Doctoral Thesis

Brownian and Nonisothermal Effects in Nucleation Theory Towards Systematic Multiscale Modeling

Author(s):
Schweizer, Marco

Publication Date:
2015

Permanent Link:
https://doi.org/10.3929/ethz-a-010523147

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
Brownian and Nonisothermal Effects in Nucleation Theory: Towards Systematic Multiscale Modeling

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

presented by

Marco Schweizer

MSc. Physics, ETH Zurich

born on 19.08.1987
citizen of
Wallisellen, Zurich, Switzerland

accepted on the recommendation of
Prof. Dr. Hans Christian Öttinger
Prof. Dr. Thierry Savin
Prof. Dr. Leonard Sagis
Prof. Dr. Jürg Diemand
Prof. Dr. David Reguera
Prof. Dr. Miguel Rubi

2015
Acknowledgements

Foremost, I thank my supervisor Hans Christian Öttinger. He is a truly extraordinary person who devotes his life to science. In my eyes, he has since ever been an ideal of science. The opportunity to work in his group was a big honor. He always gave me very sophisticated feedbacks on my manuscripts that helped me to reach a much deeper understanding of my own work, and without him this thesis would not exist in the present form.

Throughout my Ph.D I also worked intensively with my co-supervisor, Thierry Savin. I thank him deeply for having invested so much time into our work, and for always having been patient enough to wait eternities to receive my simulation data.

I thank Leonard Sagis with whom I published two of the core papers this thesis is built upon. His knowledge ranges over a remarkable variety of scientific fields and he let me profit from this invaluably.

I highly appreciated the frequent discussions about science and academic life with Martin Kröger, Patrick Ilg and Vlasis Mavrantzas.

Furthermore, I thank David Reguera, Miguel Rubi and Jürg Diemand for taking the roles of the external experts of my thesis committee, and for critically investigating my research.

I thank Harald Lehmann for supporting me when I had technical troubles.

The great assistance of Patricia Horn is also acknowledged. She reminded me of many deadlines and dealt with my peculiar requests.

I thank all friends that I gained in this group for the table soccer games we had every week, but also for the sometimes serious and cynical discussions about science, and for their support in general. In particular, I thank Maksym Osmanov, Jérome Flakowski, Ingo Füreder, Alan Luo, Alberto Montefusco, Carl Zinner, David Taj, Aparna Sreekumari, Majid Mosayebi, Orit Peleg and Monirosadat Sadati among others.

I thank Soobin Lee who represented a turning point in my life and in many respects helped me beyond academia.

I will forever look up to my parents who supported me throughout my full life. They sacrificed a lot so that I could focus entirely on my studies. In this respect I also thank my grandparents. As huge parts of my thesis concerned the implementation of computer algorithms I faced many coding problems. Concerning this I thank my brother, who is virtually dreaming in machine code, for offering me always a helping hand.

I dedicate this thesis to my family.

Zurich, 02 July 2015

M. S.
Abstract

Nucleation is the onset of a phase-transition in a metastable medium, where fragments, or nuclei, of a new phase are formed by density fluctuations in the host medium. This process is ubiquitous to understand physical mechanisms from the smallest (nanoscopic) to the largest (cosmic) length scales, and plays a key role in the design of future materials of technological relevance. We extend the state of the art literature on nucleation theory and report achievements towards the development of a modern nucleation theory that aims for real world applications.

We construct a thermodynamically guided coarse-graining procedure that obtains information about the microstructure underlining a nucleating substance directly from the atomistic scale, through efficient Monte-Carlo simulations and short-time molecular dynamics. The microscopic details are mapped in a coarse-grained way onto the proper macroscale model. Contrary to the standard procedure in the literature which, as we show, produces systematically wrong predictions in the key quantity – the nucleation rate – we take nonisothermal- and Brownian effects into account thereby reducing the aforementioned lack in predictive power significantly. Our multi-scale model is formulated for nucleation in homogeneous media. By exploiting the general structure of nonequilibrium systems we obtain complementary constitutive equations for time-dependent inhomogeneous media. In relevant special cases we establish consistency of our approach with the most recent insights in the field.

Finally, we discuss the late stage phase-separation process where two macroscopic bulk phases, separated by an interface, coexist. The classical approach to equilibrium interfacial thermodynamics describes the interface as a separate two-dimensional thermodynamic system and relies on the uniformity of intensive variables throughout the system. Therefore, it cannot be directly applied to nonequilibrium situations, where jumps in temperature and chemical potential across the interface occur. We present a conceptually clear formulation of local equilibrium for interfaces and verify the theoretical predictions by performing stringent tests with extensive high-precision nonequilibrium molecular dynamics simulations of a coexisting liquid/vapor Lennard-Jones fluid. These simulation results are further used to get deeper insights into the nature of interfacial boundary conditions.
Zusammenfassung


# Contents

Acknowledgements i

Abstract (English/Deutsch) iii

List of figures xi

List of tables xiii

List of Symbols xiii

1 Introduction 1

2 Methods 9
2.1 GENERIC Nonequilibrium Thermodynamics . . . . . . . . . . . . . . . . . . . . 10
2.2 GENERIC Coarse-Graining Procedure . . . . . . . . . . . . . . . . . . . . . . . . 11

3 Nonequilibrium Thermodynamics of Interfaces 13
3.1 Literature Overview and Achievements . . . . . . . . . . . . . . . . . . . . . . . . 13
3.2 Theory . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 14
3.3 Nonequilibrium Simulations . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 16
3.4 Results and Discussion . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 18
3.5 Conclusion and Future Work . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 22

4 Nonequilibrium Thermodynamics of Nucleation 23
4.1 Literature Overview and Achievements . . . . . . . . . . . . . . . . . . . . . . . . 23
4.2 State Variables . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 26
4.3 Isothermal Nucleation Theory . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 27
4.3.1 Energy and Entropy . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 27
4.3.2 Reversible Structure of Evolution Equations . . . . . . . . . . . . . . . . . 27
4.3.3 Irreversible Structure of Evolution Equations . . . . . . . . . . . . . . . . . 29
4.3.4 Resulting Evolution Equation . . . . . . . . . . . . . . . . . . . . . . . . . . . 30
4.4 Nonisothermal Nucleation . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 32
4.4.1 Resulting Evolution Equation . . . . . . . . . . . . . . . . . . . . . . . . . . . 32
4.5 Application: Nucleation in Supersaturated Gas . . . . . . . . . . . . . . . . . . . 34
4.5.1 Thermodynamic Model . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 34
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5.2 Detailed Results</td>
<td>36</td>
</tr>
<tr>
<td>4.6 Conclusion and Future Work</td>
<td>40</td>
</tr>
<tr>
<td>5 Nonequilibrium Statistical Mechanics of Nucleation</td>
<td>43</td>
</tr>
<tr>
<td>5.1 Literature Overview and Achievements</td>
<td>43</td>
</tr>
<tr>
<td>5.2 Derivation of Coarse-Graining Procedure</td>
<td>45</td>
</tr>
<tr>
<td>5.2.1 State Variables</td>
<td>45</td>
</tr>
<tr>
<td>5.2.2 Nonequilibrium Ensemble</td>
<td>46</td>
</tr>
<tr>
<td>5.2.3 System Entropy</td>
<td>47</td>
</tr>
<tr>
<td>5.2.4 Dissipative Bracket</td>
<td>48</td>
</tr>
<tr>
<td>5.2.5 Resulting Evolution Equation</td>
<td>48</td>
</tr>
<tr>
<td>5.3 Aspects of Coarse-Graining Procedure</td>
<td>49</td>
</tr>
<tr>
<td>5.3.1 Consistency with Nonequilibrium Thermodynamics of Nucleation</td>
<td>49</td>
</tr>
<tr>
<td>5.3.2 Nucleation Landscape in Thermodynamic Limit</td>
<td>51</td>
</tr>
<tr>
<td>5.3.3 Discussion of Temperature Fluctuations</td>
<td>54</td>
</tr>
<tr>
<td>5.3.4 Discussion of Momentum Fluctuations</td>
<td>54</td>
</tr>
<tr>
<td>5.4 Application: Mean-Field Kinetic Theory</td>
<td>55</td>
</tr>
<tr>
<td>5.4.1 Extension of State Space</td>
<td>56</td>
</tr>
<tr>
<td>5.4.2 Nucleation in Supersaturated Argon</td>
<td>56</td>
</tr>
<tr>
<td>5.5 Application: Nucleation in Lennard-Jones Gas</td>
<td>58</td>
</tr>
<tr>
<td>5.5.1 Lennard-Jones Model</td>
<td>59</td>
</tr>
<tr>
<td>5.5.2 Clustering of Particles</td>
<td>59</td>
</tr>
<tr>
<td>5.5.3 MC Simulations</td>
<td>59</td>
</tr>
<tr>
<td>5.5.4 Short-Time MD Simulations</td>
<td>61</td>
</tr>
<tr>
<td>5.5.5 Nucleation Rate</td>
<td>63</td>
</tr>
<tr>
<td>5.6 Conclusion and Future Work</td>
<td>65</td>
</tr>
<tr>
<td>6 Summary and Outlook</td>
<td>67</td>
</tr>
<tr>
<td>Bibliography</td>
<td>71</td>
</tr>
<tr>
<td>A Nonequilibrium Thermodynamics of Interfaces</td>
<td>85</td>
</tr>
<tr>
<td>A.1 Numerical Methods</td>
<td>85</td>
</tr>
<tr>
<td>A.2 Additional Remarks on Gauge Transformations</td>
<td>88</td>
</tr>
<tr>
<td>B Nonequilibrium Thermodynamics of Nucleation</td>
<td>89</td>
</tr>
<tr>
<td>B.1 Poisson Structure</td>
<td>89</td>
</tr>
<tr>
<td>B.2 Medium Evolution Equations</td>
<td>89</td>
</tr>
<tr>
<td>B.3 Entropy Production</td>
<td>90</td>
</tr>
<tr>
<td>B.4 Thermodynamic Model for Nuclei: Detailed Derivation</td>
<td>91</td>
</tr>
<tr>
<td>B.5 Stochastic Process Behind Nucleation Process</td>
<td>92</td>
</tr>
</tbody>
</table>
C Nonequilibrium Statistical Mechanics of Nucleation 93  
  C.1 Details to Derivation of Coarse-Graining Procedure 93  
  C.2 Derivation of Law of McGraw and LaViolette 95  
  C.3 Kinetic Energy as a State Variable 96  
  C.4 Saddle Point Approximation for Nucleation Rate of Extended MFKT 96  
  C.5 Nucleation Rates of MFKT Evaluated for Argon 97  
  C.6 Additional Notes on Short-Time MD for Diffusion Coefficients 98  

Curriculum Vitae 101
List of Figures

1.1 Studied nucleation rates $J_{MD}$ in selected molecular dynamics studies [29, 36, 37, 38, 39, 40, 41] of argon from 1997 – 2013 (format: first letter of name of first author and number of used atoms). The shaded area shows the experimentally accessible regime. ................................................................. 3

1.2 Left panel: activation barrier $V_S(x_{tot}, N_c)$ and its height $\Delta V_S(x_{tot}, N^*_{c})$. Right panel: multidimensional activation barrier, where size of the nuclei $N_c$ and their temperature $T_c$ (in dimensionless units), or equivalently their energy, fluctuates. Dashed lines separate the fluctuation dominated growth regime $N_c < N^*_{c}$ from the deterministic growth regime $N_c > N^*_{c}$. ................................................................. 4

3.1 (A) Snapshot of MD simulations for a Lennard-Jones fluid. In the simulation box (projected here on the $x y$-plane), a layer of liquid spontaneously forms to coexist with its vapor. The box is divided into 426 layers, and the colored layers are thermostated. (B) The surface tension measured in equilibrium at various temperatures of liquid-vapor coexistence. (C) The corresponding equilibrium chemical potential calculated using the Widom insertion method. .......... 17

3.2 Profiles of mass (A) and internal energy (B) densities in the vicinity of the interface subjected to a heat flux. (C) The excess densities $\rho^s$ and $u^s$, calculated from (A) and (B) as the shaded area between the profiles (colored curves) and their sharpened extrapolations (black lines) for various positions $x^s$ of the dividing surface. Uncertainties are below 1% of the range of values in all panels. ........... 17

3.3 Kinetic temperature profiles in the vicinity of the interface subjected to a heat flux (A) or a mass flux (B). The red and blue lines are linear extrapolation of the bulk profiles and used to define the liquid and vapor interfacial temperatures, as shown by the dashes and compared with $T^s$ (green dash). The shaded area indicates the interfacial region, with the equimolar and equipotential dividing surfaces shown by the green lines. ................................................................. 19

3.4 (A) Relative deviations of the vapor, liquid and interface temperatures from the values $T^c_{coex}$ for which Eq. (3.2a) is verified. (B) and (C) are, respectively, the relative deviations of $T^s$ from the temperature $T^c_{coex}$ that verifies Eq. (3.2b), and from the temperature $T^s_{stru}$ that verifies Eq. (3.3a). On the right side of each panel, the grey chart shows the corresponding box-and-whisker diagram in each thermodynamics situation investigated here. ................................................................. 21
4.1 Reduction in nucleation rate due to nonisothermal effects at various ambient temperatures $T$ and supersaturation ratios $S$. Solid lines are predictions of Feder [64]. Dashed lines are predictions of Barret [65] and coincide with the saddle point approximation of our theory. Symbols result from stochastic simulations of our theory. 38

4.2 Local equilibrium temperature of nuclei in dependence of deviation $\Delta N_c$ from $N_c^* \approx 15$ at $T = 0.4 T_{\text{crit}}$ and $\ln(S) = 3.5$. Our theory (dashed line – stochastic simulation results) is compared to the prediction of Feder et al. [64] (solid line). 39

4.3 Distribution $P_{\text{loc}}(T_c)$ at $T = 0.4 T_{\text{crit}}$ (black vertical line) and $\ln(S) = 3.5$ for different sizes of nuclei (black curve: subcritically sized with $N_c^* - 5$, red curve: supercritically sized with $N_c^* + 5$, dots are result of stochastic simulations of our theory). Dashed vertical lines mark local equilibrium temperatures. 39

4.4 Reduction in nucleation rate due to nonisothermal effects in dependence of coupling strength between mass and energy exchange for $T = 0.32 T_{\text{crit}}$ and $S = 5$. For rapid thermal equilibration, $\phi \to \infty$, the predictions of our theory (dashed lines: saddle point approximation, symbols: stochastic simulation) coincide with the predictions (solid lines) of Horst et al. 40

5.1 Nucleation landscape $V_S(x_{\text{tot}}, x_c)$ of liquid drop in metastable Lennard-Jones gas for nuclei composed of $N_c = 20, 40$ and $80$ particles (centered around $U_c/\epsilon = -40, -100$ and $-210$) as function of internal energy $U_c$ at $P_c = 0$. Red line shows approximate landscape (5.25) and dotted blue line exact landscape (5.22). Thermo-physical data is taken from sixth row in Table 5.3 and $\epsilon = 1.654 \times 10^{-21} J$. 53

5.2 Nucleation rates $J_{\text{MD}}$ for various temperatures $T$ and supersaturations obtained from recent large-scale molecular dynamics simulations [29] compared to original MFKT [52] (blue) and the extended MFKT (red) that takes Brownian motion and nonisothermal effects into account. Solid lines are a guide to the eyes. 58

5.3 Nucleation landscape $V_S(x_{\text{tot}}, N_c)$ at $T = 0.8 \epsilon/k_B$ and $S = 3.33$ near critical size $N_c \approx 50$. Dots are obtained from Monte Carlo simulations. The dashed black line is a fit with Eq. (5.29). This fit is unphysical for very small nuclei, here $N_c \in [0, 1]$. The red dashed line marks proper continuation to $N_c \to 0$. 60

5.4 Diffusion matrix normalized by $N_c^{2/3}$ at $T = 0.7 \epsilon/k_B$ and $S = 6.11$. Dots denote the mean-square displacement (in Lennard-Jones units) of $N_c$ with $N_c$ (red), between $N_c$ with $U_c$ (blue), between $U_c$ with $U_c$ and $P_c^x$ with $P_c^x$, where $P_c^x$ is the momentum in $x$-direction. The solid lines, the slope of which enter the prediction of the diffusion tensor, are fits to the corresponding linear regime. 63

5.5 Comparison of Lennard-Jones nucleation rate predictions of standard Monte Carlo technique (blue) with predictions of our theory (red). Also shown are the results of large-scale molecular dynamics simulations [29] (black). 64
List of Tables

4.1 Definitions of temperature $T_c$ of nuclei via internal energy $U_c$, or internal kinetic energy $E_c^{\text{kin,1}}$ as degrees of freedom in literature and in this work (GENERIC). .................................................... 25

5.1 Thermo-physical data of argon [29]. .................................................................................. 57

5.2 Nucleation rate predictions of metastable argon at various temperatures $T$ and supersaturations $S$ (and mass density $\rho$) of the ambient phase. The rates $J_{\text{MD}}$ correspond to MD simulations [29] by Diemand et al., the predictions $J_K$ to the original MFKT [52], and $J_{K,\text{ext}}$ to our extension of MFKT. .................................................... 57

5.3 Fitted parameters of the entropic potential (5.25) in Sec. 5.5.3. The reported values of the “Tolman length” $\delta$ have an error smaller or equal to $0.01 \times \sigma$. In $E_0$ and $E_s$ as well as $h_1$ the error is smaller than the number of presented digits. .................................................... 62

5.4 Fitted parameters of the diffusion tensor (5.30) with conventions Sec. 5.5.4. The error in $D^0\tau$ is discussed in App. B.VII. Errors in $D_{N_c,U_c,\epsilon}^\tau$, $\xi_{N_c,\epsilon}^\tau$, $\eta_{N_c,\epsilon}^\tau$, and $\xi^\tau_{N_c,\epsilon}^\tau$ are smaller than 0.05 and errors in $D_{N_c,U_c,\epsilon}^\tau$, $\xi_{N_c,\epsilon}^\tau$, $\eta_{N_c,\epsilon}^\tau$, and $\xi^\tau_{N_c,\epsilon}^\tau$ are smaller than 0.1. .................................................... 64

5.5 Nucleation rate predictions for a metastable Lennard-Jones gas at various temperatures $T$ and supersaturations $S$. The rates $J_{\text{MD}}$ correspond to MD simulations [29]. An asterisk on top of the data indicates that the rate is obtained through the universal scaling relation [172]. $J_{\text{MC}}$ are the predictions of the standard Monte Carlo technique, and $J_{\text{ext}}$ our predictions. $A_1 = \log\left(\frac{\alpha_{\text{non-is}}}{\alpha_{\text{is}}}\right)$ and $A_2 = \log\left(\frac{\alpha_{\text{BM}}}{\alpha_{\text{is}}}\right)$ are estimates of the correction of the nucleation rate $J_{\text{MC}}$ due to nonisothermal effects and Brownian motion. .................................................... 65

5.6 Comparison of standard literature coarse-graining expressions with our generalization. .................................................................................................................. 66

6.1 Corrections to the nucleation landscape. .................................................................................. 68

A1 Nonequilibrium simulation conditions (thermostats’ temperatures and swapping probabilities) in Lennard-Jones units. .............................................................................. 86
Nomenclature

\( D_{v,\nabla T} \)  Diffusion coefficient for coupling of velocity of nucleus with ambient temperature gradient

\( j_q \)  Diffusive heat flux in nucleus ambient phase

\( \gamma_{\infty, \delta} \)  Associated surface tension of nucleus and Tolman length

\( \langle \% \rangle \rho_{x^m, x^c(x_c)} \)  Average of % over microscopic phase space with \( \rho_{x^m, x^c(x_c)} \)

\( S^c_K \)  MFKT entropy of nucleus

\( \mathbf{s}^{P, 0}_{x^c} D_{N_c, U_c}^{k, 0} \)  Diffusion coefficients reduced by area of nucleus times \( D_{N_c, U_c}^{k, 0} \)

\( D_{0, N_c, U_c}^{k, 0}, D_{0, N_c, U_c}^{k, 0} \)  Diffusion coefficients normalized by surface area of nucleus

\([, ,] \)  Dissipative bracket

\( a_{BM}, a_{\text{non-iso}} \)  Correction to nucleation rate due to Brownian and non-isothermal effects

\( \bar{\Gamma} \)  Microscopic phase space

\( P \)  Total system momentum

\( \xi_{v_c} \)  Friction tensor for Brownian motion

\( D_{x, x_c} \)  Diffusion tensor corresponding to fluctuations in \( x_c \)

\( G \)  Hessian matrix of \( V_S(x_{env}, x_c) \) with respect to \( (N_c, U_c) \)

\( \Delta T \)  Temperature jump across interface

\( \Delta u, \Delta s, \Delta \rho \)  Jump of internal energy, entropy and mass density across interface

\( \Delta_{\tau_{GK}} \Pi_{x} \)  Deviation of \( \Pi_{x} \) during \( \tau_{GK} \)

\( \hat{\Pi}_{x_i} \)  Rapidly fluctuating part of \( \Pi_{x_i} \)

\( E_{\text{kin}}^{i, i} \)  Internal kinetic energy of a nucleus

\( E_{\text{kin}}^{i, i} \)  Total kinetic energy of nucleus

\( \Gamma \)  Gamma function
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>Macroscopic surface tension</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\lambda_{\text{min}}$</td>
<td>Unique negative eigenvalue of $\tilde{D}^* G^*$</td>
</tr>
<tr>
<td>$\lambda_c$</td>
<td>Lagrange multiplier for nucleus state</td>
</tr>
<tr>
<td>$\langle%\rangle_f$</td>
<td>Ensemble average of $%$ with $f$</td>
</tr>
<tr>
<td>$i\mathcal{L}$</td>
<td>Liouville operator governing microscopic dynamics</td>
</tr>
<tr>
<td>$\langle%\rangle_{x_{\text{tot}}}$</td>
<td>Average of $%$ over microscopic phase space with metastable phase in state $x_{\text{tot}}$</td>
</tr>
<tr>
<td>$\langle\langle%\rangle\rangle_f$</td>
<td>Ensemble and spatial average of $%$ with $f$</td>
</tr>
<tr>
<td>$N_c$</td>
<td>Number of atoms in nucleus</td>
</tr>
<tr>
<td>$N^s_c$</td>
<td>MFKT microscopic surface tension of nucleus</td>
</tr>
<tr>
<td>$N^*_c$</td>
<td>Number of atoms in critically sized nucleus</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Chemical potential of ambient phase of nuclei</td>
</tr>
<tr>
<td>$\mu_c$</td>
<td>Chemical potential of nucleus</td>
</tr>
<tr>
<td>$\mu_{\text{sat}}$</td>
<td>Chemical potential at saturation</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Momentum of nucleus</td>
</tr>
<tr>
<td>$P^{s}_c, P^{b}_c$</td>
<td>Excess momentum and bulk momentum of nucleus</td>
</tr>
<tr>
<td>$\mathcal{P}$</td>
<td>Projection onto slow microscopic variables</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Parameter regulating energy fluctuations due to collisions of atoms with nucleus</td>
</tr>
<tr>
<td>$\phi(r_i)$</td>
<td>Potential energy of interacting atoms at distance $r_i$</td>
</tr>
<tr>
<td>$\phi_S(x_{\text{tot}}, N_c)$</td>
<td>Probability of occurrence of a nucleus of size $N_c$ in metastable phase in state $x_{\text{tot}}$</td>
</tr>
<tr>
<td>$\phi_S(x_{\text{tot}}, x_c)$</td>
<td>Probability of occurrence of a nucleus in state $x_c$ in metastable phase in state $x_{\text{tot}}$</td>
</tr>
<tr>
<td>$\pi, \tau$</td>
<td>Stress tensor and extra stress tensor of ambient phase of nuclei</td>
</tr>
<tr>
<td>$\Pi^\text{kin, tot}_c, \Pi^{PO}_c$</td>
<td>Map from microscopic phase space onto total kinetic energy and potential energy of nucleus</td>
</tr>
<tr>
<td>$\Pi_{N_c, U_c}, \Pi_{\mathcal{U}^{PO}_c}$</td>
<td>Map from microscopic phase space onto nucleus states $N_c, U_c, P_c, x_c, v_c, f(x_c)$</td>
</tr>
<tr>
<td>$\Pi_N, \Pi_P, \Pi_{\mathcal{U}}, \Pi_{\mathcal{V}}, \Pi_{x_{\text{tot}}}$</td>
<td>Map from microscopic phase space onto environment states $N, P, E, V, x_{\text{tot}}$</td>
</tr>
<tr>
<td>$\Pi_{\theta(f)}$</td>
<td>Clustering of atoms as members of gas or nucleus</td>
</tr>
</tbody>
</table>

xvi
List of Tables

$\Pi_{x_i}$ Map from microscopic phase space onto $x_i$

$p^{eq,\infty}$ Saturation pressure

$\psi(T_s)$ Excess entropy in equimolar gauge

$\mathcal{Q}$ Projection onto fast microscopic variables

$\rho$ Mass density of ambient phase of nuclei

$\rho^\alpha, \rho^\beta, u^\alpha, u^\beta, s^\alpha, s^\beta$ Bulk mass, internal energy and entropy density ($\alpha = g$ (gas phase), $\beta = l$ (liquid phase))

$\rho^{eq,\infty}$ Vapor density at saturation

$\rho_c$ Mass density of nucleus

$\rho_{crit}$ Vapor density at critical temperature

$\rho_{xmc, \lambda(x)}$ Generalized mixed nonequilibrium ensemble

$\rho_{xtot, \lambda}$ Generalized mixed nonequilibrium ensemble for nucleation

$S_c$ Entropy of nucleus

$S_c^e, S_c^b$ Excess entropy and bulk entropy of nucleus

$\sigma, \epsilon$ Lennard Jones parameters

$\sigma^2_{N_c}$ Estimate for magnitude of $N_c$ fluctuations

$\sigma^2_{U_c}$ Estimate for magnitude of $U_c$ fluctuations

$S_{tot}$ Entropy of metastable phase

$\tau$ Lennard Jones time-scale

$\tau_{GK}$ Intermediate time-scale between microscopic and macroscopic dynamics

$\text{tr}\%$ Trace of matrix $\%$

$\tilde{D}$ Diffusion tensor for mass and energy transfer

$u$ Momentum density of ambient phase of nuclei

$U_c$ Internal energy of nucleus

$U_c^a, U_c^b$ Excess internal energy and bulk internal energy of nucleus

$U_c^K$ MFKT energy of nucleus

$U_c^{pot,0}$ Most probable potential energy of nucleus
List of Tables

\( \nu \) velocity of ambient phase of nuclei
\( V_c \) Volume of nucleus
\( \nu_c \) Velocity of nucleus
\( V'_c \) Nucleus volume compared to system volume
\( V \) Volume of system
\( \chi_c \) Extended state space of nucleus
\( \chi_{\text{env}} \) State of ambient phase of nuclei
\( \zeta_0 \) Coefficient related to friction coefficient for Brownian motion
\( \chi_s \) State of system
\( \chi_{\text{tot}} \) State of full metastable phase
\( \zeta \) Heat transmitted upon addition of an atom to a nucleus
\( \{\%,\%\}_H \) Poisson bracket of hydrodynamics
\( \{\%,\%\}_f \) Poisson bracket for distribution function of nuclei
\( \{\cdot,\cdot\} \) Poisson bracket
\( \{A,B\}_\text{ex} \) Poisson bracket for reversible exchange of nuclei and ambient phase
\( A_c \) Area of nucleus
\( c^P \) Specific heat capacity at constant pressure of ideal gas
\( c^P_c \) Specific heat capacity at constant pressure of nucleus
\( C_V \) Heat capacity at constant volume of ideal gas
\( c_V \) Specific heat capacity at constant volume of ideal gas
\( D_{N,N_i} \) Diffusion coefficient for mass transfer
\( D_{N_i,U_i} \) Diffusion coefficient for coupling of mass and energy transfer
\( D_{U_i,U_i} \) Diffusion coefficient for energy transfer
\( E(\chi_s) \) System energy
\( E^e_c, E^b_c \) Excess energy and bulk energy of nucleus
\( f(N_c) \) Distribution of nuclei with size \( N_c \)
\( f(\mathbf{r},\chi_c) \) Distribution of nuclei in state \( \chi_c \) at position \( \mathbf{r} \)
List of Tables

\( f(x_c) \)  Distribution of nuclei in state \( x_c \)

\( H \)  Scale, inverse to potential energy fluctuations of nucleus

\( J_K \)  MFKT nucleation rate

\( J_{N_c}, J_{U_c}, J_{M,v_c} \)  Fluxes for mass, energy and momentum transfer

\( J_{iso} \)  Nucleation rate of isothermal theory

\( J_{K, ext} \)  Nucleation rate of MFKT with extended state space

\( J_{MD} \)  Nucleation rate obtained by molecular dynamics

\( J_{non-iso} \)  Nucleation rate of non-isothermal theory

\( J_{trc} \)  Nucleation rate of truncated theory

\( L \)  Latent heat of vaporization

\( l \)  Defines family of gauge transformations

\( L(x_s) \)  Poisson matrix

\( L_0 \)  Reference value of heat of vaporization

\( M \)  Total system mass

\( m \)  mass of atom

\( M(x_s) \)  Friction matrix

\( M_c \)  Total mass of nucleus

\( M^s_c, M^b_c \)  Excess mass and bulk mass of nucleus

\( p \)  Pressure of ambient phase of nuclei

\( p_c \)  Pressure of nucleus

\( P_T(T_c) \)  Distribution of temperature of nuclei according to McGraw and LaViolette

\( p_H \)  Degree of coupling of mass and energy transfer

\( r_c \)  Radius of nucleus

\( S \)  Supersaturation ratio

\( s \)  Entropy density of ambient phase of nuclei

\( S(x_s) \)  System entropy

\( S(x_{tot}, f) \)  System entropy for nucleating system
**List of Tables**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>Temperature of ambient phase of nuclei</td>
</tr>
<tr>
<td>$T_{\text{stru}}^u$</td>
<td>Unique solution that verifies the structural interface relationship for internal energy</td>
</tr>
<tr>
<td>$T^s, \mu^s$</td>
<td>Temperature and chemical potential of interface</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Temperature of nucleus</td>
</tr>
<tr>
<td>$T_{\text{crit}}$</td>
<td>Critical temperature</td>
</tr>
<tr>
<td>$T_{\text{loc}}$</td>
<td>Local equilibrium temperature of nuclei</td>
</tr>
<tr>
<td>$u$</td>
<td>Internal energy density of ambient phase of nuclei</td>
</tr>
<tr>
<td>$u^s, s^s, \rho^s$</td>
<td>Excess internal energy, entropy and mass of interface</td>
</tr>
<tr>
<td>$V_S(x_{\text{env}}, N_c, v_c)$</td>
<td>Activation barrier of isothermal theory with Brownian motion at fixed ambient and nucleus state</td>
</tr>
<tr>
<td>$V_S(x_{\text{env}}, x_c)$</td>
<td>Generalized activation barrier at fixed ambient and nucleus state</td>
</tr>
<tr>
<td>$V_S(x_{\text{tot}}, N_c)$</td>
<td>Activation barrier height of truncated theory at fixed state of metastable phase and nucleus state</td>
</tr>
<tr>
<td>$V_S(x_{\text{tot}}, N_c)$</td>
<td>Activation barrier height of truncated theory at fixed state of metastable phase and nucleus state</td>
</tr>
<tr>
<td>$V_S(x_{\text{tot}}, x_c)$</td>
<td>Generalized activation barrier at fixed state of metastable phase and nucleus state</td>
</tr>
<tr>
<td>$x_{\mu}^s, x_p^s$</td>
<td>Location of equipotential and equimolar dividing surface</td>
</tr>
<tr>
<td>$X_{N_c}, X_U, X_M, v_c$</td>
<td>Driving force for mass, energy and momentum transfer</td>
</tr>
<tr>
<td>$Z(x_{s\mu}, \lambda_c(x_c))$</td>
<td>Partition function of $\rho x_{s\mu}, \lambda_c(x_c)$</td>
</tr>
<tr>
<td>$Z(x_{\text{tot}}, \lambda_c)$</td>
<td>Partition function of $\rho x_{\text{tot}}, \lambda_c$</td>
</tr>
<tr>
<td>$Z_{\text{tot}}$</td>
<td>Partition function of metastable phase</td>
</tr>
<tr>
<td>$Z_c^K$</td>
<td>MFKT partition function of nucleus</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Velocity gradient tensor of ambient phase of nuclei</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity of ambient phase of nuclei</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Bulk viscosity of ambient phase of nuclei</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Thermal conductivity of ambient phase of nuclei</td>
</tr>
<tr>
<td>$S(x_{\text{tot}}, x_c)$</td>
<td>Microcanonical entropy for nucleation</td>
</tr>
<tr>
<td>$Z(x_{\text{tot}}, x_c)$</td>
<td>Microcanonical partition function for nucleation</td>
</tr>
</tbody>
</table>
1 Introduction

Nucleation is the onset of a phase-transformation, an essential process throughout science and industrial engineering with numerous applications from the smallest to the largest physical length scales.

In the nano regime, future trends to design new high-performance materials increasingly rely on the nucleation process [1, 2, 3]. In 2008, for instance, the top tier company IBM together with researchers from Purdue university discovered that tiny silicon nanowires, ideal for manufacturing the future components of computers and electronics, can be produced highly reproducibly when built through a liquid to solid nucleation process [4]. A major area of investigations also concerns the tailoring of special coatings on nano-surfaces, that control, delay or avoid nucleation [5, 6, 7]. In practice, this could once substitute de-icing systems necessary to avoid nucleation of atmospheric ice on aircrafts [7] - each year commercial airports in the US spend approximately 100 million liters of de-icing agents.

On the micrometer scale, nucleation has been found to be one of the key mechanisms through which self-healing materials [8] and pharmaceutical drugs can be produced [9], creation of voids and cracks can be understood [10] or the replication of viruses such as Hepatitis B can be modeled [11].

On the upper end of length-scales, important applications of nucleation theory are especially found in climate physics. In the atmosphere primary particles such as mineral dust, sea salt or pollen are distinguished from secondary particles formed by nucleation in the atmospheric gases which, under favorable conditions, grow to seeds in clouds. The formation of these aerosol particles over oceans and other environments for the sake of weather and climate predictions has drawn a lot of scientific research [12, 13, 14, 15], but also beyond predictions [16], the direct injection of aerosol particles into rain clouds to induce droplet nucleation and rainfall has been done in reality. In this respect, China can be regarded as the world's leader in weather manipulation and puts increasing efforts in the technique to provide farmers with sufficient water for their fields. Important aspects of nucleation processes are also found in the energy industry. Natural gas constitutes approximately 25% of the total global energy...
Chapter 1. Introduction

consumption and is made accessible all over the world through pipelines. In the early history of gas pipelines it was unknown that the high-pressure conditions lead to unwanted nucleation of hydrate drops that grow to macroscopic dimension and block even the largest pipelines. To delay and suppress this effect inhibitor gases are introduced, but still substantial investments of 10−15% of the natural gas production cost are necessary to avoid hydrate nucleation [17, 18]. Hydrates also nucleate in gigantic amounts in permafrost and ocean sediments making them one of the important future energy sources [19] and it is therefore imperative to predict the location of potential hydrate reservoirs.

On astronomical scales nucleation is most relevant in the study of interstellar dust [20] constituting approximately 1% of our galaxy – gas to solid nucleation in the stellar outflows leads to the formation of grains of sizes up to 500nm that change the interstellar radiation spectrum leading to background radiation. Several space missions involving satellites, with the latest one called “Herschel” launched in 2009, extensively observed the radiation spectra of the dust to understand its size, structure and composition. Nucleation is also relevant to understand the stellar cycle: interstellar dust plays the role of a diffusive cloud that is transformed to a dense cloud and finally to a prestellar core from which a star is formed [21].

The nucleation process starts with the formation of small aggregates, or nuclei, of the new phase through density fluctuations within a metastable phase. Nuclei that exceed a certain critical size, recognized as a rare event, are likely to reach macroscopic dimension. On the contrary, sub-critically sized nuclei decay with high probability. Nucleation is an activated process - the growth beyond the critical size requires an activation barrier to be overcome and the height of the barrier determines the rate at which nuclei reach their critical size. This so called “nucleation rate” is a measure of how long it takes until the new structure emerges from the metastable phase and its estimation for various substances has drawn significant attention in both theoretical [22, 23, 24] and experimental [25, 26] work.

In order to apply theoretical models of nucleation to real world problems to predict for instance the nucleation rate, the morphology and structure of the nucleated material, or its physical properties in general we are confronted with two main difficulties: in reality nucleation nearly exclusively takes place under flow, in pressure-, or temperature gradients. Furthermore, the nuclei and their environment are intrinsically intertwined since growing nuclei deplete their ambient phase. We must hence formulate proper macroscopic equations for nucleation in inhomogeneous time-dependent media. These equations govern the evolution of the physically relevant quantities of interest, but involve unknown parameters that must be fixed based on phenomenological considerations, or by fitting experimental data, but lack a clear relation to the underlying microstructure. The second difficulty concerns the construction of a method that maps the nucleation process from the very detailed atomistic level to the coarse-grained level by translating microstructural information into the building blocks of the macroscopic description. This time- and length-scale bridging scheme in the spirit of multi-scale simulations ultimately allows for accurate quantitative predictions of the macroscale model. As we elaborate, in this thesis we report achievements for both problems.
The majority of scientific work in nucleation theory concerns nucleation in homogeneous media where a variety of methods ranging from phenomenological [27] and statistical mechanics approaches [28] to brute force molecular dynamics (MD) simulations [29] have been developed. While phenomenological and statistical approaches rely on approximations, MD simulates all involved atoms in the nucleation process and produces exact data under various initial conditions of the metastable phase. Since MD conducts computer experiments with systems of nano sized dimensions, up to a limit of a few micrometers, these studies favor regimes in which the nucleation rate is large, so that despite of the microscopic system size adequate statistics on the data can be ensured. This is in strong contrast to real experiments. Most laboratory experiments\(^\text{1}\) are restricted to measure nucleation rates less than \(10^{10}\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\) [31, 32, 33]. For the nucleation of argon experimental setups through the supersonic nozzle (SSN) experiment achieve to study nucleation rates up to \(10^{17}\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\) [34, 35]. Only recently, in 2013, large-scale MD simulations were capable to operate in the experimentally accessible regime set by the SSN [29]. In Fig. 1.1 we have reported the studied nucleation rate in MD simu-

![Figure 1.1 – Studied nucleation rates \(J_{\text{MD}}\) in selected molecular dynamics studies [29, 36, 37, 38, 39, 40, 41] of argon from 1997 – 2013 (format: first letter of name of first author and number of used atoms). The shaded area shows the experimentally accessible regime.](image)

- unless sophisticated large-scale simulations are exploited, MD studies nucleation regimes that differ by \(5 - 10\) orders of magnitude in nucleation rate from the SSN experiment and \(12 - 17\) orders of magnitude from typical experiments.

MD cannot be used to study realistic experimental regimes unless tremendous computational effort is made – only coarse-grained models offer this possibility. These models capture the relevant macroscale physics through the shape \(V_S(x_{\text{tot}}, N_0)\) and height \(\Delta V_S(x_{\text{tot}}, N_0^*)\) of the

\(^{1}\)To probe the nucleation process in experiments different methods [30] are available: diffusion cloud chambers measure nucleation rates in \(10^{-3} - 10^{2}\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\), single piston expansion chambers in \(10^2 - 10^5\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\), laminar flow diffusion chambers in \(10^3 - 10^6\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\), piston expansion wave tubes in \(10^4 - 10^8\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\), nucleation pulse chambers in \(10^5 - 10^6\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\), pulse expansion wave tubes in \(10^8 - 10^{11}\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\) and supersonic nozzle experiments in \(10^{15} - 10^{17}\) \(\text{cm}^{-3}\) \(\text{s}^{-1}\).
Chapter 1. Introduction

Figure 1.2 – Left panel: activation barrier $V_S(x_{tot}, N_c)$ and its height $\Delta V_S(x_{tot}, N^*_c)$. Right panel: multidimensional activation barrier, where size of the nuclei $N_c$ and their temperature $T_c$ (in dimensionless units), or equivalently their energy, fluctuates. Dashed lines separate the fluctuation dominated growth regime $N_c < N^*_c$ from the deterministic growth regime $N_c > N^*_c$.

activation barrier\(^2\) that prohibits small nuclei to reach the critical size $N^*_c$ in a metastable phase with properties $x_{tot}$, see also Fig. 1.2. Here, $N_c$ denotes the number of atoms in a nucleus. Throughout the past century, many phenomenological, semi-phenomenological and statistical mechanics methods have been established to predict $V_S(x_{tot}, N_c)$. In particular, the classical nucleation theory (CNT) \([27, 42, 43, 44, 45, 46]\), the internally consistent CNT (ICNT) \([47]\), the semi-phenomenological model (SP) \([48, 49, 50]\), the revised SP model (RSP) \([51]\), the mean-field kinetic theory (MFKT) \([52, 27]\), the extended modified liquid drop dynamic nucleation theory (EMLD-DNT) \([53]\), the density functional theory (DFT) \([54, 55]\), the square gradient theory (SGT) \([54]\) and many more. These theories can be split into two classes: the first type (CNT, ICNT, SP, RSP and MFKT) incorporates explicitly, or implicitly a sharp boundary between the nuclei and the ambient phase, while the latter (EMLD-DNT, DFT and SGT) are based on non-sharp, diffusive boundaries. For nucleation of argon the nucleation rate predictions of sharp boundary theories usually deviate $2 − 5$ orders of magnitude from brute-force MD simulations \([22]\), while this lack in prediction is less severe for the diffusive theories \([23]\). The CNT, ICNT, SP, RSP, MFKT and EMLD-DNT, applicable to a large range of substances, rely on the decomposition of nuclei into bulk and surface contributions (capillarity approximation), and the association of corresponding bulk and surface properties, such as a surface tension. These approximations appear rather questionable in view of the often small sizes of nuclei, of a few of tens of atoms, encountered in the studied nucleation processes. The DFT, although very accurate, is limited to very simple fluids, where the intermolecular interaction potential is spherical unless a more complicated version \([56]\) of the DFT is used, and in the SGT, the free energy density of a system at all densities, including the unstable

\(^2\)Notice, in contrast to the convention in literature, but for mathematical convenience, throughout this thesis the nucleation landscape $V_S$ is normalized by $k_B T$, where $k_B$ is the Boltzmann constant and $T$ the temperature of the metastable phase.
regions must be known.

A powerful alternative to obtain \( V_S(x_{\text{tot}}, N_c) \) free from approximations for arbitrary substances in all nucleation regimes relies on Monte Carlo (MC) simulations \([57, 58, 59, 60, 61, 62, 63]\), where microstructural information is extracted directly from the atomistic level of description. In order to obtain predictions, of say the nucleation rate \( J \), the activation barrier \( V_S(x_{\text{tot}}, N_c) \) obtained in MC simulations must however enter an adequate evolution equation obtained through supplementary dynamic considerations of the nucleation process. Many evolution equations, including the most popular one, the Zeldovich equation,

\[
\frac{\partial f(N_c)}{\partial t} = \frac{\partial}{\partial N_c} k_B D_{N_c} N_c \left[ \frac{\partial f(N_c)}{\partial N_c} + f(N_c) \frac{\partial V_S(x_{\text{tot}}, N_c)}{\partial N_c} \right],
\]

(1.1)

governing the stochastic motion of a nucleus of interest in \( N_c \)-space through the corresponding probability density \( f(N_c) \), result in \( J = J_0 e^{-\Delta V_S(x_{\text{tot}}, N_c^*)} \), where the prefactor \( J_0 \) is related to the diffusion coefficient \( D_{N_c} \) and the activation barrier shape in the vicinity of the critical size \( N_c^* \) \([27]\). Here, \( \Delta V_S(x_{\text{tot}}, N_c^*) \) denotes the height of the activation barrier.

In this thesis we show that the aforementioned nucleation rate predictions of the standard MC technique \([57, 58, 59, 60, 61, 62, 63]\) deviate 3 – 5 orders of magnitude from the exact brute-force MD simulation results \([29]\) conducted by Diemand and coworkers for nucleation of liquid drops in metastable argon. This is particularly severe since Diemand et al. consider the experimental accessible nucleation regime, see Fig. 1.1. Furthermore, argon is described by the Lennard-Jones model and this is one of the most basic and widely used microscopic models to study the nucleation process. The standard approach reported in the literature to obtain nucleation rates by MC simulations is therefore incomplete. Due to the far reaching advantages of the MC technique over other approaches, there is a desire to locate the reason for its rather poor performance in estimating nucleation rates.

We argue that the short-coming of the standard MC technique literature relies on is an artifact of the truncated state space \( x_{\text{trc}} = (N_c) \) to describe the nuclei degree of freedom on the coarse-grained scale. Our attempt to improve predictions obtained from MC simulations has its foundation in 1966 in the classical work \([64]\) by Feder et al. who already noticed the need to extend the aforementioned truncated state space in order to account for certain dynamic effects that cannot be captured by the use of a single state variable only. In particular, Feder et al. realized that in the nucleation process a significant amount of latent heat is released indicating that the nuclei exhibit rather strong energy fluctuations on top of their size fluctuations. They showed that the inclusion of the internal energy \( U_c \) into the nuclei state space leads to corrections to the nucleation rate of 1 – 3 orders of magnitude. This is confirmed by other work focusing on nonisothermal corrections \([65, 66, 67]\). Another argument in favor of equipping the state space with additional degrees of freedom traces back to the “translational-rotational paradox” initiated by Lothe and Pound around 1962 \([68]\). They realized that nuclei are not static objects, but can move and rotate within the metastable phase. Lothe and Pound tried to incorporate the translational and rotational contributions.
and ended up with corrections of $10^{17}$ to the nucleation rate. With this correction, theoretical predictions of the nucleation rate deviated from experiments so outrageously that the term “translational-rotational paradox” was coined. Many attempts tried to resolve the paradox [69, 70, 71, 72, 73, 74]. In this respect the work [74] of Reguera and Rubi presents an elegant solution by extending the state space with the momentum $P_c$ and angular momentum of the nuclei, and thereby more realistic corrections of the order of $10^2 - 10^5$ for typical nucleation regimes are obtained.

In this thesis, we notably generalize the standard MC technique to include nonisothermal effects and the Brownian motion of the nuclei, and hence operate on the extended state space $x_c = (N_c, P_c, U_c)$. We lay the basis for the corresponding nonequilibrium statistical mechanics resulting in a systematic coarse-graining procedure that is reliably predicting nucleation rates in the experimental accessible nucleation rate regime. Our coarse-graining procedure relies on the GENERIC (General Equation for Non-Equilibrium Reversible-Irreversible Coupling) nonequilibrium statistical mechanics [76, 77] that has already been successfully applied to a variety of relevant systems to predict for instance the shear behavior of unentangled polymer melts [78], the reptation time in entangled polymer melts [76], or to derive the Boltzmann equation [77] and hydrodynamics [79] from first principles. Our formalism not only generalizes the standard MC technique, by replacing the simple landscape $V_S(x_{tot}, N_c)$ through its multidimensional version $V_S(x_{tot}, x_c)$, see Fig. 1.2, but furthermore dictates the proper form of coarse-grained equations that $V_S(x_{tot}, x_c)$ enters to generate the underlying nucleation process. In particular, the stochastic evolution in $x_c$-space of a nucleus of interest is described by the associated probability density $f(x_c)$ governed by the generalization

$$\frac{\partial f(x_c)}{\partial t} = \frac{\partial}{\partial x_c} \cdot k_B D_{x_c} (x_{tot}, x_c) \cdot \left[ \frac{\partial f(x_c)}{\partial x_c} + f(x_c) \frac{\partial V_S(x_{tot}, x_c)}{\partial x_c} \right]$$

(1.2)

of the Zeldovich equation (1.1), where now $D_{x_c}$ is a diffusion tensor. We apply our approach to predict the nucleation rates obtained by Diemand et al. [29] and show that the lack in agreement of $3 - 5$ orders of magnitude of the standard MC technique can be significantly reduced by our extended theory. We illustrate further that we can conveniently extend existing phenomenological nucleation theories to richer state spaces thereby improving the quality of their predictions.

Our systematic coarse-graining procedure is applicable when the ambient phase of the nuclei is homogeneous, but the majority of potential relevant applications involves inhomogeneous, time-dependent media. The presence of spatial gradients destroys the isotropy of the system and nucleation theory of homogeneous media cannot be used anymore. The presence of a shear-flow, for instance, is known to decrease the nucleation rate significantly in certain colloidal melts [80]. On the contrary, shear can also induce nucleation and modify the mor-

---

3Angélil et al. have studied [75] the properties of nuclei in large-scale MD simulations and concluded that the angular momentum of nuclei plays a negligible role for their dynamics. Only small nuclei composed of less than 10 atoms tend to spin. In this thesis, we study nucleation regimes for which the size of critical clusters is well beyond 10 atoms.
The formation of a new phase until its completion is a combination of three mechanisms: the formation of small nuclei of the new phase and their growth beyond the critical size, systematic growth of the nuclei, and agglomeration of fragments of the new phase [86, 87]. The initial stage is governed by small nuclei that grow independently, until sufficiently many surpassed the critical size and the interaction between them becomes important. Subsequently, Ostwald ripening takes over, i.e., the growth of large nuclei on compense of small ones. And finally, when the new phase reached a macroscopic dimension, we can cleanly distinguish two coexisting bulk phases and an interface that separates them. The classical approach to equilibrium interfacial thermodynamics in phase coexistence describes the interface as a separate, autonomous two-dimensional thermodynamic system [88]. This formulation relies on the uniformity of intensive variables throughout the system. Therefore, it cannot be directly applied to nonequilibrium situations such as evaporation/condensation processes, where jumps in temperature and chemical potential across the interface can occur. Recently,
Chapter 1. Introduction

A conceptually clear formulation of local equilibrium for interfaces has been presented by Savin et al. [89]. This notion notably leads to generalized Clapeyron's relationships, valid even in nonequilibrium. The latter relationships are interpreted as boundary conditions connecting the interface and bulk phases. In this thesis, we verify the theoretical predictions of Savin et al. by performing stringent tests with extensive high-precision nonequilibrium MD simulations of a coexisting liquid/vapor Lennard-Jones fluid and hence confirm a modern implementation of local equilibrium for interfacial systems. To obtain qualitative predictions from our nonequilibrium thermodynamics approach to nucleation we perform a case study by describing the thermodynamics of nuclei through the Gibbs model: through the capillarity approximation the nuclei are assigned a well defined bulk and interface, and the modern formulation of Savin et al. will hence play a fundamental role to understand the nucleation process thermodynamically.

In Chap. 2 we introduce the nonequilibrium thermodynamics and nonequilibrium statistical mechanics in terms of the GENERIC framework as the fundamental method on which our achievements in nucleation theory are based. The main scientific milestones reported in this thesis are summarized in the following points:

2 Methods

We aim to describe a process far from equilibrium on a coarse-grained level of description. The coarse-grained dynamics of nonequilibrium systems can be obtained through two complementary approaches: based on thermodynamically motivated guidelines that fix the structure of coarse-grained evolution equations, or by using a coarse-graining technique. Coarse-graining is the art of establishing a connection between a microscopic and macroscopic level of description. This requires bridging a time- and length-scale gap to map the microscopic dynamics onto the adequate macroscopic model. The microscopic level is usually recognized as the position and momenta of all atoms involved in the process.

A widely applied framework that formulates a complete, coherent and consistent structure of the coarse-grained level of description is the GENERIC [77]. In summary, the GENERIC dictates the four building blocks of a general theory of nonequilibrium thermodynamics, see Sec. 2.1. Based on their symmetry properties, the building blocks can usually be deduced to obtain a phenomenological description that includes undetermined transport coefficients and thermophysical information. The GENERIC formalism comes however with a systematic coarse-graining technique [77, 76], see Sec. 2.2, that projects details of the underlying microstructure in a coarse-grained way onto the four building blocks, so that the coarse-grained theory allows for precise quantitative predictions.

The GENERIC is a well-established framework and has been successfully applied to study the nonequilibrium thermodynamics of simple [90] and complex fluids [77], dumbbell models [90], the Doi-Ohta model [91], Cahn-Hilliard type of models [92], plastic deformations in amorphous systems [93], special relativistic hydrodynamics [94] and more. The associated coarse-graining procedure, or nonequilibrium statistical mechanics, has shown its value and tremendous applications, for instance, in systematically predicting the shear behavior of unentangled polymer melts [95], the reptation time in entangled polymer melts [76], or to derive the Boltzmann equation [77], hydrodynamics [79], complex fluid models [96] and the equations of dissipative electromagnetism [97] from first principles.
2.1 GENERIC Nonequilibrium Thermodynamics

In the GENERIC formalism [77] the evolution equations for a set of relevant state variables $\mathbf{x}$ describing a nonequilibrium system is a simple combination of mechanics - expressed in a term of the Hamiltonian form - and a relaxation - expressed in the form of a gradient Ginzburg-Landau type dynamics - that guarantees conservation of the energy, momentum, and mass, and the growth of the entropy [84]. The dynamic behavior of a nonequilibrium system can be captured by a single compact equation,

$$\frac{d A(\mathbf{x}_s)}{dt} = \{ A(\mathbf{x}_s), E(\mathbf{x}_s) \} + [ A(\mathbf{x}_s), S(\mathbf{x}_s) ].$$ (2.1)

This is merely a decomposition of the macroscopic evolution equation of an arbitrary observable $A(\mathbf{x}_s)$, depending on the system state $\mathbf{x}_s$, into reversible and irreversible parts. The reversible evolution is generated by the system Hamiltonian $E(\mathbf{x}_s)$ and the irreversible dynamics through the total system entropy $S(\mathbf{x}_s)$. Both, reversible and irreversible dynamics are associated a bracket structure. This is the Poisson bracket $\{ \cdot, \cdot \}$ and the dissipative bracket $[\cdot,\cdot]$. The choice of the brackets is restricted by thermodynamic consistency requirements. In particular, the Poisson-Bracket must be anti-symmetric, fulfill the Jacobi identity and the entropy must be in its null-space, i.e., $\{ A, S \} = 0$, ensuring that reversible dynamics does not lead to entropy production. Correspondingly, the dissipative bracket must be positive definite, to guarantee a positive entropy production, symmetric, and the energy must be in its null-space, i.e., $[ A, E ] = 0$ for all observables $A(\mathbf{x}_s)$. The latter criterion, known as energy-degeneracy of the dissipative bracket, ensures that irreversible dynamics does not lead to energy production. The GENERIC equation (2.1) can be reformulated to access the evolution equations for the state variables $\mathbf{x}_s$ directly,

$$\frac{d \mathbf{x}_s}{dt} = L(\mathbf{x}_s) \cdot \frac{\delta E(\mathbf{x}_s)}{\delta \mathbf{x}_s} + M(\mathbf{x}_s) \cdot \frac{\delta S(\mathbf{x}_s)}{\delta \mathbf{x}_s},$$ (2.2)

where $L(\mathbf{x}_s)$ and $M(\mathbf{x}_s)$ are the Poisson and friction matrices. These must obey complementary symmetry properties [77] that define successfully a Poisson- and dissipative structure by

$$\{ A, B \} = \frac{\delta A(\mathbf{x}_s)}{\delta \mathbf{x}_s} \cdot L(\mathbf{x}_s) \cdot \frac{\delta B(\mathbf{x}_s)}{\delta \mathbf{x}_s}$$ (2.3)

and

$$[ A, B ] = \frac{\delta A(\mathbf{x}_s)}{\delta \mathbf{x}_s} \cdot M(\mathbf{x}_s) \cdot \frac{\delta B(\mathbf{x}_s)}{\delta \mathbf{x}_s}.$$ (2.4)

The brackets of many physical systems of interest are known, such as for hydrodynamic fields, complex fluids, the Boltzmann equation, dumbbell models and multiphase systems. For hydrodynamics, the Poisson-brackets can be constructed [90] based on the representation of the continuous group of space transformations on the space of hydrodynamic fields. The basic idea of such a construction is that the Poisson-bracket only involves kinematic effects and
2.2. GENERIC Coarse-Graining Procedure

these are closely related to space-transformations [90]. Along similar lines the bracket for the convection of distribution functions, necessary to treat dumbbell models and the Boltzmann equation is understood [90, 84]. For the construction of dissipative brackets intuition of the researcher on the relevant irreversible transport processes is usually required.

2.2 GENERIC Coarse-Graining Procedure

The systematic coarse-graining procedure projects atomistic dynamics onto the macroscopic theory (2.1), or respectively (2.2). This requires to go through four basic steps:

Choice of State Variables A suitable set of state variables $x_s$ must be identified for an autonomous description of the target level of coarse-graining. The state variables $x_s$ must be expressed in terms of the position and momenta of all atoms. We denote this map by $\Pi_{x_s}$, acting on the microscopic phase space and denoting the instantaneous value of $x_s$ for any microscopic configuration. The choice of the relevant variables $x_s$ is crucial since these are the observables that are averaged to obtain the building blocks in which the coarse-grained theory is encoded.

Choice of Nonequilibrium Ensemble Under the assumption that the collection of variables $x_s$ captures all relevant physical processes on the macroscopic time-scale of interest, the corresponding nonequilibrium state of the microscopic system must be characterized by an ensemble $\rho_{x_s}$. This nonequilibrium ensemble can be of canonical, microcanonical, or mixed canonical-microcanonical form, and therefore potentially contains Lagrange-multipliers. Suppose that parts of the degrees of freedom $x_s = (x_s^{mc}, x_s^c)$ are treated microcanonically, i.e., $x_s^{mc}$, and the remaining, $x_s^c$, treated canonically. Then

$$\rho_{x_s^{mc}, \Lambda^c(x_s)} = \frac{1}{Z(x_s^{mc}, \Lambda^c(x_s))} \delta (\Pi_{x_s^{mc}} - x_s^{mc}) e^{-\Lambda^c(x_s) \cdot \Pi_{x_s^c}}, \quad (2.5)$$

where $\Lambda^c(x_s)$ denotes the Lagrange multipliers chosen to produce the proper averages, i.e., $x_s = \langle \Pi_{x_s} \rangle_{\rho_{x_s^{mc}, \Lambda^c(x_s)}}$, where the brackets denote the average of $\Pi_{x_s}$ with the ensemble $\rho_{x_s^{mc}, \Lambda^c(x_s)}$ over the microscopic phase space $\bar{\Gamma}$ containing the position and momenta of all atoms. The partition function $Z(x_s^{mc}, \Lambda^c(x_s))$ serves as a normalization factor.

Calculate the Static Building Blocks The static building blocks $L(x_s)$, $E(x_s)$ and $S(x_s)$ do not depend on microscopic trajectories, but solely on microscopic configurations and can therefore be sampled through MC simulations of the atoms by imposing the nonequilibrium ensemble $\rho_{x_s^{mc}, \Lambda^c(x_s)}$. For later purpose, the reversible part of the evolution equation (2.2) emerging from coarse-graining can be brought into a form that does not highlight the decomposition in $L(x_s)$ and $E(x_s)$, but is more convenient to perform our later analysis, i.e.,
Chapter 2. Methods

\[ \langle i \mathcal{L} \Pi_{x_s} \rangle \rho^{\text{mc}, A^c(x_s)} = L(x_s) \cdot \frac{\delta E(x_s)}{\delta x_s}. \]  
(2.6)

The Liouville operator \( i \mathcal{L} \) governs the time evolution of purely reversible classic atomistic systems. Therefore, the reversible evolution is recovered by averaging \( i \mathcal{L} \Pi_{x_s} \) over the ensemble \( \rho_{x_s^\text{mc}, A^c(x_s)} \). The total system entropy associated with the ensemble (2.5) is obtained from

\[ S(x_s) = k_B \ln \left( Z(x_s^\text{mc}, A^c(x_s)) \right) - k_B A^c(x_s) \cdot x_s^c, \]  
(2.7)

where the partition function \( Z(x_s^\text{mc}, A^c(x_s)) \) must hence be sampled.

**Obtain the Dynamic Building Blocks**  
The friction matrix \( M(x_s) \) is the only dynamic building block and is connected to the evaluation of Green-Kubo formulas. To this extend a projection operator \( \mathcal{P} \) is introduced that separates the macroscopically relevant contributions \( \mathcal{P} \Pi_A \) of the atomistic expression \( \Pi_A \) of an arbitrary observable \( A \) from the irrelevant ones, \( \mathcal{Q} \Pi_A = (1 - \mathcal{P}) \Pi_A \), to be eliminated in the coarse-graining procedure - this corresponds to the separation of slow from fast microscopic degrees of freedom when switching from the detailed level of description with all atoms to the coarse-grained level characterized by \( x_s \), see also [77, 98] for more details. Introducing the intermediate time-scale \( \tau_{\text{GK}} \) separating the slow from the fast degrees of freedom, the friction matrix is

\[ M_{x_s, x_s}(x_s) = \frac{1}{k_B} \int_0^{\tau_{\text{GK}}} dt \langle \dot{\Pi}_{x_s}(t) \dot{\Pi}_{x_s}(0) \rangle \rho^{\text{mc}, A^c(x_s)}. \]  
(2.8)

Here, \( \dot{\Pi}_{x_s} = \mathcal{Q} i \mathcal{L} \Pi_{x_s} \) is the rapidly fluctuating part of the time-rate of change of \( \Pi_{x_s} \). The atomistic system must be evolved on a time-scale \( \tau_{\text{GK}} \) on which microscopic correlations drop off to obtain the atomistic trajectories from which \( \dot{\Pi}_{x_s}(t) \) can be evaluated. The average is over all trajectories for which the initial configuration is compatible with the ensemble \( \rho^{\text{mc}, A^c(x_s)} \).
3 Nonequilibrium Thermodynamics of Interfaces

3.1 Literature Overview and Achievements

Many efforts have been made in the last century to build a rigorous and thermodynamically admissible description of interfaces at equilibrium and at nonequilibrium [99, 100, 101, 102]. Broadly, we may separate these approaches into two complementary categories: the smooth - or diffuse - interface approach, and the sharp interface approach [101, 102].

The diffuse interface model relies on continuous profiles of local densities and compositions, that exhibit large but finite gradients from one phase to the other across a “thick”, three-dimensional interfacial region. The corresponding groundwork for models was laid by van der Waals [103, 104, 105] in terms of gradient theories, and further implemented by Korteweg [106] and Cahn and Hilliard [107], and many systems have been investigated using the resulting “phase field” models.

It is however challenging to experimentally access the resolution required for measuring smooth profiles of thermodynamic quantities in the vicinity of the phase interface. Hence, the validation of the aforementioned continuous approaches by experiments is often done indirectly, by relying on the observations of mesoscopic patterns of structures and dynamics that are strongly influenced by interfacial effects. As a general practice, diffusive models are successfully describing physical phenomena occurring at a length scale comparable with the thickness of the interfacial region [108] and are by nature, not well adapted for assessing macroscopic phenomena, at which scale the boundaries of bulk phases are better modeled by sharp interfaces [101, 102].

The precursors to the strictly two-dimensional model can be attributed to Gibbs [109], who first implemented the thermodynamic description of what he named the “dividing surface”. His description relies on so-called excess densities, which are thermodynamic extensive quantities assigned to the interface, considered itself as a 2D autonomous thermodynamic system [102]. Nowadays, two-dimensional equivalents of bulk models, such as the Boussinesq, Maxwell or Voigt constitutive equations, are used to describe interfacial rheometry [99, 101, 102]. The
compliance of Gibbs adsorption isotherms [110], or the description of the Marangoni effect
[111] may also be seen as celebrations of Gibbs’ model of interfacial thermodynamics. But
the ubiquitous use of surface boundary conditions in transport theories gives an even more
compelling reason for the fundamental role and success of a sharp interface approach.

Sharp interface models routinely involve intensive parameters of the interface. While the
surface tension or bending rigidity are accessible through measurements and have been
related to microstructural models [112, 113, 114, 115, 116, 117], attributing a surface tem-
perature, or surface chemical potential to the interface, which in nonequilibrium may differ
from the values in the surrounding bulk phases, has been the discussions of many attempts
[118, 119, 120, 121]. The fundamental surface thermodynamics is inherently different from
its bulk counterpart as already noticed by Gibbs since there is an unsatisfactory dependence
of surface excess densities on the chosen location of the interface. Recently this ambiguity
was resolved by Öttinger et al. by in fact exploiting it to define a gauge transformation under
which the surface thermodynamics must be invariant [122]. Savin et al. then studied the
consequences of gauge transformations on a notion of local equilibrium for interfaces [123].
A conceptually solid access to all intensive surface parameters and their equation of state even
in nonequilibrium was gained. It is the subject of this chapter to verify the model by using ex-
tensive nonequilibrium MD simulations, as well as to explore some of its consequences on the
smooth interface description. While the aforementioned attempts [118, 119, 120, 121] define
the local equilibrium hypothesis for interfaces identically to Savin et al. and obtain definitions
of the intensive surface parameters that are identical, the far reaching consequences of gauge
invariance on the surface thermodynamics have not been studied. As we will see, this leads
for instance to generalized Clapeyron’s relationships valid even in nonequilibrium.

In summary in this chapter we present the corner stone of a modern theory of interfaces [89]
and notably validate it with extensive, high-precision MD simulations:

- Sec. 3.2: Concept of gauge-transformations and local equilibrium hypothesis for inter-
  faces following Ref. [123].
- Sec. 3.3: Nonequilibrium MD simulation technique for study of liquid/vapor interface.
- Sec. 3.4: Results and Discussion.
- Sec. 3.5: Conclusion and Future Work.

3.2 Theory

Let us consider a single-component system with two phases separated by a planar dividing
surface. Calling \( x \) the coordinate normal to the interface, we write \( u(x), s(x) \) and \( \rho(x) \) the
continuous densities of internal energy, entropy and mass, respectively. To calculate the excess
mass density, we separate the variations \( \rho^\alpha(x) \) and \( \rho^\beta(x) \) of \( \rho(x) \) in each phase \( \alpha \) and
\( \beta \) (let \( \alpha \) be for smaller \( x \)) outside the interfacial layer. Upon choosing the precise location \( x^* \) of
the plane dividing the phases within the interfacial region, we then define the “sharpened” density
profile \( \rho^{\alpha,\beta}(x, x^*) = \rho^\alpha(x)\Theta(x^*-x) + \rho^\beta(x)\Theta(x-x^*) \), with the step function \( \Theta(x) = 1 \) for \( x \geq 0 \),
0 otherwise. The sharpening procedure thus requires the extrapolation of \( \rho^\alpha(x) \) and \( \rho^\beta(x) \) over the interfacial region (in equilibrium, \( \rho^\alpha \) and \( \rho^\beta \) are constant and their extrapolation is trivial). The excess mass density is then \( \rho^s(x) = \int [\rho(x) - \rho^\alpha, \beta(x, x^s)] \, dx \), and similarly for \( u^s \) and \( s^s \). Hence, all the excess densities depend on \( x^s \), chosen a priori arbitrarily. This degree of freedom is the one “apparent” lost with phase coexistence, upon invoking the Gibbs phase rule. But it raises a first problem, which is a striking and well-known paradox: interfacial thermodynamics cannot depend on the observer’s choice of a dividing surface, even though the excess densities depend on it.

When in contact with nonequilibrium bulk phases, interfaces quickly relax to states that can locally be described by the same set of variables as equilibrium interfaces, with the same thermodynamic relations between these variables. This rationale for the interfacial local equilibrium lead Savin et al. to hypothesize a generalization of Euler and Gibbs-Duhem relations for the nonequilibrium interface,

\[
\begin{align*}
  u^s &= T^s s^s + \gamma + \mu^s \rho^s, \\
  0 &= s^s dT^s + d\gamma + \rho^s d\mu^s,
\end{align*}
\]  

(3.1a) (3.1b)

where the temperature \( T^s \) and the chemical potential \( \mu^s \) must now be defined for the autonomous interface with surface tension \( \gamma \). The second problem is then to ascribe the intensive quantities \( T^s \) and \( \mu^s \) to such a 2D object.

Savin et al. used the formalism of gauge transformation to address the two problems emphasized above [123]. The gauge is the choice of \( x^s \), and the gauge transformation \( x^s \rightarrow x^s + \ell \) offsets \( x^s \) by a small displacement \( \ell \) towards the phase \( \beta \) and changes the densities to the new values, \( u^s \rightarrow u^s + \ell \Delta u \), \( s^s \rightarrow s^s + \ell \Delta s \) and \( \rho^s \rightarrow \rho^s + \ell \Delta \rho \). Here, we have called \( \Delta u = u^\beta - u^\alpha \), \( \Delta s = s^\beta - s^\alpha \) and \( \Delta \rho = \rho^\beta - \rho^\alpha \) the jumps of the corresponding bulk densities across the interface, assumed to be independent of the gauge \( x^s \). The intensive properties of the interface, \( T^s \), \( \mu^s \) and \( \gamma \), must be gauge-invariant observables, and only one of them sets the state of the interface. Since \( \gamma \) can be extracted unambiguously at both equilibrium and nonequilibrium (see later), Savin et al. suggested to use the surface tension as the thermometer of the interface: \( \gamma(T) \) is first tabulated at equilibrium, where \( T \) is the uniform bulk temperature, and then \( T^s \) is deduced from the value of \( \gamma \) in nonequilibrium \(^1\). Savin et al. then recommended that the interfacial chemical potential follows \( \mu^s = \mu(T^s) \) from the equilibrium chemical potential. To address the ambiguity in the choice of \( x^s \), we expressed the condition that the Euler and Gibbs-Duhem equations must be gauge-invariant by \( \Delta u = T^s \Delta s + \mu^s \Delta \rho \) and \( 0 = \Delta s dT^s + \Delta \rho d\mu^s \),

---

\(^1\)The reasoning relies on the structural autonomy of the interface: the interfacial region is not merely a transition zone for particles escaping one phase to join the other. Such non-autonomous interpretation of the interface would correlate its thickness with the traveling distance required by a particle for encountering enough collisions so as to join a well established phase. In the vapor-liquid system investigated here, this correlation does not exist: the width of the interfacial region increases with temperature, whereas the width of the Knudsen layer scales as the mean free path in the vapor, which decreases with the temperature.
respectively see also App. A.2. These equations are equivalent to the Clapeyron’s relationships

\[
\frac{d(\mu_s/T_s)}{d(1/T_s)} = \Delta u \frac{\Delta \rho}{\Delta \rho},
\]

(3.2a)

\[
-\frac{d\mu_s}{dT_s} = \Delta s \frac{\Delta \rho}{\Delta \rho},
\]

(3.2b)

which, if indeed proven to be generalizable to nonequilibrium, would allow to write Eqs. (3.1) into the equivalent forms:

\[
u_s(T_s, \rho_s) - \rho_s \frac{\Delta u}{\Delta \rho} \frac{d(\gamma / T_s)}{d(1/T_s)},
\]

(3.3a)

\[
u_s(T_s, \rho_s) - \rho_s \frac{\Delta s}{\Delta \rho} = -\frac{d\gamma}{dT_s}.
\]

(3.3b)

### 3.3 Nonequilibrium Simulations

We now employ nonequilibrium simulations to validate our thermodynamics description of the interface, Eqs. (3.1), by verifying Clapeyron’s Eqs. (3.2) and the local equilibrium Eqs. (3.3) with the proposed definitions for $T_s$ and $\mu_s$. We simulated\(^2\) a one-component Lennard-Jones fluid with both liquid (l) and vapor phases (g) in coexistence, $(\alpha, \beta) = (g, l)$, by using MD. Nonequilibrium situations were created for two fundamentally different transport processes: we studied systems with a heat flux or with a mass flux through the planar interface. The heat flux is imposed by tuning the temperatures of two thermostated regions in the vapor and the liquid, see Fig. 3.1A. A mass flux is created by removing particles from one phase and simultaneously inserting them in the other phase, at a given swapping rate. The temperature gradients investigated here are in the range $10^6 - 10^8$ K/m, and the speeds associated with the mass fluxes about 10 m/s (as a reference: the speed of sound in argon vapor is 319 m/s), see App. A.1. In what follows, all quantities are given in Lennard Jones units and calculated for the system’s steady state.

The surface tension $\gamma$ of the interface was calculated by integrating the difference between the pressure components normal and tangential to the interface [113]. In all the cases investigated here, the anisotropy of the pressure tensor is localized at the interface, and a spatial integration of the components’ difference does not depend on the location of the dividing surface. The surface tension is thus gauge-invariant. At equilibrium, an excellent fit of $\gamma(T)$ is $\gamma_0(1 - T/T_{\text{crit}})^\nu$, with $\gamma_0 = 2.2452$, $\nu = 1.26$ and $T_{\text{crit}} = 1.1192$ [124], see Fig. 3.1B. The fit serves as the calibration rule to extract the interface temperature $T_s = T_{\text{crit}}[1 - (\gamma/\gamma_0)^{1/\nu}]$ from the surface tension calculated in nonequilibrium situations.

Other specific atomistic expressions are time-averaged over steady state configurations to obtain $x$-dependent profiles of thermodynamic quantities. Fig. 3.2 shows typical profiles of $\rho(x)$ and $u(x)$ in a nonequilibrium situation. Along with the stress tensor, $\rho$ and $u$ are

---

\(^2\)We wrote our own simulation code from scratch in C++.
3.3. Nonequilibrium Simulations

Figure 3.1 – (A) Snapshot of MD simulations for a Lennard-Jones fluid. In the simulation box (projected here on the $x\gamma$-plane), a layer of liquid spontaneously forms to coexist with its vapor. The box is divided into 426 layers, and the colored layers are thermostated. (B) The surface tension measured in equilibrium at various temperatures of liquid-vapor coexistence. (C) The corresponding equilibrium chemical potential calculated using the Widom insertion method.

Figure 3.2 – Profiles of mass (A) and internal energy (B) densities in the vicinity of the interface subjected to a heat flux. (C) The excess densities $\rho^s$ and $u^s$, calculated from (A) and (B) as the shaded area between the profiles (colored curves) and their sharpened extrapolations (black lines) for various positions $x^s$ of the dividing surface. Uncertainties are below 1% of the range of values in all panels.
mechanical quantities whose atomistic expressions are exact in the interfacial region. The chemical potential $\mu(x)$ is obtained by the Widom insertion method [125, 126]. In equilibrium, the uniform potential can be fitted by $\mu(T) = \mu_0 + a T \ln T + b T$ with $\mu_0 = -7.6510$, $a = -4.9849$ and $b = 4.4042$, see Fig. 3.1C. In each bulk phase, the entropy density is calculated from the other profiles by invoking the Euler equation, $s(x) = u(x) T(x) - p(x) T(x) - \rho(x) T(x) T(x)$, with $p(x)$ the isotropic pressure and $T(x)$ the kinetic temperature.

We note that our simulations are significantly more precise than previous works on nonequilibrium vapor-liquid systems [124, 127]. High-precision was required to discern small gauge changes and was achieved by two means. First, for each simulation, 80 times more data were acquired as compared to Ref. [124]. Second, we eliminated any possible diffusion of the liquid film in the $x$-direction by “sticking” it to the thermostated wall, see App. A.1, instead of using the more common periodic boundaries.

### 3.4 Results and Discussion

To calculate the sharpened profile $\rho^g(x, x^s)$, we fit the bulk variations of $\rho(x)$ with linear functions of $x$ (Figs. 3.2A and 3.2B). The resulting lines deviates from the actual profile over the interfacial width $\omega$ ($\omega \sim 10$ in Fig. 3.2) which is the minimum coarse-graining scale in the sharp interface approach. Higher order extrapolations may indeed be used [118] without significantly changing the results presented here, as long as these functions do not capture variation at length scales below $\omega$. We observe that $\rho^g(x^s)$ and $u^g(x^s)$ depend linearly on $x^s$ (Fig. 3.2C), such that we may write

$$\rho^s(x^s) = \Delta \rho (x^s - x^s_\rho), \quad (3.4a)$$
$$u^s(x^s) = \Delta u (x^s - x^s_u), \quad (3.4b)$$

with $\Delta \rho = \rho^l - \rho^g$ and $\Delta u = u^l - u^g$. Here $x^s_\rho$ is the location of the “equimolar” interface such that $\rho^g(x^s_\rho) = 0$, and $x^s_u$ is the “equipotential” interface for which $u^g(x^s_u) = 0$. Importantly, there exist a non-negligible difference between $x^s_\rho$ and $x^s_u$ (see inset of Fig. 3.2C). The linearity of $\rho^s$ and $u^s$ with $x^s$ indicates that $\Delta \rho$ and $\Delta u$ do not significantly depend on the interface location, meaning that they are gauge-invariant. We initially inferred this approximation in our theoretical arguments. It comes from the fact that the bulk densities do not vary significantly over distances comparable to $\omega$, even in the extreme conditions of nonequilibrium investigated here. Hence, $\rho^g(x^s)$ varies by only a few percent when moving $x^s$ by 10, as opposed to $\rho^g(x^s)$, which can even change sign when moving the interface by $\sim 1$.

We also observe slow variations of $s(x)$ in the bulk phases, allowing us to extract, without calculating $s^s$, the interfacial jump $\Delta s = s^l - s^g$ directly from $s^l(x)$ and $s^g(x)$ and independently of any extrapolated location chosen within the interfacial region. One may wish to write $s^s$ using an expression similar to Eqs. (3.4), but it appears that an eventual “equientropic” gauge $x^s_s$ for which $s^s(x^s_s) = 0$ depends on the reference entropy. Augmenting this reference
3.4. Results and Discussion

Figure 3.3 – Kinetic temperature profiles in the vicinity of the interface subjected to a heat flux (A) or a mass flux (B). The red and blue lines are linear extrapolation of the bulk profiles and used to define the liquid and vapor interfacial temperatures, as shown by the dashes and compared with \( T^s \) (green dash). The shaded area indicates the interfacial region, with the equimolar and equipotential dividing surfaces shown by the green lines.

by \( S_0 \) translates \( s^x \) by \(-S_0 \rho^x\), \( \mu^x \) by \( S_0 T^s \) and \( \Delta s \) by \(-S_0 \Delta \rho \) (hence keeping Eqs. (3.1) and (3.2) unchanged). We prefer to express the explicit gauge dependence of \( s^x \) by also separating its reference-dependent component. Without loss of generality, we write

\[
s^x(x^s) = \Delta s (x^s - x^s_{\rho}) + \psi(T^s) \tag{3.5}
\]

where \( \psi(T^s) = s^x(x^s_{\rho}) \) is a gauge invariant thermodynamic function of the temperature only, and that does not depend on the reference entropy.

Although the temperature calculated from the kinetic energy has the classical interpretation in bulk phases, its meaning in the interfacial region is, admittedly, questionable. Nevertheless, Fig. 3.3 illustrates the conspicuous difficulty of defining a gauge-invariant interfacial temperature from such profile, since it exhibits sharp variations near the interface. The profiles of temperatures, linearly extrapolated from the bulk phases, intercept neither at a definable location, nor at the interfacial temperature \( T^s \) advocated here. Therefore, a systematic macroscopic description of the system must allow discontinuous temperatures across its interface.

The equimolar and equipotential dividing surfaces are shown in Fig. 3.3 to help outlining the interfacial region. For the mere purpose of illustrating our following arguments, \( T^s \) and \( T^l \), the vapor and liquid temperatures at the interface, are extracted at \( x^s = x^s_{\rho} \) (Fig. 3.3); but this choice has no effect on any of the conclusions in the present study.

Equipped with equilibrium and nonequilibrium values of \( \Delta \rho \), \( \Delta s \) and \( \Delta u \), we can now check the validity of the nonequilibrium Clapeyron’s relationships, Eqs. (3.2). To do so, we define the two coexistence temperatures, \( T^u_{\text{coex}} \) and \( T^s_{\text{coex}} \) that are solutions of Eqs. (3.2a) and (3.2b), respectively, for the observed jump ratios. These temperatures are uniquely defined using the fit \( \mu(T) \). If \( T = T^u_{\text{coex}} = T^s_{\text{coex}} \), then \( T \) is the best temperature choice for the interface to verify the Clapeyron’s relationships. Figure 3.4A-B reports the relative deviations of \( T^s \) from \( T^u_{\text{coex}} \).
Chapter 3. Nonequilibrium Thermodynamics of Interfaces

(Fig. 3.4A) and $T^\text{coex}_s$ (Fig. 3.4B) at equilibrium (where $T^s$ is the system’s uniform temperature) and at nonequilibrium (where $T^s$ is set by $\gamma$). It also presents the deviations of the vapor and liquid temperatures $T_g$ and $T_l$. Our definition $T^s$ consistently returns values that are, within the uncertainties, equal to the coexistence temperatures. In contrast, the vapor and liquid temperatures at the interface deviate from $T^\text{coex}_u$ and $T^\text{coex}_s$, and thus appear as inappropriate choices for the surface temperature.

We observe that $T^s$ neither correlates with the magnitudes of the heat or the mass fluxes, which quantify how far from equilibrium the system is being pushed, nor with the temperature jump $\Delta T = T^l - T^g$. Hence, discontinuities in temperature may also exist for moderate fluxes across the interface [128, 129, 130]. We verified however that despite the apparent scatter of the bulk temperatures in Fig. 3.4A, $\Delta \frac{1}{T}$ is proportional to the fluxes through the Kapitza resistances, which are indeed monotonic functions of $T^s$ [131].

We now assess the validity of the structural relationship Eq. (3.3a), which can be expressed in terms of the gauge difference

$$\Delta u (x^s_\rho - x^s_\rho) = \gamma(T^s) - T^s \gamma'(T^s),$$

(3.6)

by using Eqs. (3.4). We proceed as before by defining a structural temperature $T^\text{stru}_u$ as the unique solution of Eq. (3.6), and verify that the relative deviations of our choice of $T^s$ from $T^\text{stru}_u$ vanishes (within uncertainties) for all situations investigated here (Fig. 3.4C). This agreement is remarkable, both in equilibrium and nonequilibrium, despite the fact that Eq. (3.6) initially results from macroscale thermodynamic arguments and that $x^s_\rho - x^s_\rho$ is of the order of the molecular distances, that is, much smaller than $\omega$.

In a similar manner, we can use Eqs. (3.4a) and (3.5) to express the structural relationship Eq. (3.3b) as

$$\psi(T^s) = -\gamma'(T^s).$$

(3.7)

The direct validation of this equality requires a way to calculate $s^s$ that does not rely on thermodynamic relationships (which would inevitably assume a priori the local equilibrium of the interface). Although we could not implement such a method, we note that we have already proved $\gamma(T^s) = u^s + T^s \gamma'(T^s)$ (from Eq. (3.6)) and $s^s = \psi(T^s)$ (from Eq. (3.5)) in the equimolar gauge. This choice of gauge precludes any mass variation for the interface, and $\gamma$ then accounts for the Helmholtz free energy excess density of the interface as the amount of work per unit area that can be collected from it. Consequently, for $x^s = x^s_\rho$, we can write $\gamma(T^s) = u^s - T^s s^s$ which identifies $\psi(T^s) = -\gamma'(T^s)$, thus proving Eq. (3.7). Note that $\gamma'(T^s)$ is a gauge-invariant quantity that does not depend on the reference entropy, in accord with the requirements for $\psi(T^s)$. We have now validated Eqs. (3.1) and their gauge-invariance for a nonequilibrium vapor-liquid system where the interface has its temperature and chemical potential solely set by its surface tension.
3.4. Results and Discussion

Figure 3.4 – (A) Relative deviations of the vapor, liquid and interface temperatures from the values \( T_{\text{coex}} \) for which Eq. (3.2a) is verified. (B) and (C) are, respectively, the relative deviations of \( T^s \) from the temperature \( T_{\text{coex}}^s \) that verifies Eq. (3.2b), and from the temperature \( T_{\text{stru}}^s \) that verifies Eq. (3.3a). On the right side of each panel, the grey chart shows the corresponding box-and-whisker diagram in each thermodynamics situation investigated here.
3.5 Conclusion and Future Work

For a single-component fluid with vapor-liquid coexisting phases, the surface tension $\gamma(T)$ is the only observable required to establish the complete state of the planar interface: under constant $\gamma$, the interface will have the same intrinsic structure as in equilibrium, even if it is separating nonequilibrium phases. Stemming from this intuitive concept, and by relying on gauge transformation arguments, we were able to establish the local equilibrium status of a 2D thermodynamic system. We expect that these findings will help the development of interfacial nonequilibrium thermodynamics, even if they here concern a rather idealized situation.

The notion of local equilibrium by Savin et al. does not require to introduce a dependency of the surface entropy on the fluxes. This is required by frameworks of surface thermodynamics based on extended irreversible thermodynamics \[101\] – our simulation results clearly illustrate that this dependency is not required for establishing the concept of local equilibrium, even for interfacial systems.

To extend the applicability of our model, future studies should notably consider multicomponent systems, curved interfaces \[132\] and other coexisting phases. Nevertheless, our definition of the interface temperature, using the surface tension as the thermometer, already offers a new and practical asset to experimentalists. For a typical monoatomic fluid such as Argon, the liquid and vapor temperatures may differ from the surface temperature by a few degrees in nonequilibrium settings. Not only such differences should indeed be detectable using conventional instrumentations, they also may have heavy consequences when establishing constitutive models of interfaces. Notably, in a mass-conversion process such as condensation (or evaporation), the surface temperature can even be higher (or lower) than the surrounding bulk temperatures.
4 Nonequilibrium Thermodynamics of Nucleation

4.1 Literature Overview and Achievements

The formulation of evolution equations for nucleation in inhomogeneous time-dependent media has not received much attention in literature. This is connected to the inherent difficulty of the nucleation process associated to its nonequilibrium nature and the microscopic size of the nuclei - a successful theory must not only deal with the thermodynamics of small objects, but also treat fluctuations thermodynamically consistent as nucleation is a fluctuation dominated phenomenon. Despite of these difficulties, computational [80] and experimental studies [133, 134, 135] reveal that the presence of spatial inhomogeneities have significant influence on the nucleation process. In polymer crystallization and certain colloidal melts [80], the presence of a shear-flow suppresses the nucleation rate significantly, and, because the system is rendered non-isotropic, also drastically modifies the morphology of the nucleating material. During the nucleation process the properties of the background medium can be altered significantly. Even minor modifications of the ambient phase can lead to orders of magnitude different nucleation rates, and consequently it is of utmost importance to consistently keep track of the exchange dynamics of nuclei and the metastable phase, and in particular to deal with time-dependent environments.

Reguera and Rubi were among the first who developed within mesoscopic nonequilibrium thermodynamics a coarse-grained model for nucleation under temperature-gradients and shear flow [82, 83]. They recognized in addition to the size of nuclei, the importance of the velocity of nuclei as an internal degree of freedom that couples irreversibly to the external temperature- and velocity gradients. Several studies indicate that the state space of nuclei must also be equipped with the energy of the nuclei to treat nonisothermal effects which represent a relevant extension. This goes along with extensive studies [136, 137, 138] on two-phase systems where the coupling of energy and mass exchange have been demonstrated convincingly to be significant. In particular, in evaporation and condensation processes the exchange of particles between the phases is always accompanied by an exchange of heat, so that mass and energy transfer appear highly coupled. Even for single phase systems the
Dufour effect [139] (an energy flux driven by concentration gradients) and Soret effect [140] (mass fluxes driven by temperature gradients) illustrate that coupling of energy and mass fluxes are relevant.

We formulate here a nucleation theory of inhomogeneous media solely based on thermodynamic consistency arguments within the GENERIC [77] framework based on the assumption that the relevant internal degrees of freedom are their size $N_c$, momentum $P_c$ and internal energy $U_c$. Our work goes beyond the existing literature in that we simultaneously treat Brownian- and nonisothermal effects resulting through the mass, energy and momentum exchange between the nucleating phase and the metastable surrounding. While we treat the nucleus ambient phase through hydrodynamic fields, the dynamics of the nuclei is modeled with a Fokker-Planck equation. The latter allows a convenient solution technique by exploiting the associated stochastic process [141]. Our theory, for simplicity formulated for nucleation of a single species, is complete in the sense that all GENERIC requirements are satisfied, and we point out that effects of temperature gradients and shear-flow on nucleation can be incorporated in a straightforward manner. We identify special cases of our theory in which we recover Brownian corrections [74] as first highlighted by Reguera and Rubi, and nonisothermal contributions recognized by McGraw and Laviolette [85]. Our formulated dynamics in its most generality also represents an extension of nucleation theories of homogeneous media - we do not require concepts such as surface tension or other intensive thermodynamic quantities of microscopic nuclei nor the existence of a well-defined nuclei bulk phase. This is especially important for many substances for which the size of critical nuclei is only composed of a few tens of atoms so that the assignment of a nuclei bulk phase, or the frequently imposed capillarity approximation is doubtful [142].

As a benchmark test we study nonisothermal effects by specializing to the prototypical example of liquid drop nucleation and successfully illustrate that our thermodynamic inspired approach can indeed reproduce the fundamental results of a more microscopic approach by Barrett in 2008 [65]. Barrett studied the influence of nonisothermal effects on the nucleation rate in a supersaturated gas composed of monomers of mass $m$ within rate theory (for a detailed comparison of rate-theory and continuum approaches, see [143]). He fixed the rate at which nuclei exchange mass and energy with their surroundings by resampling to microscopic detailed balance arguments. A cluster partition function was used to obtain averaged thermodynamic properties of the nuclei. An approximate solution was given to Barrett’s rate equation whose parameters only contain the averaged thermodynamic properties of the nuclei and surrounding; it was shown that the nucleation rate $J_{\text{non-iso}}$ taking into account nonisothermal effects as compared to the rate $J_{\text{iso}}$ from the isothermal theory at temperature $T$ deviates as

$$\frac{J_{\text{non-iso}}}{J_{\text{iso}}} \bigg|_{\text{Barrett}} = \frac{1}{1 + \frac{H_{\text{Barrett}}}{2(1+\phi)}}. \quad (4.1)$$
4.1. Literature Overview and Achievements

Table 4.1 – Definitions of temperature $T_c$ of nuclei via internal energy $U_c$, or internal kinetic energy $E_{c}^{\text{kin}}$, as degrees of freedom in literature and in this work (GENERIC).

<table>
<thead>
<tr>
<th>Authors</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>McGraw/LaViolette</td>
<td>$dU_c = C_V dT_c$</td>
</tr>
<tr>
<td>Wedekind et al.</td>
<td>$E_{c}^{\text{kin}} = C_V T_c$</td>
</tr>
<tr>
<td>GENERIC</td>
<td>$1/T_c = \delta S_c(N_c,U_c)/\partial U_c$</td>
</tr>
</tbody>
</table>

Here, $H_{\text{Barrett}} = \frac{mL}{k_B T} - \frac{1}{2} - \frac{2}{3(N_c)^{1/3}k_BT} A_c^* \left( \gamma - T \frac{d\gamma}{dT} \right) + \frac{1}{2} k_BT_c$ is related\footnote{Barrett analyzed collisions of monomers with nuclei and realized that the dependence of the collision rate on the energy of colliding nuclei is related to their heat capacity at constant volume, $3/2k_BT$. But, when the increased collision rate of high energy monomers is taken into account, the dependence is on $3/2k_B + 1/2k_B$. Which is the origin of the term $1/2$ in $H_{\text{Barrett}}.$} to the change in the mean energy of the nuclei with respect to their mass at the critical size $N_c^*$. We introduced the latent heat of vaporization $L$, the surface tension $\gamma$, the area of a critically sized nucleus $A_c^*$, and the parameter $\phi \geq 0$ regulating the ability of the nuclei to accumulate energy without mass transfer. Barrett showed that depending on the thermo-physical properties nonisothermal effects can suppress the nucleation rate by $1 - 3$ orders of magnitude.

Furthermore, we will identify the limit $\phi \to \infty$ with the rapid thermal equilibration of nuclei, and recover the mesoscopic irreversible thermodynamics result [144] of Horst et al. concerning the suppression of the nucleation rate due to nonisothermal effects. Horst et al. studied nonisothermal nucleation by assigning a fixed size dependent non-fluctuating temperature contrary to our approach, where both, the size and energy, or equivalently temperature, of nuclei fluctuate.

Assigning a temperature $T_c$ to a nucleus which is inherently a small thermodynamic system is a controversial topic [40], and a bottle neck of Barrett’s work is the absence of a thermodynamic definition of the nucleus temperature $T_c$, see also Table 4.1. McGraw and LaViolette define $T_c$ via the thermodynamic relationship $dU_c = C_V dT_c$ valid for incompressible and sufficiently large nuclei [85]. Here, $U_c$ denotes the internal energy of a nucleus and $C_V$ is the heat-capacity of an ideal gas. Based on Einstein’s fluctuation theory they argue that in equilibrium the temperature $T_c$ is distributed around the ambient temperature $T$ according to $P_T(T_c) \propto e^{(C_V/k_B)\left[\ln(T_c/T) + (1 - T_c/T)\right]}$. Wedekind et al. studied [40] temperature fluctuations in direct MD simulations of the nucleation process. They measured the spontaneous internal kinetic energy $E_{c}^{\text{kin}}$ of the nuclei and defined the temperature $T_c$ via the relationship $E_{c}^{\text{kin}} = C_V T_c$ known from bulk thermodynamics. They found that in nonequilibrium $T_c$ is distributed according to $P_{T_{\text{loc}}}(T_c)$, where the “local equilibrium temperature” $T_{\text{loc}}$ of nuclei is introduced. Within our approach the definition of a nucleus temperature even in nonequilibrium is manifest and obtained through the general thermodynamic relationship
\[ T_c = \partial S_c(N_c, U_c) / \partial U_c, \] where \( S_c \) is the entropy of a nucleus. This definition is also suggested by Schmelzer et al. [145]. When restricting our approach to incompressible nuclei we will highlight that in equilibrium we obtain the law by McGraw and LaViolette, and in nonequilibrium the non-Gaussian temperature fluctuations \( P_{\text{loc}}(T_c) \) around \( T_{\text{loc}} \). In particular, we illustrate that for the case of nucleation in argon the local equilibrium temperature of nuclei is smaller than the ambient temperature \( T \) for subcritically sized nuclei and larger for critically and super-critically sized nuclei\(^2\). This insight traces back to the brute-force MD results by Wedekind [40] that have later been reconsidered by Schmelzer et al. [145]. The nonisothermal corrections implied by our framework hence reduce to up to date literature results in special cases, so that they present a plausible generalization beyond artificial assumptions on the nuclei.

In summary, guided by the GENERIC nonequilibrium thermodynamics described in detail in Sec. 2.1 we proceed as follows:

- Sec. 4.2: Introduction of the relevant state variables for the hydrodynamic fields of the environment, and for the internal degrees of freedom of the nuclei.
- Sec. 4.3: Phenomenological construction of the energy, entropy, Poisson- and dissipative bracket for isothermal nucleation / Discussion of resulting evolution equations.
- Sec. 4.4: Extension of building blocks to nonisothermal case / Discussion of resulting evolution equations.
- Sec. 4.5: Application to nucleation in a supersaturated gas / Discussion of suppression of nucleation rate due to nonisothermal effects in relation to Barrett’s theory and the theory of Horst et al. / Discussion of temperature fluctuations in relation to results of Wedekind et al. and McGraw and LaViolette.
- Sec. 4.6: Conclusion and future work.

### 4.2 State Variables

We investigate the nucleation of a one component system in a metastable phase. Every nucleus is characterized by its internal state \( x_c \). In the case of isothermal nucleation theory this state is given by \( x_c = (N_c, v_c) \), where \( v_c \) is the velocity of the nucleus and \( N_c \) its size. For nonisothermal nucleation processes we will extend the state space by incorporating the nucleus internal energy, so that \( x_c = (N_c, v_c, U_c) \). To describe the dynamics of the process, we use the density \( f(r, x_c) \) of nuclei with degree of freedom \( x_c \) at location \( r \). The mass of one unit or atom is \( m \), so that the total nucleus mass is \( M_c(N_c) = N_c m \). Every nucleus possesses a volume \( V_c(N_c) \) that solely depends on the size \( N_c \). From the distribution \( f \) the total number of nuclei \( \int d^3r dN_c \ f(r, x_c) \) can be obtained. The total number of nuclei in a nucleation process are not necessarily constant since nuclei can be spontaneously created from density fluctuations in

\(^2\)Notice, while Wedekind et al. identify the temperature of nuclei via their instantaneous internal kinetic energy, we rely on the use of the entropy of nuclei. These apparent different definitions of \( T_c \) lead however to similar fluctuation laws. We resolve this issue more cleanly in Chap. 5.
the metastable environment, however, the total particle number of the system is indeed a conserved quantity. The dynamics of the metastable medium is governed by its mass density \( \rho(r) \), the momentum density \( u(r) \) and the internal energy density \( u(r) \) at the position \( r \). Here, \( \rho, u \) and \( u \) exclude the nuclei contributions. We denote by \( v = \frac{u}{\rho} \) the velocity field of the metastable phase. The system is fully characterized by the state variables \( x_s = (\rho, u, u, f) \).

### 4.3 Isothermal Nucleation Theory

#### 4.3.1 Energy and Entropy

For convenience we introduce the notation \( \langle \ldots \rangle_f = \int dx_c \langle \ldots \rangle_f(r, x_c) \) for the ensemble average at a particular location \( r \) and double brackets \( \langle\langle \ldots \rangle\rangle_f = \int d^3r dx_c \langle \ldots \rangle_f(r, x_c) \) for spatially integrated and ensemble averaged quantities. We decompose the total system energy,

\[
E(x_s) = \int d^3r \left( \frac{u^2}{2\rho} + u \right) + \left\langle \frac{1}{2} M_c(N_c) v_c^2 + U_c(N_c) - \left( \frac{u^2}{2\rho} + u \right) V_c(N_c) \right\rangle_f,
\]

into contributions associated with the ambient phase and parts attributed to the nuclei. The last term in Eq. (4.2) takes into account the excluded volume that is occupied by the nuclei and where hence the metastable phase is absent. This subtle term arises since a fragment of a new phase is created at the expense of the metastable phase. The total system entropy is

\[
S(x_s) = \int d^3r \left( \frac{u^2}{2\rho} + u \right) + \left\langle S_c(x_c) - k_B \ln \left( \langle f \rangle s(\rho, u) V_c(N_c) \right) \right\rangle_f,
\]

and consists of the entropy of the metastable phase and a contribution due to the presence of nuclei. The latter consists of the logarithmic term known for distribution functions, and an additional entropy \( S_c(x_c) \) associated to every nucleus. The presence of this entropy is a result of coarse-graining from the atomistic level to our current mesoscopic level [77]. In particular, since the presence of a nucleus requires the absence of bulk phase, the entropy (or work) of formation of a single nucleus is naturally given by the difference \( S_c(x_c) - V_c(N_c) s(\rho, u) \).

#### 4.3.2 Reversible Structure of Evolution Equations

We decompose the Poisson structure into parts involving solely the nucleus contributions, \( \{ A, B \}_f \), parts containing only the hydrodynamic fields of the metastable phase, \( \{ A, B \}_H \), and an exchange bracket \( \{ A, B \}_{ex} \), so that the total Poisson bracket is given by

\[
\{ A, B \} = \{ A, B \}_H + \{ A, B \}_f + \{ A, B \}_{ex}.
\]

---

\(^3\)Notice, \( \langle\langle 1 \rangle \rangle_f = \langle 1 \rangle \langle f(r, x_c) \rangle \) is the density of nuclei at \( r \), and \( \langle\langle 1 \rangle \rangle_f \) the total number of nuclei in the system.
This Poisson-Bracket must be constructed such that all symmetries are obeyed for all observables $A$. In App. B.1 we show how the Poisson structure can be obtained by studying the related brackets of the effective bulk densities $\bar{\rho} = \rho (1 - \langle V_c \rangle_f)$, $\bar{u} = u (1 - \langle V_c \rangle_f)$, and $\bar{s} = s (1 - \langle V_c \rangle_f)$, and assuming that the distribution $f$ is naturally convected according to the usual geometric structure familiar from Boltzmann equations. We obtain:

$$\{A, B\}_H = -\int d^3r \, \rho \left( \frac{\partial A}{\partial u} \cdot \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial B}{\partial \rho} - \frac{\partial B}{\partial u} \cdot \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial A}{\partial \rho} \right)$$

$$- \int d^3r \, u \left( \frac{\partial A}{\partial u} \cdot \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial B}{\partial u} - \frac{\partial B}{\partial u} \cdot \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial A}{\partial u} \right)$$

$$- \int d^3r \, u \left( \frac{\partial A}{\partial u} \cdot \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial B}{\partial u} - \frac{\partial B}{\partial u} \cdot \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial A}{\partial u} \right)$$

$$- \int d^3r \, u \left( \frac{\partial A}{\partial u} \cdot \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial B}{\partial u} - \frac{\partial B}{\partial u} \cdot \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial A}{\partial u} \right),$$

where $p$ denotes the thermodynamic pressure of the metastable phase. The expression for the Poisson-bracket (4.5) for the hydrodynamic fields of the metastable phase is standard and its first instances in connection with the GENERIC framework can be traced back to the work of Grmela and Öttinger [90] where it is shown that this Poisson bracket indeed reproduces the reversible parts of the evolution equations of hydrodynamics. The nucleus distribution function is convected as [77]

$$\{A, B\}_f = \int d^3r \, dx_c \, f \left( \frac{\partial A}{\partial v_c} \frac{\partial}{\partial f} - \frac{\partial B}{\partial v_c} \frac{\partial}{\partial f} \right).$$

In order to highlight the structure of the exchange bracket $\{A, B\}_\text{ex}$ we introduce the notation

$$A = \rho \frac{\partial A}{\partial \rho} + u \frac{\partial A}{\partial u} + (u + p) \frac{\partial A}{\partial u},$$

so that the bracket takes the form:

$$\{A, B\}_\text{ex} = \int d^3r \, dx_c \, f \left( \frac{\partial A}{\partial v_c} \frac{\partial}{\partial f} \right) \left( \frac{\partial}{\partial r} \frac{V_c}{1 - \langle V_c \rangle_f} \right) - \left( \frac{\partial B}{\partial v_c} \frac{\partial}{\partial f} \right) \left( \frac{\partial}{\partial r} \frac{V_c}{1 - \langle V_c \rangle_f} \right).$$

The resulting Poisson bracket $\{A, B\}$ is such that the total mass of the system

$$M = \int d^3r \, \rho + \langle M_c (N_c) - \rho V_c (N_c) \rangle_f,$$

the total momentum

$$P = \int d^3r \, u + \langle M_c (N_c) u_c - u V_c (N_c) \rangle_f,$$

and the entropy $S$ fall in its null-space, i.e., $\{A, M\} = 0$, $\{A, P\} = 0$ and $\{A, S\} = 0$, so that not only energy, but also mass and momentum are conserved under reversible dynamics. Similar
4.3. Isothermal Nucleation Theory

Bracket structures for exchange mechanisms of two phases have been obtained in [122], where boundary conditions at the interface between two phases have been taken into account explicitly. An analogous term to Eq. (4.8) was added to ensure consistency of the GENERIC with the chain rule of functional calculus in the presence of moving and deforming interfaces. The term was noticed [122] to be crucial in obtaining mass and momentum conservation across phase boundaries, but upon introducing it, the Jacobi identity of the resulting Poisson bracket was lost. Despite having a similar structure, the exchange term $\{A, B\}_{ex}$ in this work has an entirely different status, but actually guarantees the validity of the conservation laws and the Jacobi identity. In our theory, the presence of a nucleating phase only modifies the metastable phase slightly, so that the resulting theory is more an effective medium theory than a theory that can cleanly distinguish two distinct bulk phases through the presence of a localized interface. The Poisson structure $\{A, B\}_{ex}$ implicitly assumes that there is no reversible exchange of mass between the nucleus and the metastable phase on our coarse-grained description of nucleation.

4.3.3 Irreversible Structure of Evolution Equations

We split the total dissipative bracket $[A, B]$ into a part $[A, B]_H$ attributed to the hydrodynamic fields ($\rho, u, u$), with the familiar irreversible dynamics of hydrodynamics, and a bracket $[A, B]_{ex}$ governing the irreversible exchange dynamics:

$$[A, B] = [A, B]_H + [A, B]_{ex}. \quad (4.11)$$

The hydrodynamic part $[A, B]_H$ is given by:

$$[A, B]_H = \int d^3 r 2\eta T \left[ \left( \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c f \rangle} \frac{\partial A}{\partial u} \right)^s - \kappa^s \left( \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c f \rangle} \frac{\partial B}{\partial u} \right) \right] :$$

$$+ \int d^3 r \kappa T \left( \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c f \rangle} \frac{\partial A}{\partial u} - \text{tr} \kappa \frac{1}{1 - \langle V_c f \rangle} \frac{\partial A}{\partial u} \right)$$

$$+ \int d^3 r \lambda T \left( \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c f \rangle} \frac{\partial A}{\partial u} \right) \left( \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c f \rangle} \frac{\partial B}{\partial u} \right) \left( \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c f \rangle} \frac{\partial B}{\partial u} \right), \quad (4.12)$$

where $\eta$ is the viscosity, $\kappa$ the bulk viscosity, $\lambda$ the thermal conductivity, and $\kappa$ is the velocity gradient tensor in the metastable phase. A superscript “s” on top of a tensor denotes the
symmetrized traceless part of that tensor. For the exchange bracket \([A, B]_{\text{ex}}\) we obtain:

\[
[A, B]_{\text{ex}} = \int d^3 r d x_c \left\{ \frac{\partial}{\partial x_c} \left[ \delta A \frac{M_c - \rho V_c}{1 - \langle V_c \rangle_f} \frac{\delta A}{\delta \rho} - \frac{M_c v_c - u V_c}{1 - \langle V_c \rangle_f} \frac{\delta A}{\delta u} \right] - \frac{1}{2} M_c (v - v_c)^2 + U_c - u V_c \frac{\delta A}{\delta u} \right\}.
\]

This bracket results solely from the requirement of producing an evolution equation for \(f\). That is of the Fokker-Planck type, together with the thermodynamic consistency requirements that the total mass, momentum and energy must clearly be in the null-space, i.e., \([A, M]_{\text{ex}} = 0\), \([A, P]_{\text{ex}} = 0\) and \([A, E]_{\text{ex}} = 0\), so that mass, momentum and energy are conserved quantities during the exchange process from the metastable bulk phase into the nuclei. Feedback effects on the environment are completely incorporated: any growth of the nucleus is accompanied by momentum and energy exchange. The phenomenological diffusion tensor \(D_{x, x_c}(r, x_c)\) contains the friction matrix \(\xi_{v_c}\) regulating the Brownian motion of nuclei in the metastable phase, and the coefficient \(D_{N, N_c}\) corresponding to mass-exchange:

\[
D_{x, x_c} = \begin{pmatrix} T \xi_{v_c}(N_c) & 0 \\ 0 & D_{N, N_c}(N_c) \end{pmatrix}.
\]

The transfer mechanisms of mass and momentum are assumed to be decoupled and independent of velocity. For an isotropic medium, \(\xi_{v_c} = \frac{1}{3} \text{tr}(\xi_{v_c}) I_{3 \times 3}\), where \(I_{3 \times 3}\) is the \(3 \times 3\) unit matrix.

### 4.3.4 Resulting Evolution Equation

Through the GENERIC equation (2.1) the dynamics of the host medium and the nuclei are now specified. We postpone the discussion of the dynamics of the ambient phase to nonisothermal nucleation, and restrict to the evolution equation of nuclei:

\[
\frac{\partial f}{\partial t} = - \frac{\partial}{\partial r} (v_f + f) + k_B M_c \frac{\partial}{\partial v_c} \cdot (v_c - v) f + k_B T \frac{\partial}{\partial v_c} \cdot \xi_{v_c} \cdot v_c \frac{1}{M_c} \frac{\partial}{\partial v_c} \cdot f \frac{\partial V_c}{\partial r} + \frac{\partial}{\partial N_c} D_{N, N_c} \left[ k_B \frac{\partial f}{\partial N_c} - f \frac{\partial}{\partial N_c} \left( S_c - \frac{U_c}{T} - V_c \frac{p}{T} + M_c \frac{\mu}{T} - M_c (v_c - v)^2 \right) \right].
\]
The Brownian motion of the nuclei results in the kinetic correction already discovered by Bashkirov in his statistical mechanics of Brownian motion [146]. Unlike other attempts to describe Brownian motion in inhomogeneous media [147], we recover this term since we keep rigorous track of the tiny volume terms in our derivation. The term on the second line describes the mass-accumulation and loss of the nuclei. Nucleation takes place in the nucleation landscape

\[ k_B V_S(x_{\text{env}}, N_c, \nu_c) = -\left(S_c - \frac{U_c}{T}\right) + \left(V_c \frac{p}{T} - M_c \frac{\mu}{T}\right) + \frac{1}{2} M_c \left(\nu_c - \nu\right)^2, \quad (4.16) \]

where \( x_{\text{env}} = (\rho, \mathbf{u}, \mu) \) denotes the state of the environment. In principle, Eq. (4.15) must be supplemented by boundary conditions on \( f(x_c) \) for small nuclei sizes \( N_c = 1 \). From a rigorous point of view this would require us to introduce in addition to the Poisson- and dissipative brackets also the corresponding boundary brackets for the distribution function \( f(x_c) \). Guidelines for such a procedure have recently been developed [148, 122]. Here we will motivate the boundary conditions on \( f(x_c) \) from a physical perspective when we apply our framework to a specific example, see also Sec. 4.5.

To investigate the nucleation landscape \( V_S \) in more detail, we assume that the nuclei are sufficiently large so that they can be attributed thermodynamic bulk and surface properties. Since we consider the process to be isothermal, the temperature of nuclei coincides with the ambient temperature \( T \). The internal energy of a nucleus is composed of bulk \( U_c^b \) and surface contributions \( U_c^s \), i.e., \( U_c = U_c^b + U_c^s \), where \( U_c^s \) is the excess internal energy of the interface separating the nucleus from the ambient phase. Similarly, the entropy \( S_c = S_c^b + S_c^s \) and mass \( M_c = M_c^b + M_c^s \) can be decomposed into bulk, \( S_c^b \) and \( M_c^b \), and excess contributions, \( S_c^s \) and \( M_c^s \). For the bulk terms, the Euler equation \( TS_c^b = U_c^b + p_c V_c - \mu_c M_c^b \) holds, where \( p_c \) is the bulk pressure of the nucleus and \( \mu_c \) its chemical potential. The surface satisfies the analogous relation \( TS_c^s = U_c^s - \gamma A_c - \mu_c M_c^s \), where \( \gamma \) is the surface tension of the nucleus and \( A_c \) its surface area. We assume that the chemical potential of the interface and bulk phase of the nucleus coincide. Exploiting the Euler equations for the bulk and the surface, the nucleation landscape is given by

\[ k_B V_S(x_{\text{env}}, N_c, \nu_c) = -M_c \left(\frac{\mu - \mu_c}{T}\right) + V_c \left(\frac{p - p_c}{T}\right) + \frac{1}{2} M_c \left(\frac{\nu - \nu_c}{T}\right)^2 + \frac{\gamma}{T} A_c. \quad (4.17) \]

The Brownian motion of the nuclei results in the kinetic correction already discovered by Reguera and Rubi [74]. Omitting the kinetic correction, we obtain the standard nucleation barrier [149, 27]. But here, we solely derived this result by exploiting the symmetries of the

---

3The bulk quantities \( M_c^b, S_c^b, U_c^b \) and \( V_c \), and the excess quantities \( M_c^s, S_c^s, U_c^s \) and \( A_c \), depend on the choice of the location of the dividing surface (interface) that separates the bulk phase of the nucleus from the ambient phase, see also Chap. 3. Therefore also \( M_c = M_c^b + M_c^s \) depends on this choice. We show, see Sec. 4.4.1, that the nucleation landscape \( V_S \) is independent on this choice if and only if \( TS_c^s = U_c^s - \gamma A_c - \mu_c M_c^s \) is independent on it. The latter statement is known as the gauge invariance of the local equilibrium hypothesis [123]. In Chap. 3 we validated this hypothesis thoroughly, so that \( V_S \) is invariant under the choice of the dividing surface.

---
dissipative bracket structure.

4.4 Nonisothermal Nucleation

Subsequently, we will seek the GENERIC building blocks for non-isothermal nucleation, where the internal state of the nucleus is characterized by \( x_c = (N_c, v_c, U_c) \), that is, the previously non-fluctuating internal energy \( U_c(N_c) \) becomes an independent dynamic variable. Abusing notation, \( x_c = (N_c, v_c) \rightarrow x_c = (N_c, v_c, U_c) \), we can directly adopt the expression of the total system energy (4.2), the total system entropy (4.3), and the Poisson- and dissipative brackets, see Sec. 4.3.3 and Sec. 4.3.2. Compared to the isothermal case, the state space \( \dot{x}_c \) is now extended, so that the diffusion tensor (4.14) has one additional row and column to account for energy fluctuations:

\[
D_{\dot{x}_c, \dot{x}_c} = \begin{pmatrix}
T \xi_{v_c}(N_c) & 0 & 0 \\
0 & D_{N_c N_c}(N_c) & D_{N_c U_c}(N_c) \\
0 & D_{N_c U_c}(N_c) & D_{U_c U_c}(N_c)
\end{pmatrix},
\]

where we assumed that energy fluctuations are decorrelated from Brownian motion. In the study of interfacial systems, the off-diagonal elements \( D_{N_c U_c} \) describing the interplay between mass and energy exchange of the nucleus with the metastable surrounding are known to be highly significant [136, 137, 138]. If we consider for illustration purposes a metastable gas phase where liquid drops are nucleating, then the coupling \( D_{N_c U_c} \) is related to the heat exchange in evaporation and condensation of particles. We assumed that the coefficients do not depend on the internal energy \( U_c \). Such a dependency is completely natural and can readily be implemented. In particular, in nuclei with high internal energy, nuclei constituents are more likely to escape [150], so that the coefficients would indeed depend on \( U_c \).

4.4.1 Resulting Evolution Equation

The dynamics of the nuclei is given by:

\[
\frac{\partial f}{\partial t} = -\nabla \cdot v_c f + k_B M_c \frac{\partial}{\partial v_c} \xi_{v_c} \cdot (v_c - v) f + k_B T \frac{\partial}{\partial v_c} \xi_{v_c} \cdot \frac{\partial f}{\partial v_c} + \frac{1}{M_c} \frac{\partial}{\partial v_c} \cdot f \frac{\partial V_c p}{\partial r} \\
+ \frac{\partial}{\partial N_c} D_{N_c N_c} \left[ k_B \frac{\partial f}{\partial N_c} - f \frac{\partial}{\partial N_c} \left( S_c - \frac{U_c}{T} - V_c \frac{p}{T} + M_c \frac{\mu}{T} - M_c \frac{(v_c - v)^2}{2T} \right) \right] \\
+ \frac{\partial}{\partial U_c} D_{N_c U_c} \left[ k_B \frac{\partial f}{\partial U_c} - f \frac{\partial}{\partial U_c} \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} \right) \right] \\
+ \frac{\partial}{\partial U_c} D_{U_c U_c} \left[ k_B \frac{\partial f}{\partial U_c} - f \frac{\partial}{\partial U_c} \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} \right) \right].
\]

(4.19)
4.4. Nonisothermal Nucleation

The driving force for energy fluctuations is the difference of the associated inverse temperature $\frac{1}{T} = \frac{\delta S}{\delta A}^{\text{bulk}}$ of a nucleus and inverse bulk temperature $\frac{1}{T}$. The evolution equation for $f(x_c)$ is supplemented by the medium evolution equations, discussed in App. B.2, where we also show the entropy generating processes, see App. B.3.

Assuming that the nuclei can be attributed thermodynamic bulk and surface properties, we proceed as in Sec. 4.3.4 to get further insight into the driving force for mass-transfer associated with the nucleation landscape $V_S$ that has the form (4.16), but with $U_c$ being now and independent variable. Notice, in absence of reversible effects, Eq. (4.19) can be cast into Eq. (1.2). It is useful to switch to the temperature $T_c$ obtained by inverting the relationship $U_c = U_c(T_c, N_c)$. As in Sec. 4.3.4, we introduce the bulk and surface contributions of $M_c$, $S_c$ and $U_c$, and write the Euler equation $T_cS_c^b = U_c^b + p_cV_c - \mu_cM_c^b$ for the bulk and surface, $T_cS_c^s = \gamma A_c - \mu_cM_c^s$. We assume that the surface temperature and surface chemical potential coincide with the corresponding bulk values. We also assume that the surface tension $\gamma = \gamma(T_c)$ depends solely on the temperature of the nucleus, see Chap. 3. The nucleation landscape is then given by

$$k_B V_S(x_{\text{env}}, x_c) = -M_c \left( \frac{\mu}{T} - \frac{\mu_c}{T_c} \right) + V_c \left( \frac{p}{T} - \frac{p_c}{T_c} \right) - \left( \frac{1}{T_c} - \frac{1}{T} \right) U_c + \frac{\gamma(T_c)}{T_c} A_c + \frac{1}{2} M_c \left( \mathbf{v} - \mathbf{v}_c \right)^2.$$  

(4.20)

Setting formally $T = T_c$ recovers the landscape (4.17) of the isothermal case. Ignoring the kinetic contribution in Eq. (4.20), the nucleation landscape (4.20) coincides with the equilibrium work of formation of nuclei, as obtained in recent work on the thermodynamics of nonisothermal nucleation by Alekseechkin [151]. Notice however, that the very origin of the nucleation landscape (4.20) emerges in our approach from dynamical considerations through the friction mechanism $[A, B]_{\text{exc}}$. The choice of the location of the dividing surface separating the bulk phase of the nucleus from the ambient phase is ambiguous up to a resolution $l$ comparable to the width of the corresponding interfacial transition zone, for more details, see also Chap. 3. Hence, suppose that the nucleus is spherical with a radius $r_c$, then $r_c$ is ambiguous within the length scale $l$. The mass of the surrounding ambient phase $M_{\text{env}|r_c}$, the excess mass of the interface $M_c^s|_{r_c}$, and the bulk mass of the nucleus $M_c^b|_{r_c}$ depend on the choice of $r_c$, but the total mass in the system, $M_{\text{env}|r_c} + M_c^s|_{r_c} + M_c^b|_{r_c}$, must be independent on this choice. This implies that the excess mass of different choices of $r_c$ are related, i.e., $M_c^s|_{r_c+l} = M_c^s|_{r_c} + 2A_c|_{r_c} + 2(l/r_c)A_c|_{r_c}$, and the volume $V_c|_{r_c+l} = V_c|_{r_c} + 2A_c|_{r_c}$ and surface $A_c|_{r_c+l} = A_c|_{r_c} + 2(l/r_c)A_c|_{r_c}$, for the nucleus transform under different reference choices of $r_c$. The entropies $S_c^b$ and $S_c^s$, and the momenta $P_c^b$ and $P_c^s$ obey similar transformation laws as $M_c^b$ and $M_c^s$. It is suggested [132], see also App. A.2, that in the presence of kinetic effects, also the total energy of the bulk phase $E_c^b = U_c^b + \frac{1}{2}P_c^b \cdot \mathbf{v}_c$ of the nucleus, and the surface energy $E_c^s = U_c^s + \frac{1}{2}P_c^s \cdot \mathbf{v}_c$, where we assume that the surface velocity coincides with the velocity of the nucleus, transform according to

---

5Since we inscribed thermodynamic bulk and interfacial properties to the nucleus, the nucleus must be sufficiently large so that a well defined bulk phase and interfacial transitions zone exists.
Chapter 4. Nonequilibrium Thermodynamics of Nucleation

\[ E^b_{r_c+1} = E^b_{r_c} + l A_c (u + u \cdot v/2) - 3(l/r_c) E^b_{r_c} + 3(l/r_c) E^b_{r_c} \]. The intensive parameters \( T_c, \mu_c, \gamma \) and \( \nu_c \) are invariant under transformations. The Euler equation for the surface can be rewritten in terms of the variables that exhibit the natural transformation behavior introduced above, i.e., \( T_c S^s_c = E^s_c - P^s_c \cdot v_c/2 - \gamma A_c - \mu_c M^b_c \). In a similar way, the nucleation landscape (4.20) can be rewritten in terms of the variables for which we introduced the transformation. By studying the transformation behavior of the nucleation landscape \( V^s(x_{env}, x_c) \) and the Euler equation for the surface it can be shown that \( V^s(x_{env}, x_c) \) is invariant if and only if the Euler equation for the surface is invariant. The validity of the invariance of the Euler equation for the surface has been suggested in [123], and is also verified in detail in Chap. 3, so that \( V^s(x_{env}, x_c) \) is indeed independent on the ambiguous choice of \( r_c \). This invariance allows us to express the nucleation landscape equally for any choice of the dividing surface, in particular for the choice of \( r_c \) where \( M^c_c = 0 \) (equimolar location, where \( M^b_c = M^b \)), using \( S^s_c = -A_c d\gamma/dT_c \) (see Chap. 3), we find

\[
k_B V^s(x_{env}, x_c) = -M_c \left( \frac{\mu_c}{T} \frac{\rho_c}{T_c} \right) + V_c \left( \frac{p_c}{T} - \frac{p_c}{T_c} \right) \left( \frac{1}{T_c} - \frac{1}{T} \right) U^b_c
\]

\[ + \frac{\gamma(T_c)}{T_c} A_c + \left( \frac{1}{T} - \frac{1}{T_c} \right) \left( \gamma(T_c) - T_c \frac{d\gamma}{dT_c} \right) A_c + \frac{1}{2} M^b_c(v - \nu_c)^2 \]  

This form highlights that the surface contributions to \( V^s(x_{env}, x_c) \) are solely related to the surface tension. This will be particularly useful for the subsequent application of our theory.

4.5 Application: Nucleation in Supersaturated Gas

Subsequently we study the evolution equations, (4.15) and (4.19), for the isothermal and nonisothermal nucleation processes when the metastable phase is a heat bath with fixed temperature \( T \) and density \( \rho \). Consequently, we neglect depletion effects in the environment, modeled as static background medium. Concretely, we investigate a supersaturated gas phase in which high density, incompressible liquid drops, or nuclei, are formed and grow. We treat the gas phase under the assumptions of ideality and investigate the instances that lead to suppression of the nucleation rate as compared to the isothermal case. We assume that the nuclei can be attributed bulk and interfacial thermodynamic properties, so that the validity of the specific forms for the nucleation landscapes (4.17) and (4.21), for isothermal- and nonisothermal nucleation is guaranteed.

4.5.1 Thermodynamic Model

The nucleation landscapes (4.17) and (4.21) require the equations of state of the nuclei, or alternatively, the explicit form of \( S_c(x_c) \). To this extend we postulate a local equilibrium hypothesis according to which the thermodynamic equations of state of the nuclei are the same whether they are in equilibrium, or nonequilibrium with their ambient phase. This raises the question of the definition of “equilibrium” for the nucleation phenomenon [27]. Here,
4.5. Application: Nucleation in Supersaturated Gas

to construct the equation of state for the nuclei we rely on the notion [152] of equilibrium, as the stable equilibrium of a nucleus of size \( N_c \) in a finite volume with its ambient phase at temperature \( T \) and mass density \( \rho_c^{eq,N_c}(T) \). In this equilibrium state, the Laplace-equation holds, which connects the surface tension of the nucleus with the pressure drop across its interface, but also the Clausius Clapeyron equation connecting the corresponding energy jumps with the surface tension holds [123, 153]. Assuming that the density \( \rho_c \) of nucleating liquid drops is much larger than the density \( \rho \) of the metastable gas and \( \rho_c^{eq,N_c}(T) \), our notion of equilibrium can be related to the state of phase-coexistence at saturation of a macroscopic liquid phase in contact with its vapor separated by a flat interface at temperature \( T \). We denote the density of the latter vapor by \( \rho_c^{eq,\infty}(T) \), and obtain through these considerations, see also App. B.4 for more details, the nucleation landscape of nonisothermal nucleation\(^6\)

\[
k_B V_S(x_{env}, x_c) = -N_c k_B \ln(S) + \frac{\gamma(T)}{T} A_c + \frac{1}{2} N_c m \frac{\nu_c^2}{T} - N_c c_P^c \left[ \ln \left( \frac{T_c}{T} \right) + \left( 1 - \frac{T_c}{T} \right) \right]
\]

(4.22)

and the caloric equation of state \( U^c_c(N_c, T_c) = C_V T_c - N_c (mL_c(T_c) - k_b T_c) \), where we assumed [65] that the latent heat of evaporation \( L \) is a function of temperature and obeys \( mL_c(T_c) = mL_0 + (c_P^c - \tilde{c}_P^c) T_c \), where \( c_P^c \) and \( \tilde{c}_P^c \) are the heat capacities at constant pressure per monomer of the saturated gas and the nuclei. We introduced the saturation ratio \( S = \rho / \rho_c^{eq,\infty}(T) \). The three first terms in Eq. (4.22) define the nucleation landscape of the isothermal theory. The fourth term involves non-isothermal corrections and is known from an analysis of temperature fluctuations by McGraw and LaViolette [85]. Resampling to the equilibrium solution \( f_{eq} \propto \exp(-V_S) \) of the evolution equation (4.19), the nucleus temperature \( T_c \) fluctuates around the ambient temperature \( T \) for any fixed size \( N_c \) in a non-Gaussian way. Within our thermodynamic analysis we however find corrections to the temperature fluctuations as proposed by McGraw and LaViolette involving the surface tension. Although in many studies the change of surface tension with temperature is ignored, for a variety of substances \( d\gamma / dT_c \) is comparable to \( \gamma / T_c \) and therefore non-negligible [66]. The surface tension correction to the nucleation potential vanishes in two prominent instances often encountered in literature; when \( \gamma \) is a constant independent on temperature and when \( \gamma \) is a linear function of temperature.

Finally, we specify further the functional form of the dissipative diffusion coefficients. We assume that the velocity friction is given by the Stokes-Einstein scaling:

\[
M_c \xi_{v_c}(N_c) = \xi_0 \rho_c^{-1/3} M_c^{1/3} I_{3 \times 3},
\]

(4.23)

where \( \xi_0 \) is a positive constant. The accumulation of mass and energy must scale with the surface area \( A_c \propto (M_c/\rho_c)^{2/3} \) of the nuclei, but also with the hitting frequency \( \propto \rho \) of gas

---

\(^6\)The volume term \( V_c \left( p/T - p_c/T_c \right) \) in Eq. 4.21 is negligible due to the assumptions \( \rho, \rho_c^{eq,N_c} \ll \rho_c \).
Chapter 4. Nonequilibrium Thermodynamics of Nucleation

molecules onto the nuclei, i.e.,

\[
\tilde{D} = \begin{pmatrix}
D_{N_e} & D_{N_e, U_e} \\
D_{N_e, U_e} & D_{0, N_e, U_e}
\end{pmatrix}
= \begin{pmatrix}
D_{0, N_e, N_e} & D_{0, N_e, U_e} \\
D_{0, N_e, U_e} & D_{0, U_e, U_e}
\end{pmatrix} \rho \left( \frac{M_e}{\rho_c} \right)^2,
\]

where \( D_{0, N_e, N_e}, D_{0, N_e, U_e} \) and \( D_{0, U_e, U_e} \) denote coefficients independent on \( N_e \).

4.5.2 Detailed Results

As specific model of liquid drop nucleation we investigate the nucleation of argon droplets in a metastable gas. In the text, we set the temperature at the critical point \( k_B T_{\text{crit}} = 1 \), the vapor mass density at the critical point \( \rho_{\text{crit}} = 1 \), the mass of monomers \( m = 1 \) and \( k_B D_{0, N_e, N_e} = 1 \) to define the dimensionless units. As model parameters we used for the heat capacity \( c_p = c_V = 3/2 k_B \), for the heat of evaporation \( L_0 = 4.7 \), for the mass density of the nuclei \( \rho_c = 2 \), for the friction coefficient \( \zeta_0 = 1 \) and finally the surface tension was chosen to be of the linear form \( \gamma(T_c) = 3.5 \times (1 - T_c/T_{\text{crit}}) \).

Here, we are interested in the correction of the nucleation rate due to nonisothermal effects, and following Kramer \[ 155\], the nucleation rate is obtained by solving the Fokker-Planck equations (4.15) and (4.19) for the isothermal- and nonisothermal nucleation process in the stationary limit. To this purpose, we exploit stochastic simulations, see also App. B.5. Roughly, the Fokker-Planck equations can be solved by resampling to their underlying stochastic process in the \( x_c \)-space, and the restriction to a stationary solution implies the proper boundary conditions on the stochastic process for small nuclei, \( N_e = 1 \), and large nuclei, \( N_e \gg N^*_e \). We compared our numerical results to an approximate solution of the stationary Fokker-Planck equation obtained via the well-known saddle-point approximation described in \[ 64, 156\]. We obtain

\[
\frac{J_{\text{non-iso}}}{J_{\text{iso}}} = \frac{1}{D_{N_e, N_e} \omega \sqrt{|\det G^*|}} |\lambda_{\text{min}}|,
\]

where \( \lambda_{\text{min}} \) is the negative eigenvalue of the \( 2 \times 2 \) matrix \( \tilde{D}^* G^* \). Here the superfix * indicates that the functions are evaluated at the saddle point \( (N_e = N^*_e, U_e = 0, T_e = T) \) of \( V_S(x_{\text{env}}, x_c) \), where \( V_S(x_{\text{env}}, x_c) \) is given in Eq. (4.22). Here, \( G^* \) is the Hessian of \( V_S(x_{\text{env}}, x_e) \) with respect to \( (N_e, U_e) \) at the critical size (note: at the saddle point \( P_e = 0 \)), and given by

\[
G^* = \frac{\zeta}{\sigma^2 U_e} \left( \begin{array}{cc}
1 - \frac{\omega^2}{\zeta^2} & \frac{1}{\zeta} \\
\frac{1}{\zeta} & \frac{1}{\zeta^2}
\end{array} \right).
\]

\( \text{Thermophysical data for argon is taken from [154]. Notice, the surface tension and heat of evaporation in [154] exhibit nonlinear temperature dependences in contrast to our model assumptions. We however analyze the nucleation process in a rather narrow range for values of the ambient temperature } T_e \text{ so that the nonlinear contributions are of minor importance. Here we do not analyze the effects of Brownian motion explicitly, and set the friction coefficient } \zeta_0 \text{ to the fixed arbitrary value } \zeta_0 = 1. \)
The coefficients are given by\(^8\)

\[
\sigma^2_{Uc} = C^*_V T - T^2 A^*_c \frac{d^2 \gamma}{dT^2}\bigg|_{T_c = T},
\]

\[
\frac{1}{\sigma^2_{Nc}} = -\gamma(T)\frac{d^2 A_c}{dN^2_c}\bigg|_{N_c},
\]

\[
\omega^2 = \frac{\sigma^2_{Uc}}{\sigma^2_{Nc}},
\]

\[
\zeta = mL(T) - \frac{5}{2} k_B T - \frac{dA_c}{dN_c}\bigg|_{N_c} \left(\gamma(T) - T \frac{d\gamma}{dT}\bigg|_{T_c = T}\right),
\]

\[
\xi = mL(T) - \frac{5}{2} k_B T - \frac{dA_c}{dN_c}\bigg|_{N_c} \left(\gamma(T) - T \frac{d\gamma}{dT}\bigg|_{T_c = T}\right),
\]

The reduction in nucleation rate as given by Eq. (4.25) is independent on the Brownian motion of the nuclei characterized by the friction coefficient \(\xi\), because both, the isothermal and nonisothermal theory, are evaluated in the presence of Brownian motion; In the saddle point approximation the Brownian motion correction to the isothermal theory and to the nonisothermal theory are identical. We can interpret \(TG^{-1}\) as the variance of the fluctuating quantities \(N_c\) and \(U_c\). Then the magnitude of fluctuations in energy roughly scale with \(\sigma^2_{Uc}\) while size fluctuations scale with \(\sigma^2_{Nc}\). In equilibrium this becomes evident by approximating the distribution function of nuclei near the saddle point

\[
f_{eq}(x_c) \propto \exp\left(-\frac{M_c v_c^2}{2k_B T}\right)\exp\left(-\frac{(N_c - N^*_c, U_c - U^*_c) G^*(N_c - N^*_c, U_c - U^*_c)}{2k_B T}\right),
\]

and in stationary nonequilibrium a more involved approximate solution exists [64, 156] that however offers the same interpretation of \(\sigma^2_{Uc}\) and \(\sigma^2_{Nc}\). In the limit of small energy fluctuations as compared to size fluctuations, identified with \(\omega^2 / \zeta \, \xi \ll 1\), we obtain

\[
\frac{J_{\text{non-iso}}}{J_{\text{iso}}} \bigg|_{\xi \, \omega^2 \ll 1} = \frac{1}{1 + \left(\frac{D_{0,Nc,Uc}}{D_{0,Nc,Nc}} + \frac{D_{0,Uc,Uc}}{D_{0,Nc,Nc}}\right)^2}.
\]

If we now take the statistical expressions obtained from rate theory for the coefficients of the diffusion matrix [66], \(D_{0,Nc,Uc} / D_{0,Nc,Nc} = 2k_B T\), \(D_{0,Uc,Uc} / D_{0,Nc,Nc} = 6(k_B T)^2 (1 + \phi)\) and we neglect the heat capacity of the interface related to the second derivative of temperature of the surface tension, we recover Eq. (4.1) of Barrett’s work. This is remarkable since Barrett’s work is based on statistical arguments within a rate theory approach while we entirely relied on thermodynamic arguments. Here, \(\phi \geq 0\) defines the ability of a nucleus to exchange energy without mass transfer.

We compare the saddle point solution (4.29) in different temperature regimes with the solution of the stochastic simulation as visualized in Fig. 4.1 for the coefficients of the diffusion matrix as

\[^8\]These coefficients turn out to be the same as derived by Barrett [65], because in the saddle point approximation the nucleation landscape (4.22) (quadratic expansion of \(V_S(x_{\text{env}}, x_c)\) around the saddle point) coincides with the one derived by Barrett. Note however, that the stochastic simulations of nucleation that we perform capture the nucleation landscape exactly.
Chapter 4. Nonequilibrium Thermodynamics of Nucleation

proposed by Barrett with $\phi = 0$. We also show the original theoretical results by Feder [64] that

\[ T / Equal 0.56 T_{crit} \]
\[ T / Equal 0.4 T_{crit} \]
\[ T / Equal 0.32 T_{crit} \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.1.png}
\caption{Reduction in nucleation rate due to nonisothermal effects at various ambient temperatures $T$ and supersaturation ratios $S$. Solid lines are predictions of Feder [64]. Dashed lines are predictions of Barret [65] and coincide with the saddle point approximation of our theory. Symbols result from stochastic simulations of our theory.}
\end{figure}

neglect the temperature dependence of the surface tension. Notice, we expect nonisothermal corrections to be most significant at low supersaturation. Decreasing the ambient temperature $T$ also amplifies nonisothermal effects.

Wedekind et al. argued [40] that in nonequilibrium the temperature $T_c$ fluctuates around the local equilibrium temperature $T_{loc}$ in the same way as $T_c$ fluctuates around the ambient temperature $T$ in equilibrium. The so called local equilibrium temperature $T_{loc}$ introduced by Wedekind et al. was then shown within MD simulations of nucleation of liquid argon drops to be smaller than the ambient temperature $T$ for subcritical nuclei and always larger for super critical nuclei. Around the critical size, the nuclei were observed to be hotter than the bath temperature $T$ as later also argued by Schmelzer et al. [145], where the MD simulations of Wedekind et al. [40] were reconsidered. We analyzed the local equilibrium temperature $T_{loc}$ in Fig. 4.2 for a supersaturation ratio of $\ln(S) = 3.5$ and ambient temperature $T = 0.4 T_{crit}$. The local equilibrium temperature $T_{loc}$ is obtained, see also Fig. 4.3, by fitting the temperature distribution $P_{T_{loc}}(T_c)$ in the stochastic simulations with

\[ P_{T_{loc}}(T_c) \propto \exp\left\{ N_c (c_v / k_B) [\ln (T_c / T_{loc}) + (1 - T_c / T_{loc})]\right\}. \]

We observe that the local equilibrium temperature of nuclei is smaller than the ambient temperature for subcritically sized nuclei, and larger for critically and supercritically sized nuclei. In general, the conclusion drawn on the temperature $T_c$ and its $N_c$-dependence crucially depends on its definition as already indicated by the work of Wedekind et al.[40]. This is also illustrated in the extensive study [67] of Wyslouzil and Seinfeld, and the more recent work by Barrett [157], where an average temperature $T_{av}$ is introduced via $\langle U_c \rangle_f = N_c c_v (T_{av} - T)$, and the average over $U_c$ is taken for the stationary nonequilibrium situation described by $f$. With this definition, contrary to $T_{loc}$, the temperature $T_{av}$ is always higher than the ambient temperature. But, unlike $T_{loc}$, the
4.5. Application: Nucleation in Supersaturated Gas

average temperature $T_{av}$ has no strict thermodynamic meaning. In Fig. 4.2 we also illustrate the prediction by Feder et al. – in their work $T_{loc}$ is obtained analytically in the saddle point approximation. In this approximation logarithmic fluctuations in $P_{T_{loc}}(T_c)$ would appear as centered Gaussians around $T_c = T$ which is the reason why the analytics of Feder et al. yield a local equilibrium temperature of $T_c = T$ at $N_c^*$.  

We have also studied, see Fig. 4.4, the reduction in nucleation rate when we vary the coupling coefficient $D_{0,N,U}$ from the case of completely coupled $p_H = 1$ to completely decoupled $p_H = 0$ heat and mass exchange between nuclei and surrounding, where $p_H = D_{0,N,U}^2 (D_{0,N,U}, D_{0,U,U}, u)$. We observe that when the exchange processes are highly coupled, the nonisothermal rate is drastically suppressed. But even when the processes are decoupled,
Chapter 4. Nonequilibrium Thermodynamics of Nucleation

nucleation is suppressed. Hence, temperature fluctuations push the nuclei to an unfavorable entropic state so that the energetic barrier they need to surmount to reach the critical size is generally larger. In a recent study [144] by Horst et al. it was argued within mesoscopic nonequilibrium thermodynamics that the nonisothermal nucleation rate is suppressed by

\[ J_{\text{non-iso}} / J_{\text{iso}} = (1 - p_H) / (1 + L(T)D_0, N, U_c / D_0, U_c, U_c). \]

In their study, the cluster temperature \( T_c \) does not fluctuate, but is set to a fixed value that depends on the size of the nucleus. That energy fluctuations lead to significant corrections for small values of \( \phi \) is illustrated in Fig. 4.4 where we compare the result of Horst et al. with our framework. It is the limit \( \phi \to \infty \) identified

![Graph showing the reduction in nucleation rate due to nonisothermal effects in dependence of coupling strength between mass and energy exchange for \( T = 0.32 T_{\text{crit}} \) and \( S = 5 \). For rapid thermal equilibration, \( \phi \to \infty \), the predictions of our theory (dashed lines: saddle point approximation, symbols: stochastic simulation) coincide with the predictions (solid lines) of Horst et al.](image)

with rapid thermal equilibration in which our results coincide with the study of Horst et al.

4.6 Conclusion and Future Work

We have formulated the nonequilibrium thermodynamics of nucleation under incorporation of Brownian- and nonisothermal effects within the GENERIC framework. Our approach applies to a wide spectrum of systems composed of a metastable phase treatable with hydrodynamic equations, and nuclei described by internal degrees of freedom. The evolution equations are complete in the sense that all structural requirements of the GENERIC formalism are satisfied. As a specific model system, we applied our approach to study the nucleation of incompressible liquid drops in a metastable gas and recovered the recent more microscopically derived results by Barrett [65] for the suppression of the nucleation rate due to nonisothermal effects. We also showed that when mass- and energy exchange between nuclei and ambient phase are highly coupled, the nucleation rate is more suppressed and in this respect recovered the literature result of Horst et al. [144]. We were able to reproduce the insight
by Wedekind et al. [40, 145] who studied the nucleation process within MD and found that the local equilibrium temperature of subcritically sized nuclei is always smaller than the ambient temperature in contrast to critically- and supercritically sized clusters which are warmer than their surrounding. We also showed that our approach recovers the proper energy fluctuations of nuclei which in equilibrium reduce to the law derived by McGraw and LaViolette [85], and in nonequilibrium to its extension [40] recognized by Wedekind and coworkers.

We did not apply our approach to time-dependent environments, where growing nuclei could deplete their ambient phase. We expect this to be most important in small finite systems, where it would be interesting to quantify confinement effects on the nucleation rate. These effects can suppress nucleation completely below certain threshold system sizes [158, 159], but have never been studied under incorporation of nonisothermal, and Brownian effects. We also found that pressure gradients in the environment couple reversibly to the velocity of the nuclei. This novel mechanism is a necessity to guarantee a thermodynamically admissible reversible structure of evolution equations. Further work is desirable to shed light on the importance of this new term.

A relevant generalization of our study concerns the extension of the dissipative bracket $[\cdot,\cdot]_{ex}$ to incorporate the effects of temperature gradients or shear-flows on nucleation. This can be achieved by taking into account cross correlations between environment fluxes associated with the dissipative bracket $[\cdot,\cdot]_H$ and fluxes describing the exchange of mass, momentum and energy in $[\cdot,\cdot]_{ex}$. Due to Curie’s principle, which roughly states that thermodynamic forces and fluxes of different tensorial character do not couple, the temperature gradient, for instance, solely couples to the momentum exchange mechanism in $[\cdot,\cdot]_{ex}$, and for this purpose the dissipative bracket

$$[A,B]_{ex,VT} = \int d^3 r d x_c \left\{ \frac{\partial}{\partial v_c} \left[ \frac{\delta A}{\delta f} - \frac{M_c - \rho V_c \delta A}{1 - \langle V_c \rangle_f} \frac{\delta A}{\delta \rho} - \frac{M_c v_c - u V_c}{1 - \langle V_c \rangle_f} \frac{\partial A}{\partial u} \right] \right\} \cdot D_{\nu_c,VT}(r, x_c) f(x_c) \cdot \left( \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial B}{\partial u} \right)$$

$$- \frac{1}{2} M_c (v - v_c)^2 + U_c - u V_c \frac{\delta A}{\delta u} \right\} \cdot D_{\nu_c,VT}(r, x_c) f(x_c) \cdot \left( \frac{\partial}{\partial r} \frac{1}{1 - \langle V_c \rangle_f} \frac{\partial A}{\partial u} \right)$$

must be added, where the $3 \times 3$ matrix $D_{\nu_c,VT}$ describes the coupling between temperature gradient and the velocity of nuclei. The evolution equations (4.15) and (4.19) for the nuclei are then supplemented by the term $-(\partial / \partial v_c) \cdot (k_B D_{\nu_c,VT}(r, x_c)) \cdot (\partial (1/T) / \partial r)$ already recognized by Reguera and Rubi in their mesoscopic nonequilibrium thermodynamics approach [82].
5 Nonequilibrium Statistical Mechanics of Nucleation

5.1 Literature Overview and Achievements

The nonequilibrium thermodynamics approach to nucleation in Chap. 4 yields evolution equations that directly describe the macroscopic quantities of interest. The phenomenological parameters, including the diffusion coefficients, and the specific functional form of the entropy must be fixed based on kinetic, and thermodynamic considerations, or can be used to fit experimental data, but lack a clear microscopic foundation. This drawback makes it difficult to investigate the influence of the microstructure on the nucleation process. The advantage is however the applicability in a wide range of practically relevant physical regimes. In contrast, MD obtains exact results, but is limited to rather high nucleation rates, see also Fig. 1.1. Only a systematic coarse-graining procedure that operates simultaneously on the microscopic and macroscopic levels of description offers the key to benefit from the known microstructure and the fact that only a few relevant macroscopic variables are physically relevant.

The widely used standard method reported in the literature [57, 58, 59, 60, 61, 62, 63] to obtain first principle based quantitative predictions, of for instance the nucleation rate, relies on the use of the Zeldovich equation (1.1) governing the dynamics of the probability \( f(N_c) \) that a nucleus of interest has \( N_c \) atoms. The diffusion coefficient \( D_{N_c,N_c} \) and nucleation landscape \( V_S(x_{\text{tot}}, N_c) \) can be extracted from simulations of atomistic systems: restricting to nucleation in a one-component system, standard MC simulations exploit small systems with \( N \) atoms, pressure \( P \) and temperature \( T \) to sample the probability \( \phi_S(x_{\text{tot}}, N_c) \) of occurrence of a nucleus of size \( N_c \).\(^1\) The link of the microscopically obtained probability \( \phi_S(x_{\text{tot}}, N_c) \) with the macro-physics manifests in the relationship \( V_S(x_{\text{tot}}, N_c) = -\ln(\phi_S(x_{\text{tot}}, N_c)) \). To obtain the diffusion coefficient \( D_{N_c,N_c} \), short-time MD simulations are exploited to measure the mean-square displacement in \( N_c \) that is directly related to \( D_{N_c,N_c} \) [160, 161].

The Zeldovich equation (1.1) can be solved in the stationary limit to obtain the nucleation rate

\(^1\)The choice of the isobaric-isothermal ensemble in computer simulations mimics the conditions of many real experiments which control exactly these variables to induce the nucleation process. Therefore the state of the system is characterized by \( x_{\text{tot}} = (N, P, T) \).
as \( J = J_0 e^{-\Delta V_S(x_{\text{tot}}, N^*_c)} \), where the prefactor \( J_0 \) is related to \( D_{N_c} \) and the nucleation landscape around the critical size \( N^*_c \), and \( \Delta V_S(x_{\text{tot}}, N^*_c) \) is the activation barrier high \( \text{(27)} \), see also Fig. 1.2. Sampling of \( V_S(x_{\text{tot}}, N_c) \) and \( D_{N_c} \) from atomistic simulations should hence imply first principle based nucleation rate predictions, but in this chapter we show that these predictions deviate 3–5 orders of magnitude from the exact nucleation rates obtained in the recent large-scale MD simulations \( \text{(29)} \) by Diemand et al. conducted in the experimental accessible supersaturation regime for nucleation in a metastable Lennard-Jones gas. This is particularly severe, since the Lennard-Jones gas is the most basic and frequently studied system, and the failure occurs in the experimentally accessible regime.

We argue that this failure is due to the truncated state space literature relies on, where the number of atoms \( N_c \) in a nucleus is considered the only relevant order parameter. Certain dynamic effects can only be captured by equipping the internal degrees of freedom of nuclei with additional order parameters as already recognized in work \( \text{(64, 65, 67)} \) focusing on non-isothermal corrections, work \( \text{(74)} \) treating translational and rotational effects, work \( \text{(162, 163)} \) analyzing the significance of shape and volume fluctuations of nuclei, and attempts \( \text{(164, 165)} \) dealing with potential energy fluctuations of nuclei.

In this chapter we go beyond the existing literature in that we formulate the nonequilibrium statistical mechanics of nucleation under incorporation of Brownian- and nonisothermal effects to obtain a complete and coherent procedure that not only dictates the structure of coarse-grained equations, but also the way microstructural information enters the equations in a coarse-grained way. We notably generalize the standard MC technique to obtain the nucleation landscape of the extended theory. By combining efficient MC simulations with short-time MD of small atomistic systems, we determine the thermo-physical information, and transport coefficients that enter the macroscopic model, which we conveniently solve with stochastic simulations to obtain quantitative predictions – we show that our extended model explains the lack in agreement between the MD simulations by Diemand et al. and the standard literature procedure formulated on the truncated state space. We demonstrate on the example of MFKT \( \text{(52)} \) that existing nucleation theories formulated on the truncated state space can be extended to our more general state space thereby improving the quality of their prediction. The MFKT, a non-perturbative approach to obtain the entropy associated to nuclei by assuming that the environment acts as a mean-field, is chosen since it relies on attributing a partition function to nuclei in a way that fits particularly well in our framework.

For the first time we are capable to show rigorously from a nonequilibrium statistical mechanics approach that the internal energy of nuclei indeed exhibit the equilibrium fluctuations \( \text{(85)} \) first derived by McGraw and LaViolette up to a modification that concerns the compressibility of nuclei which goes hence beyond the case captured by McGraw and LaViolette. Our approach also offers for the first time a microscopic justification for recent observations \( \text{(40, 75)} \) in direct MD simulations of nucleation that observed that the kinetic energy of nuclei fluctuate according to the law derived by McGraw and LaViolette without modifications, see also Sec. 4.1
and Table 4.1. Furthermore, we also recover the Brownian motion correction\(^2\) as suggested by Reguera and Rubi [74], and our nonequilibrium thermodynamics treatment in Chap. 4.

In summary, guided by the GENERIC nonequilibrium statistical mechanics described in detail in Sec. 2.2 we proceed as follows:

- **Sec. 5.2:** Construction of macroscopic model from microscopic considerations: microscopic definition of state variables, appropriate nonequilibrium ensemble, entropy functional, dissipative bracket, resulting macro-scale equations.
- **Sec. 5.3:** Discussion of various aspects of coarse-graining procedure: reproduce phenomenological dissipative bracket (4.13), “thermodynamic limit” of nucleation landscape, energy fluctuations, Brownian motion corrections.
- **Sec. 5.4:** Extension of MFKT to include nonisothermal- and Brownian effects, and application to argon nucleation.
- **Sec. 5.5:** Application of coarse-graining procedure to nucleation in Lennard-Jones gas: show that literature overestimates nucleation rate by \(3 - 5\) orders of magnitude, show that predictions are significantly improved by our coarse-graining procedure.
- **Sec. 5.6:** Conclusion and future work.

## 5.2 Derivation of Coarse-Graining Procedure

### 5.2.1 State Variables

We investigate nucleation in a metastable one component system. We characterize the state \(x_c = (N_c, P_c, U_c)\) of the nuclei by means of their number of atoms \(N_c\), their total momentum \(P_c\) and their internal energy \(U_c\). The incorporation of the total momentum allows for Brownian motion of the nuclei and the total energy as an additional variable is necessary to treat nonisothermal effects. The dynamics of a single nucleus is captured by the distribution function \(f(x_c)\) describing the probability that the nucleus has degrees of freedom \(x_c\).\(^3\) The nuclei are assumed to evolve independently, so that the evolution of each nucleus does not affect other nuclei and the single-nucleus distribution function \(f(x_c)\) is sufficient to capture the relevant macro-scale physics. We hence neglect the break-up of a nucleus into several nuclei and coalescence effects. We further characterize the full system in which nucleation takes place by its total energy \(E\), total number of particles \(N\), total momentum \(P\) and volume \(V\) so that its state is captured by \(x_{\text{tot}} = (N, P, E, V)\). Clearly, as \(x_{\text{tot}}\) consists of conserved quantities, the state vector \(x_{\text{tot}}\) is a constant of motion. The state variables \(x_c\) (or respectively \(f(x_c)\)) and \(x_{\text{tot}}\) are merely a splitting of degrees of freedom to capture the essential characteristics of the nucleus and its environment. However, \(x_{\text{tot}}\) is not the state of the nucleus ambient phase, but involves both, the nucleus and ambient phase degrees of freedom. In Sec. 5.3.1 we show

---

\(^2\)The Brownian correction to the nucleation barrier must however be supplemented with additional logarithmic corrections in the size of nuclei.

\(^3\)In the phenomenological approach, Chap. 4, \(f(r, x_c)\) denotes the number of nuclei per unit volume with properties \(x_c\) at \(r\). This is to be distinguished from the present definition of \(f(x_c)\).
Chapter 5. Nonequilibrium Statistical Mechanics of Nucleation

that upon a suitable transformation, the variables \( x_{\text{tot}} \) and \( x_c \) can indeed be used to split the degrees of freedom into nucleus, \( x_c \), and environment degrees of freedom, \( x_{\text{env}} \).

The macroscopic state variables must be computable by exploiting specific microscopic expressions. On this more detailed level of description, the system is characterized by \( N \) atoms with mass \( m \), position \( r_i \) and momentum \( p_i \) in a box of volume \( V \). All atoms build the microscopic phase space \( \tilde{\Gamma} = (r_1, p_1, \ldots, r_N, p_N) \). In order to distinguish particles that are part of our nucleus of interest from the remaining ones we introduce the function \( \Pi_{\theta(\Gamma)} \) on \( \tilde{\Gamma} \). We use the simple position dependent rule \( \Pi_{\theta(\Gamma)}(r_i) = 1 \) if particle \( i \) is part of the nucleus and 0 otherwise.\(^4\) Popular cluster criteria \( \Pi_{\theta(\Gamma)} \) of the kind are the Stillinger-cluster definition \([166]\), and its extension presented by ten Wolde and Frenkel \([63, 166]\), see also Sec. 5.5.2. We obtain the subsequent microscopic definition of the macro-variables \( x_c \) and \( f(x_c) \) characterizing the state of the nucleus:

\[
\begin{align*}
\Pi_{N_c} &= \sum_i \Pi_{\theta(\Gamma)}(r_i), \\
\Pi_{P_c} &= \sum_i p_i \Pi_{\theta(\Gamma)}(r_i), \\
\Pi_{I_{2c}} &= \sum_i \left[ \frac{(p_i - m \Pi_{E_c})^2}{2m} + \phi(r_i) \right] \Pi_{\theta(\Gamma)}(r_i), \\
\Pi_{f(x_c)} &= \delta(x_c - x_c),
\end{align*}
\tag{5.1}
\]

where \( \phi(r_i) \) denotes the total interaction potential of particle \( i \) due to all other particles. Using the shorthand notation \( \Pi_{x_c} = (\Pi_{N_c}, \Pi_{P_c}, \Pi_{I_{2c}}) \) we also introduced the atomistic expression for the distribution function \( f(x_c) \) in Eq. (5.1). The velocity \( \Pi_{P_c} \) of the nucleus is obtained from \( \Pi_{N_c} \Pi_{P_c} \) as the microscopic expressions for \( x_{\text{tot}} \) are introduced analogously.\(^5\): \( \Pi_N = N, \Pi_V = V, \Pi_P = \sum_i p_i \) and \( \Pi_E = \sum_i \left( \frac{p_i^2}{2m} + \phi(r_i) \right) \).

5.2.2 Nonequilibrium Ensemble

Under the assumption that the collection of variables \( (\Pi_{x_{\text{tot}}}, \Pi_f) \) captures all relevant physical processes on the macroscopic time-scale of interest, the nonequilibrium state of the system is characterized by the generalized mixed ensemble \([76, 77]\):

\[
\rho_{x_{\text{tot}}, \lambda_c} = \frac{1}{Z(x_{\text{tot}}, \lambda_c)} \delta(x_{\text{tot}} - x_{\text{tot}}) \exp \left( \int dx_c \lambda_c (x_{\text{tot}} - x_c) \Pi_{f(x_c)} \right),
\tag{5.2}
\]

where \( Z(x_{\text{tot}}, \lambda_c) \) is the partition function corresponding to \( \rho_{x_{\text{tot}}, \lambda_c} \), see Sec. 2.2. In particular, the Lagrange multipliers \( \lambda_c \) must be chosen to guarantee for the proper macroscopic averages of the slow variables, i.e., \( f(x_c) = \langle \Pi_{f(x_c)} \rangle \rho_{x_{\text{tot}}, \lambda_c} \), where the brackets denote an average over

\(^4\)We do not take into account the interaction between nuclei. Therefore, to study the nucleation process it is sufficient to consider a microscopic system that contains exactly one nucleus, so that the cluster criterion makes sense.

\(^5\)Following the notation of Sec. 2.2 we have \( x_c = (x_{\text{tot}}, f(x_c)) \) and \( \Pi_{x_c} = (\Pi_{x_{\text{tot}}}, \Pi_{f(x_c)}) \).
the entire phase space with respect to the ensemble $\rho_{x_{\text{tot}},\lambda_c}$. We also have $x_{\text{tot}} = \langle \Pi x_{\text{tot}} \rangle_{\rho_{x_{\text{tot}},\lambda_c}}$. While the variables $x_{\text{tot}}$ are treated microcanonically since the total system is closed and the quantities $x_{\text{tot}}$ rigorously conserved, the nucleus, as an open system, must be treated canonically through the use of Lagrange multipliers.

### 5.2.3 System Entropy

We first derive a useful identity which relies on the observation that the nonequilibrium ensemble can be rewritten as

$$
\rho_{x_{\text{tot}},\lambda_c} = \frac{1}{Z(x_{\text{tot}},\lambda_c)} \delta(\Pi x_{\text{tot}} - x_{\text{tot}}) e^{-\lambda_c(x_{\text{tot}},\Pi x_{\text{tot}})},
$$

and therefore the distribution $f(x_c)$ can be cast into the form

$$
f(x_c) = \langle \Pi f(x_c) \rangle_{\rho_{x_{\text{tot}},\lambda_c}} = \frac{Z(x_{\text{tot}},x_c)}{Z(x_{\text{tot}},\lambda_c)} \exp(-\lambda_c(x_{\text{tot}},x_c)).
$$

Here, $Z(x_{\text{tot}},x_c)$ is the microcanonical counterpart of $Z(x_{\text{tot}},\lambda_c)$,

$$
Z(x_{\text{tot}},x_c) = \int d\bar{\Gamma} \delta(\Pi x_{\text{tot}} - x_{\text{tot}}) \delta(\Pi x_c - x_c),
$$

and we associate it with the entropy $S(x_{\text{tot}},x_c) = k_B \ln(Z(x_{\text{tot}},x_c))$ of the system in state $x_{\text{tot}}$ with the nucleus of interest having properties $x_c$. This allows us to obtain the total system entropy $S(x_{\text{tot}},f)$, see Sec. 2.2, as

$$
S(x_{\text{tot}},f) = k_B \ln(Z(x_{\text{tot}},\lambda_c)) - k_B \int dx_c \lambda_c(x_{\text{tot}},x_c) f(x_c)
$$

$$
= -k_B \int dx_c \ln \left( \frac{e^{-\lambda_c(x_{\text{tot}},x_c)}}{Z(x_{\text{tot}},\lambda_c)} \right) f(x_c)
$$

$$
= -k_B \int dx_c \left[ k_B \ln(f(x_c)) - S(x_{\text{tot}},x_c) \right] f(x_c)
$$

$$
= -k_B \int dx_c f(x_c) \ln \left( \frac{f(x_c)}{\phi_S(x_{\text{tot}},x_c)} \right) + S_{\text{tot}}(x_{\text{tot}}),
$$

where $S_{\text{tot}}(x_{\text{tot}}) = k_B \ln(Z_{\text{tot}})$ is the entropy of the full metastable phase and contains its total partition function

$$
Z_{\text{tot}} = \int d\bar{\Gamma} \delta(\Pi x_{\text{tot}} - x_{\text{tot}})
$$

$$
= \int x_{\text{tot}} d\bar{\Gamma}.
$$
Chapter 5. Nonequilibrium Statistical Mechanics of Nucleation

In the last line of Eq. (5.7) the integration is over the full phase space compatible with the system state $x_{\text{tot}}$. The expression for the entropy $S(x_{\text{tot}}, f)$ contains

$$\phi_S(x_{\text{tot}}, x_c) = \langle \delta(\Pi_{x_c} - x_c) \rangle_{x_{\text{tot}}} \equiv \int_{x_{\text{tot}}} d\Gamma \delta(\Pi_{x_c} - x_c) \int_{x_{\text{tot}}} d\tilde{\Gamma},$$

(5.8)

as the probability of occurrence of a nucleus with properties $x_c$ in a system described by $x_{\text{tot}}$.

5.2.4 Dissipative Bracket

We require the dissipative bracket $[A, B]$ acting on the space of observables $A$ and $B$ that depend on $(x_{\text{tot}}, f)$. In App. C.1, based on the GENERIC nonequilibrium statistical mechanics, we show that:

$$[A, B] = \int d\bar{x}_c \left( \frac{\partial}{\partial \bar{x}_c} \frac{\delta A}{\delta f(x_c)} \cdot D_{x_c, \bar{x}_c}(x_{\text{tot}}, x_c) f(x_c) \cdot \frac{\partial}{\partial \bar{x}_c} \frac{\delta B}{\delta f(x_c)} \right),$$

(5.9)

where the elements of the diffusion tensor are

$$D_{x_c, \bar{x}_c}(x_{\text{tot}}, x_c) = \frac{1}{2k_B \tau_{\text{GK}}} \langle \Delta_{\text{GK}} \Pi_{x_c} \Delta_{\text{GK}} \Pi_{x_c} \rangle_{(x_{\text{tot}}, x_c)}.$$

(5.10)

The average $\langle ... \rangle_{(x_{\text{tot}}, x_c)}$ is over all configurations compatible with the state $x_{\text{tot}}$ of the total system and the initial state $x_c$ of the nucleus. Here, $\Delta_{\text{GK}} \Pi_{x_c} = \Pi_{x_c}(\tau_{\text{GK}}) - \Pi_{x_c}(0)$, where $\tau_{\text{GK}}$ is a time-scale on which the microscopic correlations drop off and the right hand-side in Eq. (5.10) reaches a plateau value. For the nucleation of liquid drops in a metastable gas, we recognize $\tau_{\text{GK}}$ as the intermediate time-scale between the collision time of gas particles with the nucleus and the time-scale on which changes in the nucleus state are recognizable on the coarse-grained level of description.

5.2.5 Resulting Evolution Equation

Through Eq. (2.1), where here the Poisson-bracket contribution is absent, see App. C.1, we find with the total system entropy (5.6) and dissipative bracket (5.9) the evolution equations:

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial x_c} \left( k_B D_{x_c, x_c}(x_{\text{tot}}, x_c) \left( \frac{\partial f}{\partial x_c} f(x_c) \frac{\partial V_S(x_{\text{tot}}, x_c)}{\partial x_c} \right) \right),$$

$$\frac{\partial x_{\text{tot}}}{\partial t} = 0.$$

(5.11)

The nucleation landscape $V_S(x_{\text{tot}}, x_c) = -\ln(\phi_S(x_{\text{tot}}, x_c))$ is related to the probability (5.8). When nucleation is treated with the truncated state space $x_{c, \text{trc}} = (N_c)$, i.e., when the nucleus is in isothermal equilibrium with its surrounding at temperature $T$ and Brownian motion of the nucleus is not taken into account, the Zeldovich equation (1.1) is recovered.
We reformulate our theory in terms of the state variables (5.9) in the new variables is now stated as A is absent, the observables by means of the usual chain rule of functional calculus [77]. Again, the reversible evolution f function V not have spatial variations, and are defined within the volume graining theory under the assumptions of homogeneity of the environment, these fields do not have spatial variations, and are defined within the volume V. Introducing the average \( \langle A \rangle_f = \int dx_c f(x_c) A \) of a coarse-grained variable A(x_c, x_{tot}) with respect to the distribution function f, and the volume \( V_c(x_c) \), and relative volume \( V_c' = V_c/V \) of a nucleus, we relate (x_{env}, f) to (x_{tot}, f):

\[
\begin{align*}
V(1 - \langle V'_c \rangle_f) \rho &= mN - m \langle N_c \rangle_f \\
V(1 - \langle V'_c \rangle_f) u &= P - \langle P_c \rangle_f \\
V(1 - \langle V'_c \rangle_f) u &= E - \left( U_c + \frac{P_c^2}{2mN_c} \right)_f - \frac{p^2}{2mN}.
\end{align*}
\] (5.12)

The GENERIC equation (2.1) and building blocks can be transformed from (x_{tot}, f) to (x_{env}, f) by means of the usual chain rule of functional calculus [77]. Again, the reversible evolution is absent, the observables A and B are now defined on the state space (x_{env}, f), and the dissipative bracket (5.9) in the new variables is now stated as

\[
[A, B]_{ex} = \int dx_c \left\{ \frac{\partial}{\partial x_c} \left[ \frac{\delta A}{\delta f} - \frac{M_c - \rho V_c}{1 - \langle V'_c \rangle_f} \frac{\delta A}{\delta \rho} - \frac{P_c - u V_c}{1 - \langle V'_c \rangle_f} \frac{\delta A}{\delta u} \right] - \frac{1}{2} \frac{M_c (v - v_c)^2 + U_c - u V_c}{1 - \langle V'_c \rangle_f} \frac{\delta A}{\delta u} \right\} \\
[5.13]
\]

\[
D_{x \cdot x} (x_{env}, f(x_c)) = \int dx_c \left\{ \frac{\partial}{\partial x_c} \left[ \frac{\delta B}{\delta f} - \frac{M_c - \rho V_c}{1 - \langle V'_c \rangle_f} \frac{\delta B}{\delta \rho} - \frac{P_c - u V_c}{1 - \langle V'_c \rangle_f} \frac{\delta B}{\delta u} \right] - \frac{1}{2} \frac{M_c (v - v_c)^2 + U_c - u V_c}{1 - \langle V'_c \rangle_f} \frac{\delta B}{\delta u} \right\}.
\]
where we introduced the velocity of the environment \( v(\rho, u) = u/\rho \) and the velocity \( v_c(\mathbf{N}_c, \mathbf{P}_c) = \mathbf{P}_c/(m_N N_c) \) of the nucleus. We hence recover the phenomenological bracket (4.13) specialized to nonisothermal nucleation in Sec. 4.4. The integral over space in Eq. (4.13) is now absent, and the nucleus volume \( V_c \) replaced by \( V_c' \) as an artifact of considering in the coarse-graining approach the distribution function \( f(x_c) \) that is not spatially resolved to \( f(r, x_c) \) like in the phenomenological approach.

The variables \( (x_{\text{env}}, f) \) also allow for a straightforward interpretation of thermodynamics. To this extend the total system entropy is represented as \( S(x_{\text{env}}, f) = S(x_{\text{tot}}(x_{\text{env}}, f), f) \) and similarly \( S(x_{\text{env}}, x_c) = S(x_{\text{tot}}(x_{\text{env}}, x_c), x_c) \) in Eq. (5.6). In the variables \( (x_{\text{env}}, f) \) it is natural to assume that the entropy \( S(x_{\text{env}}, x_c) \) splits into an environment entropy density \( s(x_{\text{env}}) \) depending only on the environment state and an entropy \( S_c(x_c) \) attributed to the nucleus, so that \( S(x_{\text{env}}, x_c) = V \left( 1 - \langle V'_c \rangle \right) f(x_{\text{env}}) + S_c(x_c) \), and therefore the total system entropy (5.6) follows the phenomenological equation (4.3):

\[
S(x_{\text{tot}}, f) = V s(x_{\text{env}}) - \langle S_c(x_c) - k_B \ln(f) - s(x_{\text{env}}) V_c \rangle f. \tag{5.14}
\]

The representation in terms of the new variables defines hence naturally the nucleus ambient phase temperature \( T \) through \( 1/T = \partial s(x_{\text{env}})/\partial u \), and the chemical potential \( \mu \) as \( \mu / T = -\partial s(x_{\text{env}})/\partial \rho \). The temperature \( T_c \) of the nucleus can be defined thermodynamically by observing changes in the entropy when the nucleus internal energy \( U_c \) changes at fixed environment state, i.e., \( 1/T_c = \partial S(x_{\text{env}}, x_c)/\partial U_c = \partial S_c(x_c)/\partial U_c \). In the variables \( (x_{\text{tot}}, x_c) \) the thermodynamic relationships are less intuitive, and we find for instance

\[
\frac{\partial V_S(x_{\text{tot}}, x_c)}{\partial U_c} = \frac{1}{k_B T} - \frac{1}{k_B T_c}. \tag{5.15}
\]

The environment variables \( x_{\text{env}} \), unlike \( x_{\text{tot}} \), have non-trivial evolution equations. Here, we do not show the evolution equations for \( x_{\text{env}} \), but focus on the dynamics for \( f \) that is now obtained from the dissipative bracket and the total system entropy as

\[
\frac{df}{dt} = \frac{\partial}{\partial x_c} \cdot k_B \mathbf{D}_{x_c x_c}(x_{\text{env}}, x_c) \cdot \left( \frac{\partial f}{\partial x_c} + f \frac{\partial V_S(x_{\text{env}}, x_c)}{\partial x_c} \right). \tag{5.16}
\]

Nucleation takes place in the nucleation landscape

\[
k_B V_2(x_{\text{env}}, x_c) = -\left( S_c(x_c) - \frac{U_c}{T} \right) + \left( V_c \frac{\mu}{T} - m_N c \frac{(v_c - v)^2}{2T} \right) + m_N c \frac{(v_c - v)^2}{2T} + \frac{3}{2} k_B \ln(N_c). \tag{5.17}
\]

This is the expression of the nucleation landscape in the nonequilibrium thermodynamics description of the nucleation process, see also in Sec. 4.4.1. Here, the entropy of the nucleus seemingly depends on the momentum \( \mathbf{P}_c \), but it can be shown through statistical mechanics arguments [167] that the entropy \( S_c(x_c) \) is related to the entropy \( S_c(N_c, U_c) \), where the momen-
We introduced the atomistic expression $\Pi$ we integrate out the momentum degrees of freedom. The momentum and position degrees of freedom of the atoms can be separated, so that version (5.8) involving microcanonical averaging must be used.

5.3.2 Nucleation Landscape in Thermodynamic Limit

Sampling the probability $\phi_S(x_{\text{tot}}, x_c)$, see Eq. (5.8) requires, to calculate the probability of occurrence of a nucleus with properties $x_c$ in the microcanonical ensemble defined by the state $x_{\text{tot}}$. In the prominent case of a sufficiently large system ensemble averages become identical and instead of averaging over the microcanonical ensemble we can sample over the isobaric-isothermal ensemble with fixed number of particles $N$, fixed pressure $p$ and temperature $T$. By Galilean invariance we can set $P = 0$ without loss of generality. We define the corresponding system state by $x_{\text{tot}} = (N, p, T, P = 0)$. To evaluate the probability (5.8) we hence obtain the alternative expression

$$\phi_S(x_{\text{tot}}, x_c) = \frac{\int d\Gamma \delta(\Pi_{x_c} - x_c) e^{-\frac{1}{k_B T}(\Pi_{\text{kin}} - p \Pi_{\text{V}})}}{\int d\Gamma e^{-\frac{1}{k_B T}(\Pi_{\text{kin}} - p \Pi_{\text{V}})}}. \quad (5.18)$$

In this section, we abuse notation and denote the average over the isobaric-isothermal ensemble also by $\langle \ldots \rangle_{\text{int}}$ due its statistical equivalence to the microcanonical average, see Eq. (5.8), for large systems. By the same argument other ensembles can be used to sample $\phi_S$, such as the canonical or grandcanonical. Only when the system size is small, the rigorous exact version (5.8) involving microcanonical averaging must be used.

The momentum and position degrees of freedom of the atoms can be separated, so that $\phi_S(x_{\text{tot}}, x_c)$ can be sampled by MC simulations on the position of the particles. To this extent we integrate out the momentum degrees of freedom\(^6\):

$$\phi_S(x_{\text{tot}}, x_c) = \int dE_c' \left\langle \delta(\Pi_{N_c} - N_c) \delta(\Pi_{P_c} - P_c) \delta \left( \Pi_{U_c}^{\text{pot}} + E_c' - U_c \right) \delta \left( \Pi_{E_c^{\text{kin}, t}} - \frac{p_c^2}{2mN_c} - E_c' \right) \right\rangle_{x_{\text{tot}}} \propto \frac{1}{N_c^{3/2} \Gamma(C_V k_B + 1)} \int_0^\infty dE_c' \left( \frac{E_c'}{k_B T} \right)^{C_V / k_B} e^{-\frac{1}{k_B T}\left( E_c' + \frac{p_c^2}{2mN_c} \right)} \phi_S(x_{\text{tot}}, N_c, U_c - E_c'). \quad (5.19)$$

\(^6\)Notice, $\phi_S(x_{\text{tot}}, x_c)$ is normalized in $x_c$. 

We introduced the atomistic expression $\Pi_{U_c}^{\text{pot}}$ of the potential energy of the nucleus as the sum of the potential energies of its atoms, analogous to Eq. (5.1). Analogously, $\Pi_{E_c^{\text{kin}, t}}$ is the total...
kinetic energy of a nucleus as the sum of the kinetic energy of its atoms. The integration over $E'_c$ is over all possible internal kinetic energy contributions. Here, $\phi_S(x_{tot}, N_c, U_c - E'_c)$ denotes the probability that in the isobaric-isothermal ensemble the nucleus of interest has size $N_c$ and potential energy $U_{pot}^c = U_c - E'_c$. Furthermore, $C_V = \frac{3}{2} k_B N_c - \frac{5}{2} k_B$ is the heat-capacity of an ideal gas, and $\Gamma$ the Gamma-function. The probability $\phi_S(x_{tot}, N_c, U_{pot}^c)$ can conveniently be sampled by means of MC simulations since it does not depend on the momentum of atoms.

To gain further insight, we approximate the probability $\phi_S(x_{tot}, N_c, U_{pot}^c)$ by the saddle point approximation in the potential minimum $U_{pot,0}^c(N_c) = \arg\min_{U_{pot}^c} \phi_S(x_{tot}, N_c, U_{pot}^c)$. We evaluate the second derivative of $\phi_S(x_{tot}, N_c, U_{pot}^c)$ with respect to $U_{pot}^c$ around $U_{pot,0}^c(N_c)$, which we denote by $H(N_c)$, and find:

$$\phi_S(x_{tot}, N_c, U_{pot}^c) \propto \sqrt{H(N_c)} \phi_S(x_{tot}, N_c) e^{-H(N_c)} \frac{(U_{pot}^c - U_{pot,0}^c)^2}{2}.$$  \hspace{1cm} (5.20)

The factor of $\sqrt{H(N_c)}$ is arising for normalization reasons. The relevant probability $\phi_S(x_{tot}, N_c)$ of the truncated theory is recovered from

$$\phi_S(x_{tot}, N_c) = \int dU_{pot}^c \phi_S(x_{tot}, N_c, U_{pot}^c)$$
$$= \int dU_{pot}^c \left\langle \delta(\Pi_{N_c} - N_c) \delta(U_{pot}^c - U_{pot}^c) \right\rangle_{x_{tot}}$$
$$= \left\langle \delta(\Pi_{N_c} - N_c) \right\rangle_{x_{tot}},$$

and we can define the corresponding nucleation landscape $V_S(x_{tot}, N_c) = -\ln(\phi_S(x_{tot}, N_c))$. With the approximation (5.20) we can solve the integral in Eq. (5.19) analytically. A more elegant way is to rewrite $\phi_S(x_{tot}, x_c)$ in the form

$$\frac{\phi_S(x_{tot}, x_c)}{\phi_S(x_{tot}, N_c)} \propto \sqrt{H(N_c)} e^{-\frac{U_{pot}^c - U_{pot,0}^c}{2}} \int_0^\infty dE'_c e^{-H\left(\frac{U_c - E'_c - U_{pot,0}^c}{2} - \frac{E'_c}{k_B} + \Gamma(C_V/k_B)\ln\left(\frac{E'_c}{k_B}\right)\right)}.$$  \hspace{1cm} (5.22)

We approximate the exponent in the integral to second order around the saddle point $E'_c = E'_c(N_c, U_c)$ and we are then able to calculate the resulting Gaussian integral. The lower integration boundary can be shift to $-\infty$ since the main contribution of the integral comes from values $E'_c > 0$ so that the nucleation landscape $V_S(x_{tot}, x_c) = -\ln(\phi_S(x_{tot}, x_c))$ is given by

$$V_S(x_{tot}, x_c) = V_S(x_{tot}, N_c) + \frac{p_c^2}{2mN_c k_BT} + \frac{3}{2} \ln(N_c) + \ln(\Gamma(C_V/k_B) + 1) + H\left(\frac{U_c - E'_c - U_{pot,0}^c}{2}\right)^2$$
$$+ \frac{E'_c}{k_BT} - (C_V/k_BT)\ln\left(\frac{E'_c}{k_BT}\right) + \frac{1}{2} \ln\left(1 + \frac{C_V/k_BT}{(E'_c)^2}\right) + \text{const}(T)$$

(5.23)

that turns out to compare excellently with the true solution (5.22) down to $N_c = 5$, see also
Fig 5.1. To gain further insight, we introduce the thermodynamic definition of the nucleus

\[ \phi_S(x_{\text{tot}}, N_c) \]}

temperature \( T_c \) via Eq. (5.15). Employing now the specific expression (5.23) for the purpose of evaluating the left hand-side of Eq. (5.15) we find the caloric equation of state\(^7\),

\[ U_c = C_V T_c + U_c^{\text{mol,0}} + \frac{P_c^2}{2 k_B T m N_c} + 2 \ln(N_c) - \frac{(C_v / k_B)}{\ln(T_c/T)} + \left( 1 - \frac{T_c}{T} \right) \]

and with this, the saddle point in Eq. (5.22) can be represented as \( E^*_c = C_V T_c \). The internal energy of a nucleus is hence given by the kinetic term \( C_V T_c \) and a potential energy contribution involving the most probable potential energy \( U_c^{\text{mol,0}} \) at a given nucleus size \( N_c \), and a correction for nonisothermal effects. When \( T = T_c \), the nucleus is in the potential minimum of the landscape \( \phi_S(x_{\text{tot}}, x_c) \) at fixed \( N_c \) and \( P_c \). Plugging Eq. (5.24) and \( E^*_c = C_V T_c \) back into the expression (5.23) and expanding the logarithm of the \( \Gamma \)-function with Stirling’s approximation, we obtain the final form for the nucleation landscape\(^8\)

\[ V_S(x_{\text{tot}}, N_c) = V_S(x_{\text{tot}}, N_c) + \frac{P_c^2}{2 k_B T m N_c} + 2 \ln(N_c) - \frac{(C_v / k_B)}{\ln(T_c/T)} + \left( 1 - \frac{T_c}{T} \right) \]

\[ + \frac{1}{2 k_B^2 H} \left( \frac{1}{T} - \frac{1}{T_c} \right)^2 + \theta \left( \frac{1}{N_c} \right) + \text{const}(T). \]

Note, \( V_S(x_{\text{tot}}, N_c) \) is the usual barrier to nucleation in the absence of Brownian-motion and non-isothermal effects. In particular, \( 3/2 \ln(N_c) \) of the correction are due to the introduction of the momentum \( P_c \) into the nucleus state space and \( 1/2 \ln(N_c) \) through the Stirling approximation.

\(^7\)To obtain Eq. (5.24) we ignored the second last term in Eq. (5.23) since compared to the other terms it is of subleading order in \( N_c \).

\(^8\)The surface tension corrections to the nucleation landscape of the phenomenological approach, see Eq. (4.22) are not recovered. This might be an artifact of choosing the harmonic form (5.20) for \( \phi_S(x_{\text{tot}}, N_c, U_c^{\text{mol}}) \).
Chapter 5. Nonequilibrium Statistical Mechanics of Nucleation

mation on the Gamma function \( \Gamma \left( \frac{C_V}{k_B} + 1 \right) \). We here recover all corrections reported in the literature, including the momentum contribution obtained through entirely thermodynamic arguments by Reguera and Rubi [74], and the fourth term governing temperature fluctuations derived by McGraw and LaViolette for incompressible nuclei [85]. The additional temperature fluctuation contribution proportional to \( \frac{1}{H} \) has not been reported in the literature to our knowledge. We postpone further discussion of the temperature fluctuations to Sec. 5.3.3, and the discussion of the momentum corrections to Sec. 5.3.4.

5.3.3 Discussion of Temperature Fluctuations

It has been convincingly demonstrated in MD simulations [40, 75] of nucleation that when only the properties \( x_c^\text{red} = (N_c, E_{\text{kin},1}) \) of a nucleus are measured, the temperature \( T_c \) can be defined by \( T_c = E_{\text{kin},1}/C_V \) and its equilibrium fluctuations obey the law derived by McGraw and LaViolette, \( P_T(T_c) \propto \exp\left(\frac{C_V}{k_B} \ln \left( \frac{T_c}{T} \right) + \left( 1 - \frac{T_c}{T} \right) \right) \). In App. C.2 we derive this assertion rigorously based on our nonequilibrium statistical mechanics.

By working with the state space \( x_c = (N_c, P_c, U_c) \) we have knowledge of the potential energy contributions through \( U_c \) and it is then natural, that these contributions give rise to the more complicated caloric equation of state (5.24) rather than \( E_{\text{kin},1} = C_V T_c \). The law derived by McGraw and LaViolette is strictly only valid for incompressible nuclei, and the internal kinetic energy \( E_{\text{kin},1} \) does not invoke information about the nucleus volume, so that the temperature definition via \( E_{\text{kin},1} = C_V T_c \) naturally gives rise to the fluctuations derived by McGraw and LaViolette. When the state space \( x_c \) is used, where the temperature \( T_c \) is assigned though the internal energy \( U_c \), then \( T_c \) implicitly has information about the compressed state of the nucleus, since in \( U_c \) the potential energy is hidden, which in return depends strongly on the volume of the nucleus. Therefore, the additional contribution in Eq. 5.25, proportional to \( \frac{1}{H} \), takes the compressed state of the nucleus into account.

5.3.4 Discussion of Momentum Fluctuations

The momentum \( P_c \) in the state space leads to the kinetic term \( P_c^2/(2k_B T m N_c) \) in the nucleation landscape, see Sec. 5.3.1 or Eq. (5.25), but also to the complementary term \( 3/2 \ln(N_c) \). In Sec. 5.3.1 this can be derived based on considerations of the partition function underlying the entropy \( S(x_{\text{tot}}, x_c) \), and in Eq. (5.25) the logarithmic term is an artefact of the normalization condition of \( \phi_S(x_{\text{tot}}, x_c) \) with respect to \( P_c \). In the nonequilibrium mesoscopic thermodynamics approach of Reguera and Rubi [74], but also our earlier work on the nonequilibrium thermodynamics of nucleation, see Chap. 4, solely the kinetic term is present - entirely nonequilibrium thermodynamics inspired approaches generally suffer from the difficulty in obtaining consistently all logarithmic corrections in \( N_c \) [168]. As such the logarithmic correction of \( 1/2 \ln(N_c) \) in Eq. (5.25) resulting from the Stirling approximation of the exact nucleation landscape (5.23) can probably not be thermodynamically derived.
5.4. Application: Mean-Field Kinetic Theory

In their work [74] about rotational and translational effects in nucleation theory Reguera and Rubi describe the nucleation process in terms of \((N_c, v_c)\), and the dynamics of the distribution \(f(N_c, v_c)\) is driven by a nucleation landscape of the form \(V_{S}^{RR}(x_{\text{tot}}, N_c, v_c) = V_S(x_{\text{tot}}, N_c) + m N_c v_c^2/(2 k_B T)\). They then argue that a clear separation of time-scales between relaxation in \(v_c\) and \(N_c\) exists that allows them to eliminate \(v_c\) adiabatically from the Fokker-Planck equation for \(f(N_c, v_c)\) to obtain a reduced description, similar to the Zeldovich equation (1.1), in terms of the distribution function \(V_{S}^{RR}(x_{\text{tot}}, N_c) = V_S(x_{\text{tot}}, N_c) + 3/2 \ln(N_c)\). Consequently, the nucleation barrier that enters the nucleation rate prediction is increased by \(3/2 \ln(N_c)\).

In Sec. 5.5 we evaluate the diffusion tensor (5.10) within MD for nucleation in a Lennard-Jones gas and we cannot confirm the aforementioned time-scale separation. In this case, the adiabatic elimination of variables cannot be performed to obtain a simple Fokker-Planck equation for \(f(N_c)\) which allows a straightforward nucleation rate prediction through the usual saddle-point approximation. But instead, we can rely on the multidimensional generalization [156, 66] of the saddle-point approximation. Neglecting energy fluctuations (and the term \(1/2 \ln(N_c)\) in Eq. (5.25) resulting from the aforementioned Striling approximation) for this discussion, the nucleation landscape of our theory is stated in the form \(V_{S}^{RR}(x_{\text{tot}}, N_c, P_c) = V_S(x_{\text{tot}}, N_c) + 3/2 \ln(N_c) + P_c^2/(2 k_B T m N_c)\). But evaluating this barrier at the saddle point \((N_c^*, P_c^*)\), where clearly \(P_c^* = 0\), we obtain \(V_{S}(x_{\text{tot}}, N_c^*, P_c^*) = V_S(x_{\text{tot}}, N_c^*) + 3/2 \ln(N_c^*)\), so that the final nucleation barrier entering the nucleation rate prediction coincides with the discussion of Reguera and Rubi, see also App. C.4.

If Reguera and Rubi had used the multidimensional generalization of the saddle-point approximation to evaluate the nucleation rate, they would not have observed a reduction in nucleation rate due to Brownian effects. From a nonequilibrium statistical mechanics perspective, the kinetic term \(P_c^2/(2 k_B T m N_c)\) must be accompanied by \(3/2 \ln(N_c)\), and in this respect we regard the statistical approach as the correct one.

We also remark, that the equivalent momentum corrections to the nucleation landscape (5.25) can alternatively be obtained by deriving the nonequilibrium statistical mechanics with the state space \((N_c, P_c, U_c)\), \((N_c, P_c^2, U_c)\), or \((N_c, E_{\text{kin}}^{\text{i}} U_c)\) since for the case of homogeneous environments we consider, momentum has no preferential direction, see App. C.3.

5.4 Application: Mean-Field Kinetic Theory

At the example of the MFKT of nucleation [27] we illustrate that our work represents a powerful tool to extend existing nucleation theories to our richer state space. Concretely, we here rely on the results of Sec. 5.3.1.

In his work [52], Kalikmanov derived a non-perturbative expression for the partition function \(Z_{S}^{F}(N_c, T)\) of a nucleus by microscopic considerations, assuming that the ambient phase acts as a mean-field on the nucleus. His theory is valid for isothermal nucleation at temperature \(T\)
and in particular he finds

\[
\ln(Z^K_c(N_c, T)) = -N_c \frac{\mu_{\text{sat}}(T)}{T} - [N^0_c(N_c, T) - 1] \theta_{\text{micro}}(T) + \ln \left( V \frac{\rho_{\text{eq},\infty}(T)}{m} \right),
\]

(5.26)

where the chemical potential \( \mu_{\text{sat}}(T) \), the mass density \( \rho_{\text{eq},\infty}(T) \) at saturation, and the mass of atoms \( m \) are introduced. Here, \( N^0_c \) can be interpreted as the number of particles located at the surface of the nucleus and \( \theta_{\text{micro}} \) is a “microscopic” surface tension.

The entropy \( S^K_c(N_c, T) \) and internal energy \( U^K_c(N_c, T) \) of the nucleus of the isothermal theory are then given by

\[
S^K_c(N_c, T) = k_B \ln(Z^K_c(N_c, T)) + k_B T \frac{\partial Z^K_c(N_c, T)}{\partial T},
\]

\[
U^K_c(N_c, T) = k_B T^2 \frac{\partial Z^K_c(N_c, T)}{\partial T},
\]

(5.27)

by means of the usual definitions of statistical mechanics.

### 5.4.1 Extension of State Space

We exploit a local equilibrium hypothesis to extend the entropy obtained by Kalikmanov to nonisothermal nucleation. To this extent, notice that the entropy \( S_c(N_c, T) \) of a nucleus can be viewed as a property of the nucleus only and in this sense does not depend on the state of the environment. In isothermal nucleation the temperature of the nucleus \( T_c \) coincides with the ambient temperature, so that \( T = T_c \) and we can equally write \( S_c = S_c(N_c, T_c) \). We postulate the hypothesis of local equilibrium in the sense that a nucleus in nonisothermal nucleation that can be assigned the temperature \( T_c \) has the same properties as a nucleus in isothermal nucleation that takes place at temperature \( T = T_c \). Since the entropy, and analogously the internal energy of the nucleus are solely a property of the nucleus and do only depend on the nucleus state, we hence find the generalizations \( S_c(N_c, T_c) = S_c^K(N_c, T_c) \) and \( U_c(N_c, T_c) = U_c^K(N_c, T_c) \) of the entropy and energy of the nucleus to describe nonisothermal nucleation. The temperature \( T_c \) is now related to \( U_c \) and \( N_c \) by \( 1/T_c(N_c, U_c) = \partial S_c/\partial U_c \). This implies \( S_c(N_c, U_c) = S_c(N_c, T_c(N_c, U_c)) \). The associated nucleation landscape is obtained by means of the analysis presented in Sec. 5.3.1.

### 5.4.2 Nucleation in Supersaturated Argon

As a specific model system we consider the nucleation of argon\(^9\) droplets in a supersaturated gas in the low-supersaturation regime studied by Diemand et al. through brute-force MD simulations [29]. This allows to compare our predictions directly with first hand exact results on the nucleation rate. We have computed, see App. C.4 and App. C.5, the isothermal MFKT

---


\(^9\)We state thermophysical data of argon and the the evaluated nucleation rates in terms of the Lennard-Jones parameters \( \sigma = 3.822 \times 10^{-10} \text{ m}, \epsilon = 1.654 \times 10^{-21} \text{ J} \) and \( m = 6.690 \times 10^{-26} \text{ kg} \), see also Sec. 5.5.1.
Table 5.1 – Thermo-physical data of argon [29].

<table>
<thead>
<tr>
<th>$k_B T / \epsilon$</th>
<th>$p_{eq,\infty}^s / \epsilon^3$</th>
<th>$\gamma \sigma^2 / \epsilon$</th>
<th>$\rho \sigma^3 / m$</th>
<th>$B_2 / \sigma^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>$2.55 \times 10^{-2}$</td>
<td>0.453</td>
<td>0.696</td>
<td>-5.26</td>
</tr>
<tr>
<td>0.8</td>
<td>$4.53 \times 10^{-3}$</td>
<td>0.863</td>
<td>0.797</td>
<td>-7.75</td>
</tr>
<tr>
<td>0.7</td>
<td>$1.37 \times 10^{-3}$</td>
<td>1.09</td>
<td>0.813</td>
<td>-9.65</td>
</tr>
<tr>
<td>0.6</td>
<td>$2.54 \times 10^{-4}$</td>
<td>1.33</td>
<td>0.882</td>
<td>-12.9</td>
</tr>
<tr>
<td>0.5</td>
<td>$2.54 \times 10^{-5}$</td>
<td>1.57</td>
<td>0.921</td>
<td>-18.15</td>
</tr>
</tbody>
</table>

Table 5.2 – Nucleation rate predictions of metastable argon at various temperatures $T$ and supersaturations $S$ (and mass density $\rho$) of the ambient phase. The rates $J_{MD}$ correspond to MD simulations [29] by Diemand et al., the predictions $J_K$ to the original MFKT [52], and $J_{K,ext}$ to our extension of MFKT.

<table>
<thead>
<tr>
<th>$k_B T / \epsilon$</th>
<th>$S$</th>
<th>$\rho \sigma^3 / m$</th>
<th>$\log \left( \frac{J_{MD}}{\sigma^3 \tau} \right)$</th>
<th>$\log \left( \frac{J_K}{\sigma^3 \tau} \right)$</th>
<th>$\log \left( \frac{J_{K,ext}}{\sigma^3 \tau} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>72.8</td>
<td>0.008</td>
<td>-11.36 ± 0.03</td>
<td>-9.15</td>
<td>-12.14</td>
</tr>
<tr>
<td>0.5</td>
<td>59.2</td>
<td>0.007</td>
<td>-13.01 ± 0.02</td>
<td>-10.41</td>
<td>-13.44</td>
</tr>
<tr>
<td>0.5</td>
<td>48.7</td>
<td>0.005</td>
<td>-15.07 ± 0.04</td>
<td>-11.83</td>
<td>-14.92</td>
</tr>
<tr>
<td>0.6</td>
<td>16.9</td>
<td>0.008</td>
<td>-11.75 ± 0.01</td>
<td>-9.53</td>
<td>-12.42</td>
</tr>
<tr>
<td>0.6</td>
<td>15.6</td>
<td>0.007</td>
<td>-12.64 ± 0.02</td>
<td>-10.17</td>
<td>-13.10</td>
</tr>
<tr>
<td>0.6</td>
<td>14.0</td>
<td>0.006</td>
<td>-14.39 ± 0.05</td>
<td>-11.16</td>
<td>-14.15</td>
</tr>
<tr>
<td>0.6</td>
<td>12.0</td>
<td>0.005</td>
<td>-16.32 ± 0.73</td>
<td>-12.88</td>
<td>-15.93</td>
</tr>
<tr>
<td>0.8</td>
<td>4.02</td>
<td>0.030</td>
<td>-9.08 ± 0.01</td>
<td>-7.36</td>
<td>-10.08</td>
</tr>
<tr>
<td>0.8</td>
<td>3.55</td>
<td>0.025</td>
<td>-11.70 ± 0.01</td>
<td>-8.87</td>
<td>-11.70</td>
</tr>
<tr>
<td>1.0</td>
<td>1.66</td>
<td>0.062</td>
<td>-10.94 ± 0.01</td>
<td>-8.83</td>
<td>-11.79</td>
</tr>
<tr>
<td>1.0</td>
<td>1.63</td>
<td>0.060</td>
<td>-11.90 ± 0.07</td>
<td>-9.38</td>
<td>-12.36</td>
</tr>
<tr>
<td>1.0</td>
<td>1.60</td>
<td>0.058</td>
<td>-12.92 ± 0.07</td>
<td>-9.96</td>
<td>-13.00</td>
</tr>
</tbody>
</table>

The nucleation rate $J_K$ and the corrected rate $J_{K,ext}$ taking into account nonisothermal effects and Brownian motion, and compared it to the MD simulations by Diemand et al. for various temperatures $T$ and supersaturations $S$ (and mass density $\rho$) of the ambient phase, see also Table 5.2. Therefore we use thermophysical data of argon obtained through MD simulations [29], see also Table 5.1. Here, $p_{eq,\infty}^s(T)$ is the gas pressure at saturation at temperature $T$.

In Fig. 5.2 and Table 5.2 we illustrate the predictions of the standard isothermal MFKT and the extended version. The truncated theory deviates systematically from the exact MD rates $J_{MD}$ by 2–4 orders of magnitude. Our theory successfully eliminates this deviation. We traced back the reduction of the nucleation rate due to the logarithmic corrections $3/2 \ln(N_c)$ associated to Brownian motion, and due to nonisothermal effects. For high temperatures, $k_B T / \epsilon = 1$, the nonisothermal corrections, of about 0.5 orders of magnitude, are nearly negligible, but by progressively lowering the temperature to $k_B T / \epsilon = 0.5$ these corrections are 1.5 orders of magnitude, constituting a relevant decrease in the nucleation rate.
The excellent performance of our extension of MFKT must be enjoyed with care. It is known that for certain substances, such as water, MFKT underestimates the nucleation rate [52], so that the agreement of our extension would possibly become worse. However, MFKT constitutes phenomenological components and the real benchmark test of our coarse-graining procedure is performed in Sec. 5.5, where we apply our coarse-graining procedure to direct atomistic systems, so that no phenomenology enters the prediction. The basic insight that we gain is that in the supersaturation regime analyzed by Diemand et al. our theory predicts corrections to the nucleation rate of the truncated theory in the range of 2−4 orders of magnitude.

5.5 Application: Nucleation in Lennard-Jones Gas

We study the nucleation of liquid drops in a metastable Lennard-Jones gas in the supersaturation regime considered by the large-scale MD simulations [29] by Diemand and coworkers. We employ the same Lennard-Jones system as Diemand et al., see Sec. 5.5.1, and consider nucleation in the limit of a large ambient phase at temperature $T$ and pressure $P$. We aim to obtain the static building block $Φ_S(x_c, x_{tot})$ and the dynamic information $D_{x_c, x}$ from atomistic simulations. These then determine the coarse-grained model composed of the evolution equation (5.11), the diffusion coefficients (5.10) and the nucleation landscape (5.25). We apply the following scheme to obtain predictions of the nucleation rate:

1. Sample configurations $C$ of $N$ atoms at pressure $p$ and temperature $T$ containing the nucleus of interest to obtain $Φ_S(x_{tot}, N_c, U_{pot}^c)$, here approximated by Eq. (5.20). Construct the nucleation barrier $V_S(x_{tot}, X_c)$ in Eq. (5.25).
2. Use the configurations $C$ as input in short-time MD simulations to obtain $D_{x_c, x}$.
3. Solve the Fokker-Planck equation (5.11) in the stationary limit to obtain the nucleation
rate prediction.

Subsequently we offer more details to each of the steps.

5.5.1 Lennard-Jones Model

We simulate the interaction between atoms through the Lennard-Jones potential, expressed at a separating distance $r$ by

$$\phi(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6,$$

except cutoff, and shifted at $r_c = 5\sigma$. Typical values of $\sigma$ and $\epsilon$ for a mono-atomic Lennard-Jones system, made of argon-like particles, are $\sigma = 3.822 \times 10^{-10}$ m and $\epsilon = 1.654 \times 10^{-21}$ J, with a particle’s mass $m = 6.690 \times 10^{-26}$ kg. We also introduce the typical time-scale $\tau = \sqrt{\sigma^2 m \epsilon}$ on which the atomistic dynamics takes place. We performed both, the MC and MD simulations with $N = 1000$ particles in the isobaric-isothermal ensemble. We used periodic boundary conditions in all directions. With 1000 particles system size effects are negligible [158] and we benefit from the fact that the system is small enough so that only one nucleus is formed in the system.

5.5.2 Clustering of Particles

For our simulations we need to formulate the microscopic cluster criterion $\Pi_{\theta(i)}(\Gamma)$ introduced in Sec. 5.2.1 to evaluate the properties of the nucleus. We here rely on the extension [63] of ten Wolde and Frenkel (tWF) of the most popular and simple scheme, the Stillinger-cluster definition where nearby atoms, within a distance smaller than a cutoff distance $r_c = 1.5\sigma$ are considered part of the same cluster. Ten Wolde and Frenkel further distinguish between particles with a liquid like and vapor like environment. A particle has a liquid like environment if it has at least 5 neighbours as defined by the Stillinger-criterion. All liquid like particles which are connected are considered part of the same nucleus. The tWF scheme is computationally cheap and has been shown by Wedekind et al. [166] to offer several advantages over the simple Stillinger definition.

5.5.3 MC Simulations

To sample $\phi_S(\mathbf{x}_{\text{tot}}, N_c, U^{\text{pot}}_c)$ we exploit standard MC simulations\textsuperscript{10} in the isobaric-isothermal ensemble with fixed number of particles $N$, pressure $P$ and temperature $T$. The formation of a nucleus in the low supersaturation regime of the Lennard-Jones gas is a rare event and so we use an importance sampling technique to investigate regions in phase space that contain a nucleus. We use the umbrella sampling technique [63] to bias the simulation with the bias

\textsuperscript{10}We wrote our own simulation code from scratch in C++.
potential
\[ \Pi_{N_c, \text{bias}} = -\frac{1}{2} k (\Pi_{N_c} - N_c)^2 \] (5.28)

that favours the presence of a nucleus with size \( N_c \) in the system. We use different umbrella windows corresponding to different choices of \( N_c \). In particular, we take umbrella windows from \( N_c = 10 \) to 140 usually in steps of 10. The bias strength is chosen as \( k = 0.25\epsilon \). The size 140 is in all simulations beyond the critical size \( N_c^* \). In our MC simulations of the \( NPT \) ensemble, we attempt at each step a volume changing move with probability \( 1/N \). If the volume changing move does not take place, each particle is moved with a probability of \( 5/N \) in this step. The maximum distance in any direction a particle can move is set to 0.4\( \sigma \). This ensures in all our simulations an average acceptance probability of volume moves and particle moves of 50%. To sample each umbrella window we first initialize homogeneously distributed particles in space so that their density coincides with the density of the metastable state at the temperature and supersaturation we are investigating, see also Table 5.3. Subsequently we perform an equilibration run of \( 10^7 \) MC steps and then start averaging for \( 10^8 \) MC steps to obtain \( \phi_S(x_{\text{tot}}, N_c, U_{\text{pot}}^c) \). We have only sampled down to nuclei with \( N_c > 6 \), i.e., nuclei that consist of at least 6 cluster like particles as defined by the tWF scheme. We however fit the data obtained for \( V_S(x_{\text{tot}}, N_c) \) in Eq. (5.25) for \( V_S(x_{\text{tot}}, x_c) \) between \( N_c = 6 \) and 140 and assume this fit can be extrapolated down to \( N_c = 0 \):

\[ V_S(x_{\text{tot}}, N_c) = -N_c \ln(S) + \frac{4\pi r_c^2(N_c)}{k_B T} \gamma_\infty \left( 1 - \frac{2\delta}{r_c(N_c)} \right), \] (5.29)
5.5. Application: Nucleation in Lennard-Jones Gas

where the radius of the nucleus is defined by \( r_c(N_c) = (3mN_c/(4\pi \rho_c))^{1/3} \) with the bulk density \( \rho_c \) in Table 5.1. The form (5.29) may misleadingly suggest that the nuclei have a well defined bulk and surface phase, but here, we do not test this assertion, but solely aim to fit \( V_S(x_{tot}, N_c) \) with two parameters - the “surface tension” \( \gamma_{c0} \) and the associated “Tolman correction” \( \delta \) depending on the temperature \( T \) and supersaturation\(^1\) \( S \), see Table 5.3. The surface tension \( \gamma_{c0} \) deviates by about \( 10 - 20\% \) from the macroscopic surface tension \( \gamma \) of a Lennard-Jones liquid-vapor interface in coexistence. The Tolman length approaches the value \( 0.20 \times \sigma \) for the lower temperatures in our simulations\(^1\). This convergence has been reported in literature \([170, 171]\). Notice, since we work with the tWF cluster definition, the height of the nucleation barrier of the truncated theory is obtained from \( \Delta V_S(x_{tot}, N_c^*) = V_S(x_{tot}, N_c^*) - V_S(x_{tot}, N_c = 0) \), and \( V_S(x_{tot}, N_c = 1) \) would correspond to the work of formation of a tWF cluster of size one, i.e., a liquid like particle surrounded by a halo of at least 5 atoms. The functional form of \( V_S(x_{tot}, N_c) \) invokes the problem that an unphysical local minimum, usually between \( N_c = 0 \) and 1 is present. To avoid this, we use for small nuclei, \( N_c < 3 \) an extrapolation to \( N_c = 0 \) of a cubic polynomial fit to \( V_S(x_{tot}, N_c = 0) \) obtained in the interval \( N_c \in [3,10] \), see also Fig. 5.3 for a typical nucleation landscape. Furthermore, we fit the remaining coefficients for \( V_S(x_{tot}, x_c) \) in Eq. (5.25)\(^\text{13}\): the potential minimum \( U_c^{\text{pot},0}(N_c) = E_0N_c + E_1N_c^{2/3} \) and \( H(N_c) = h_1N_c^{-3/2} \), see also Table 5.3. Here, \( E_0 \) can be interpreted as the bulk energy per particle of a nucleus, and \( E_s \) as its corresponding surface energy.

5.5.4 Short-Time MD Simulations

The atomic positional configurations harvested from MC simulations are used as initial conditions for our short-time MD simulations\(^1\) in the microcanonical ensemble. We can equally use the isobaric-isothermal ensemble at temperature \( T \) and pressure \( P \) to sample the short-time correlations of fluctuations determining the diffusion coefficient since on these short time-scales the macroscopic state of the system cannot be affected. Microcanonical simulations are more robust since there is no thermostat that can affect the state of the nucleus. If the isobaric-isothermal ensemble is used, the thermostats corresponding to \( T \) and \( P \) must be ensured to produce system relaxation times of the thermostated variables that drop off much slower than the time-scale on which relevant microscopic correlations drop off. Otherwise, the momentum and energy of the nucleus can be affected through the thermostat on the same time-scale as microscopic collisions of atoms of the ambient phase and the nucleus take place \([40]\), resulting then in erroneous estimates of the diffusion tensor. For simplicity we have sampled the initial momentum of all atoms in our MD simulations with a Gaussian

\[ U_c^{\text{pot},0}(N_c) = E_0N_c + E_1N_c^{2/3} \]

\[ H(N_c) = h_1N_c^{-3/2} \]

\(^1\)The supersaturation ratio is defined by \( S = p/p_{eq}^{\infty} \) where \( p \) is the initial pressure of the metastable gas at temperature \( T \) and \( p_{eq}^{\infty} \) the saturation pressure at temperature \( T \).

\(^1\)As argued by Kalikmanov \([52]\) the Tolman length interpreted as a curvature correction to the surface tension of a planar interface is strictly only valid for extremely large nuclei, \( N_c \gg 10^5 \), and also Nair and Sathian report \([169]\) that the Tolman length for microscopic nuclei is a controversial issue. Here, we do not intend to interpret \( \delta \) in any physical way, but solely use it as fitting parameter.

\(^1\)Note that \( V_S(x_{tot}, x_c) \) in Eq. 5.25 is ill-behaved near \( N_c \rightarrow 0 \). We apply the same polynomial fitting procedure as for \( V_S(x_{tot}, N_c) \) to extrapolate \( V_S(x_{tot}, x_c) \) to \( N_c = 0 \) to avoid singularities.

\(^1\)We wrote our own simulation code from scratch in C++.
Chapter 5. Nonequilibrium Statistical Mechanics of Nucleation

Table 5.3 – Fitted parameters of the entropic potential (5.25) in Sec. 5.5.3. The reported values of the “Tolman length” $\delta$ have an error smaller or equal to $0.01 \times \sigma$. In $E_0$ and $E_s$ as well as $h_1$ the error is smaller than the number of presented digits.

<table>
<thead>
<tr>
<th>$k_B T / \epsilon$</th>
<th>$S$</th>
<th>$\rho \sigma^3 / m$</th>
<th>$\gamma_{\infty} \sigma^2 / \epsilon$</th>
<th>$\delta / \sigma$</th>
<th>$E_0 / \epsilon$</th>
<th>$E_s / \epsilon$</th>
<th>$h_1 \epsilon^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>2.98</td>
<td>0.0200</td>
<td>1.083 ± 0.005</td>
<td>0.39</td>
<td>−4.8</td>
<td>5.4</td>
<td>6.8</td>
</tr>
<tr>
<td>0.8</td>
<td>3.11</td>
<td>0.0211</td>
<td>1.085 ± 0.006</td>
<td>0.36</td>
<td>−4.7</td>
<td>5.3</td>
<td>6.6</td>
</tr>
<tr>
<td>0.8</td>
<td>3.33</td>
<td>0.0230</td>
<td>1.086 ± 0.006</td>
<td>0.36</td>
<td>−4.7</td>
<td>5.1</td>
<td>6.6</td>
</tr>
<tr>
<td>0.8</td>
<td>3.55</td>
<td>0.0250</td>
<td>1.086 ± 0.008</td>
<td>0.35</td>
<td>−4.6</td>
<td>4.9</td>
<td>6.5</td>
</tr>
<tr>
<td>0.7</td>
<td>5.30</td>
<td>0.0106</td>
<td>1.230 ± 0.008</td>
<td>0.30</td>
<td>−4.9</td>
<td>5.1</td>
<td>7.5</td>
</tr>
<tr>
<td>0.7</td>
<td>6.11</td>
<td>0.0125</td>
<td>1.228 ± 0.006</td>
<td>0.26</td>
<td>−4.8</td>
<td>4.9</td>
<td>8.5</td>
</tr>
<tr>
<td>0.6</td>
<td>11.95</td>
<td>0.005</td>
<td>1.376 ± 0.01</td>
<td>0.24</td>
<td>−5.3</td>
<td>5.7</td>
<td>6.4</td>
</tr>
<tr>
<td>0.6</td>
<td>14.00</td>
<td>0.0065</td>
<td>1.381 ± 0.006</td>
<td>0.23</td>
<td>−5.3</td>
<td>5.8</td>
<td>5.3</td>
</tr>
<tr>
<td>0.6</td>
<td>15.60</td>
<td>0.0073</td>
<td>1.374 ± 0.008</td>
<td>0.22</td>
<td>−5.3</td>
<td>5.8</td>
<td>5.1</td>
</tr>
<tr>
<td>0.6</td>
<td>16.90</td>
<td>0.0080</td>
<td>1.375 ± 0.009</td>
<td>0.21</td>
<td>−5.3</td>
<td>5.7</td>
<td>4.8</td>
</tr>
<tr>
<td>0.5</td>
<td>39.37</td>
<td>0.0021</td>
<td>1.539 ± 0.010</td>
<td>0.19</td>
<td>−5.6</td>
<td>6.3</td>
<td>5.1</td>
</tr>
<tr>
<td>0.5</td>
<td>43.31</td>
<td>0.0023</td>
<td>1.541 ± 0.011</td>
<td>0.20</td>
<td>−5.6</td>
<td>6.2</td>
<td>5.2</td>
</tr>
<tr>
<td>0.5</td>
<td>48.70</td>
<td>0.0026</td>
<td>1.558 ± 0.009</td>
<td>0.20</td>
<td>−5.6</td>
<td>6.3</td>
<td>5.4</td>
</tr>
</tbody>
</table>

distribution at the temperature $T$ we are investigating. In this work we omit studying the energy dependence of the diffusion tensor and solely capture its size dependence. To sample the diffusion tensor at the critical size for any given temperature and supersaturation regime, we take 32 configurations harvested from MC runs that contain a nucleus of the critical size and then run the MD simulation for a total time of $25 \tau$ around five times larger than the collision time-scale $\tau_{\text{GK}} \approx 5 \tau$ of gas particles with the nucleus. By averaging the dynamics of all 32 simulations we are able to obtain the required mean-square displacements (5.10). The corresponding correlation functions $\langle \Delta_{\tau_{\text{GK}}} \Pi_{x,c} \Delta_{\tau_{\text{GK}}} \Pi_{x,c} \rangle(x_{\text{tot}},x_c)$ are illustrated in Fig. 5.4. A linear regime is recognizable from which the diffusion coefficient can be obtained. In Table 5.4 we have listed all obtained diffusion coefficients with the convention

$$D_{x_c,x_c}(x_{\text{tot}},x_c) = \begin{pmatrix} \xi_{P_c} I_{3\times3} & 0 \\ 0 & 1 \\ 0 & D_{N_c,U_c}^{0,0} \\ D_{N_c,U_c}^{0,0} & D_{U_c,U_c}^{0,0} \end{pmatrix} D_{N_c,N_c}^{0,0} N_c^{2/3}. \quad (5.30)$$

We also evaluated the diffusion coefficients for the temperature $T = 0.7$ and supersaturation ratio 6.11 for sizes of the nucleus distinct from the critical size and realized that they are well approximated by Eq. (5.30) for nuclei down to $N_c = 15$. The scaling (5.30) was also valid in the post-critical regime. We hence assume the validity of Eq. (5.30) for all $N_c$. In his work [66, 65], Barret gives explicit expressions for the coefficients $D_{N_c,U_c}^{0,0}$ and $D_{U_c,U_c}^{0,0}$ derived by kinetic theory arguments, see also Sec. 5.4.2. We did not find his theoretical predictions to match with our computer experiments. The derivation of the diffusion coefficients by Barrett invokes many

---

15 This convention is not compatible with the form (4.23) for the friction coefficient for Brownian motion chosen in the phenomenological approach. However, the MD simulation results support the validity of the scaling in Eq. (5.30).
5.5. Application: Nucleation in Lennard-Jones Gas

Figure 5.4 – Diffusion matrix normalized by $N_c^{2/3}$ at $T = 0.7e/k_B$ and $S = 6.11$. Dots denote the mean-square displacement (in Lennard-Jones units) of $N_c$ with $N_c$ (red), between $N_c$ with $U_c$ (blue), between $U_c$ with $U_c$ and $P^x_c$ with $P^x_c$, where $P^x_c$ is the momentum in $x$-direction. The solid lines, the slope of which enter the prediction of the diffusion tensor, are fits to the corresponding linear regime.

assumptions, and a future study would be desirable to explore the origin of the discrepancy between our numerical values of the diffusion coefficients and Barrett’s predictions. But we found rather good agreement of his prediction of $D_{N_c,N_c}^0$ with ours. For more details on the evaluation of the diffusion coefficients, see App. C.6. We realized, see also Fig. 4.4 for $\phi \approx 0$ in Chap. 4, that for a large range of values of coupling coefficients the nonisothermal corrections are not too sensitive, so that the discrepancy has no huge effects on nucleation rate prediction.

5.5.5 Nucleation Rate

The nucleation rate prediction for the truncated theory using $x_{trc}^0 = (N_c)$ as state variable is given by the classical formula

$$J_{trc} = \sqrt{\frac{1}{2\pi} \frac{\partial^2 V_S(x_{tot},N_c)}{\partial N_c^2}} \rho \frac{m}{N_c^2} D_{N_c,N_c}^0 (N_c^*)^2 \ e^{-\Delta V_S(x_{tot},N_c^*)},$$

(5.31)

where $\rho$ is the mass density of the metastable gas at temperature $T$ and supersaturation $S$, and $N_c^*$ is the critical size of the truncated nucleation landscape $V_S(x_{tot},N_c^*)$ and $\Delta V_S(x_{tot},N_c^*)$ the barrier height, see also Eq. (5.29). In order to obtain the nucleation rate of the full theory $J_{ext}$, we performed stochastic simulations of the full Fokker-Planck equation (5.11) and the Fokker-Planck equation of the truncated theory (1.1) to obtain the correction to the nucleation rate (5.31) through nonisothermal effects and Brownian motion, see also App. B.5 for details. In Table 5.5 we tabulated the different obtained rates and corrections $\alpha_{non-isoto}$ and $\alpha_{BM}$ to $J_{trc}$ through nonisothermal and Brownian effects. We roughly estimated these correction by first performing the stochastic simulations in an isothermal setup, but with the correction
Table 5.4 – Fitted parameters of the diffusion tensor (5.30) with conventions Sec. 5.5.4. The error in $D_0$ is discussed in App. B.VII. Errors in $D^{0}_N$, $D^{r,0}_N$, $e^2$ and $\xi^{r,0} me$ are smaller than 0.05 and errors in $D^{r,0}_U$, $e^4$ smaller than 0.1.

<table>
<thead>
<tr>
<th>$k_B T / \epsilon$</th>
<th>$S$</th>
<th>$D^0_\tau$</th>
<th>$D^{r,0}_N$, $e^2$</th>
<th>$D^{r,0}_U$, $e^4$</th>
<th>$\xi^{r,0} me$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>2.98</td>
<td>0.089</td>
<td>0.72</td>
<td>1.79</td>
<td>0.77</td>
</tr>
<tr>
<td>0.8</td>
<td>3.11</td>
<td>0.132</td>
<td>0.71</td>
<td>1.50</td>
<td>0.62</td>
</tr>
<tr>
<td>0.8</td>
<td>3.33</td>
<td>0.229</td>
<td>0.68</td>
<td>1.15</td>
<td>0.50</td>
</tr>
<tr>
<td>0.8</td>
<td>3.55</td>
<td>0.314</td>
<td>0.68</td>
<td>0.88</td>
<td>0.39</td>
</tr>
<tr>
<td>0.7</td>
<td>5.30</td>
<td>0.054</td>
<td>0.75</td>
<td>1.42</td>
<td>0.80</td>
</tr>
<tr>
<td>0.7</td>
<td>6.11</td>
<td>0.145</td>
<td>0.74</td>
<td>1.16</td>
<td>0.37</td>
</tr>
<tr>
<td>0.6</td>
<td>11.95</td>
<td>0.025</td>
<td>0.74</td>
<td>1.42</td>
<td>0.81</td>
</tr>
<tr>
<td>0.6</td>
<td>14.00</td>
<td>0.032</td>
<td>0.68</td>
<td>1.20</td>
<td>0.77</td>
</tr>
<tr>
<td>0.6</td>
<td>15.60</td>
<td>0.038</td>
<td>0.61</td>
<td>1.03</td>
<td>0.63</td>
</tr>
<tr>
<td>0.6</td>
<td>16.90</td>
<td>0.056</td>
<td>0.54</td>
<td>0.89</td>
<td>0.49</td>
</tr>
<tr>
<td>0.5</td>
<td>39.37</td>
<td>0.013</td>
<td>0.70</td>
<td>1.00</td>
<td>0.62</td>
</tr>
<tr>
<td>0.5</td>
<td>43.31</td>
<td>0.012</td>
<td>0.67</td>
<td>0.85</td>
<td>0.56</td>
</tr>
<tr>
<td>0.5</td>
<td>48.70</td>
<td>0.012</td>
<td>0.58</td>
<td>0.69</td>
<td>0.48</td>
</tr>
</tbody>
</table>

for Brownian motion activated to obtain $\alpha_{BM}$ and subsequently we performed stochastic simulations incorporating all state variables and the additional correction was attributed to $\alpha_{non-iso}$. The nonisothermal corrections obtained with Barrett’s rate theory [65], see also Sec. 4.5, of nonisothermal nucleation agree remarkably well with the values of $\alpha_{non-iso}$ we obtained, usually by a difference of 20%. The treatment of Barrett follows closely the original work [64] of Feder et al. with the important difference, that the temperature dependence of the surface tension is accounted for. We observed that in lowering the ambient temperature $T$ the nonisothermal effects become more pronounced and comparable with the Brownian effects. In the high temperature regime however, Brownian effects dominate. In Fig 5.5 we compare

![Figure 5.5 – Comparison of Lennard-Jones nucleation rate predictions of standard Monte Carlo technique (blue) with predictions of our theory (red). Also shown are the results of large-scale molecular dynamics simulations [29] (black).](image-url)
We have derived a systematic coarse-graining procedure that extracts microstructural information from atomistic dynamics and projects it onto the proper macroscopic model. This procedure is formulated to take into account the Brownian motion of nuclei and nonisothermal effects. Within our approach we derived the correction of the nucleation landscape due to energy- and momentum fluctuations of nuclei, and reproduced up to date results. This includes the non-Gaussian energy fluctuations inherent for small nuclei following a generalized form of the law of McGraw and LaViolette [85], and the Brownian motion contribution already obtained within mesoscopic nonequilibrium thermodynamics by Reguera and Rubi [74]. The latter, as we found, must be corrected by a logarithmic term in the size of nuclei that arises from statistical mechanics arguments, and can probably not be obtained by bare thermodynamic argumentation.

5.6 Conclusion and Future Work

Table 5.5 – Nucleation rate predictions for a metastable Lennard-Jones gas at various temperatures $T$ and supersaturations $S$. The rates $J_{\text{MD}}$ correspond to MD simulations [29]. An asterisk on top of the data indicates that the rate is obtained through the universal scaling relation [172]. $J_{\text{trc}}$ are the predictions of the standard Monte Carlo technique, and $J_{\text{ext}}$ our predictions. $A_1 = \log\left(\frac{J_{\text{MD}}}{\sigma^{\tau}}\right)$ and $A_2 = \log\left(\frac{J_{\text{BM}}}{\sigma^{\tau}}\right)$ are estimates of the correction of the nucleation rate $J_{\text{trc}}$ due to nonisothermal effects and Brownian motion.

<table>
<thead>
<tr>
<th>$k_B T / e$</th>
<th>$S$</th>
<th>$\log\left(\frac{J_{\text{MD}}}{\sigma^{2\tau}}\right)$</th>
<th>$\log\left(\frac{J_{\text{trc}}}{\sigma^{2\tau}}\right)$</th>
<th>$\log\left(\frac{J_{\text{ext}}}{\sigma^{2\tau}}\right)$</th>
<th>$A_1$</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>2.98</td>
<td>$-16 \pm 0.5$</td>
<td>$-11.59 \pm 0.31$</td>
<td>$-16.24 \pm 0.61$</td>
<td>-1.0</td>
<td>-3.7</td>
</tr>
<tr>
<td>0.8</td>
<td>3.11</td>
<td>$-15.53^*$</td>
<td>$-11.41 \pm 0.25$</td>
<td>$-16.01 \pm 0.42$</td>
<td>-1.0</td>
<td>-3.6</td>
</tr>
<tr>
<td>0.8</td>
<td>3.33</td>
<td>$-13.47 \pm 0.07$</td>
<td>$-9.76 \pm 0.31$</td>
<td>$-14.39 \pm 0.58$</td>
<td>-1.2</td>
<td>-3.4</td>
</tr>
<tr>
<td>0.8</td>
<td>3.55</td>
<td>$-11.90 \pm 0.02$</td>
<td>$-8.60 \pm 0.35$</td>
<td>$-13.20 \pm 0.60$</td>
<td>-1.4</td>
<td>-3.2</td>
</tr>
<tr>
<td>0.7</td>
<td>5.30</td>
<td>$-16.24^*$</td>
<td>$-12.25 \pm 0.34$</td>
<td>$-16.76 \pm 0.59$</td>
<td>-1.2</td>
<td>-3.3</td>
</tr>
<tr>
<td>0.7</td>
<td>6.11</td>
<td>$-13.28^*$</td>
<td>$-10.71 \pm 0.35$</td>
<td>$-15.11 \pm 0.68$</td>
<td>-1.3</td>
<td>-3.1</td>
</tr>
<tr>
<td>0.6</td>
<td>11.95</td>
<td>$-16.45 \pm 0.98$</td>
<td>$-11.60 \pm 0.28$</td>
<td>$-15.68 \pm 0.36$</td>
<td>-1.2</td>
<td>-2.8</td>
</tr>
<tr>
<td>0.6</td>
<td>14.00</td>
<td>$-14.58 \pm 0.07$</td>
<td>$-10.37 \pm 0.21$</td>
<td>$-14.41 \pm 0.29$</td>
<td>-1.3</td>
<td>-2.6</td>
</tr>
<tr>
<td>0.6</td>
<td>15.60</td>
<td>$-12.81 \pm 0.04$</td>
<td>$-9.71 \pm 0.24$</td>
<td>$-13.53 \pm 0.35$</td>
<td>-1.3</td>
<td>-2.5</td>
</tr>
<tr>
<td>0.6</td>
<td>16.90</td>
<td>$-11.96 \pm 0.01$</td>
<td>$-9.04 \pm 0.35$</td>
<td>$-12.72 \pm 0.62$</td>
<td>-1.4</td>
<td>-2.3</td>
</tr>
<tr>
<td>0.5</td>
<td>39.37</td>
<td>$-16.77^*$</td>
<td>$-12.61 \pm 0.26$</td>
<td>$-16.51 \pm 0.48$</td>
<td>-1.5</td>
<td>-2.4</td>
</tr>
<tr>
<td>0.5</td>
<td>43.31</td>
<td>$-15.89^*$</td>
<td>$-11.97 \pm 0.24$</td>
<td>$-15.96 \pm 0.40$</td>
<td>-1.7</td>
<td>-2.3</td>
</tr>
<tr>
<td>0.5</td>
<td>48.70</td>
<td>$-15.27 \pm 0.05$</td>
<td>$-11.34 \pm 0.21$</td>
<td>$-15.58 \pm 0.34$</td>
<td>-1.7</td>
<td>-2.5</td>
</tr>
</tbody>
</table>

The predictions $J_{\text{ext}}$ with the brute-force MD rates $J_{\text{MD}}$ obtained by Diemand et al. [29] and plotted it in a manner that highlights the intrinsic universal scaling behavior suggested by Tanaka et al. [172], where the MD nucleation rate is recognized as a universal function of $\ln(S)/(T_{\text{crit}} - T)^{1.3}$ with $T_{\text{crit}} = 1.312e/k_B$ the critical temperature. The rates obtained by the standard truncated theory deviate by $3 - 5$ orders of magnitude from the exact MD rates whereas our approach yields a quite excellent agreement.
We have shown that nucleation rate predictions of the coarse-graining technique in literature [57, 58, 59, 60, 61, 62, 63] operating on the truncated state space, where only the number of atoms in a nucleus is a relevant dynamic variable, leads to systematically erroneous predictions of 3 – 5 orders of magnitude for the prototypical studied nucleation of liquid drops in a supersaturated Lennard-Jones gas. Our coarse-graining procedure significantly reduces this lack in prediction. More generally, we recognized that our thermodynamic guided coarse-graining procedure results in atomistic expressions for the nucleation landscape and the diffusion tensor that appear to be simple generalizations of the standard procedure, see Table 5.6.

Angélil et al. have studied [75] the properties of nuclei in large-scale MD simulations and concluded that the spin of nuclei plays a negligible role for their dynamics. In particular, only small nuclei composed of less than 10 atoms tend to spin. In our simulations the critical size of nuclei was well beyond 10 (probably comparable to a tWF cluster size of 5) so that these corrections are irrelevant.

It might be interesting to account for additional state variables such as the shape of the nuclei but also to include additional atomic species and generalize our coarse-graining procedure to multicomponent system for more realistic applications. As a next major step the environment could also be rendered inhomogeneous, and the coarse-graining procedure should then be formulated to project atomistic dynamics on the hydrodynamic equations for the ambient phase, and the present Fokker-Planck type description for the nucleating phase. This will also give detailed expressions for the coupling of temperature gradients and shear-flow to the nucleation process, see also Sec. 4.6.

More fundamentally, our work relies on a cluster definition to group the atoms as members of the gas phase or the nucleus of interest. Some work has been done avoiding the introduction of an artificial cluster criterion and we also expect useful extensions of our work in this directions, possibly following the lines of Kusaka et al. [57, 164].
We studied in detail nucleation under incorporation of Brownian motion and nonisothermal effects within the GENERIC framework. When the ambient phase is inhomogeneous we derived evolution equations that obey the severe structural restrictions of nonequilibrium thermodynamics. This approach contains material parameters that must be fixed based on phenomenological considerations but lack a clear connection to the underlying microstructure. When the environment is rendered homogeneous we notably derived a systematic coarse-graining procedure that unambiguously connects microstructural information with the macroscopic model where the latter can conveniently be solved through stochastic simulations. Our highly efficient multi-scale procedure constructs the activation barrier for nucleation via MC simulations performed on the atomistic level, and obtains kinetic coefficients by evaluating Green-Kubo expressions in short-time MD. The standard coarse-graining procedure reported in the literature maps atomistic dynamics onto the evolution of a single order-parameter and we showed that this leads to systematically wrong predictions of 3 – 5 orders of magnitude in the key quantity, the nucleation rate. In addition to the size of nuclei, we also took their momentum and energy fluctuations into account and thereby reduced this lack in prediction significantly.

More technically, our approach to construct the nucleation landscape $V_S(x_{tot}, x_c)$, or respectively the activation barrier, is entropy based, and the cornerstone of our considerations is the concept of an entropy of formation of nuclei. This contradicts the central paradigm of many other attempts [66, 65, 144] to formulate nonisothermal nucleation theories which rely in first instance on the Gibbs-free energy of formation. We exploited the existence of an entropy $S_c(x_c)$ of nuclei to associate naturally a temperature $T_c$ to the nucleation process via $1/T_c = \partial S_c/\partial U_c$, and with this we casted the nucleation landscape in the form $V_S(x_{tot}, x_c) = V_S(x_{tot}, N_c) + \Delta U_c + \Delta N_c$. Here, $\Delta U_c$ and $\Delta N_c$ are nonisothermal and Brownian corrections, and $\Delta N_c$ statistical mechanics corrections. We obtained these coefficients for nucleation of drops in a metastable gas, first by specializing our nonequilibrium thermodynamics (NEQ-TD) approach to incompressible high-density nuclei, and then through nonequilibrium statistical mechanics (NEQ-SM) free from approximations, see Table. 6.1. We
Chapter 6. Summary and Outlook

Table 6.1 – Corrections to the nucleation landscape.

<table>
<thead>
<tr>
<th>Case</th>
<th>$\Delta T_c/T$</th>
<th>$\Delta P_c$</th>
<th>$\Delta N_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEQ-TD</td>
<td>$P_c^2/(2k_BTmN_c)$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>NEQ-SM</td>
<td>$P_c^2/(2k_BTmN_c)$</td>
<td>$2\ln(N_c)$</td>
<td></td>
</tr>
</tbody>
</table>

classified the absence of the additional corrections in $\Delta T_c/T$ proportional to $(1 - T/T_c)^2$ in NEQ-TD as an artifact of the incompressibility assumption. The corrections $\Delta N_c$ arising in the NEQ-SM approach are recognized as absolutely essential to guarantee the proper normalization of the probability $\phi_S(x_{\text{tot}}, x_c)$ that defines in the NEQ-SM approach the nucleation landscape by $V_S(x_{\text{tot}}, x_c) = -\ln(\phi_S(x_{\text{tot}}, x_c))$. In particular, the NEQ-TD approach does not take into account the proper normalization of the nucleation landscape. In this respect we believe that the NEQ-SM result is the appropriate one since it is derived from first principles, while thermodynamic approaches are likely to be incapable to capture consistently all logarithmic corrections in $N_c$ to the nucleation landscape.

We also studied phase-transitions beyond nucleation, where we considered the flow of mass, momentum and energy across interfaces that separate two macroscopic bulk phases. This physics is significantly different from nucleation, since small nuclei, usually composed of some tens of atoms, cannot be attributed an interface nor a well-defined bulk phase. Phase-separation in its final stage is governed by boundary conditions imposed at the interface on the hydrodynamic fields that describe the bulk dynamics. The interface can be equipped with a notion of local-equilibrium even under nonequilibrium situations and we were notably able to unambiguously prove this hypothesis, formulated in 2012 by Savin et al. [89], and its far reaching consequences through extensive, high-precision MD simulation studies on a vapor-liquid interface. In particular, for a one-component system we showed that the interface has the same intrinsic structure in equilibrium, and nonequilibrium under constant surface tension. This state also defines the jump ratio in entropy, and internal energy normalized by the jump in mass density across the bulk phases via generalized Clapeyron relationships. Profiles of intensive quantities through the interfacial layer are thermodynamically meaningless, but the surface tension allows to unambiguously reconstruct the intensive state of the interface treated rigorously as a two-dimensional autonomous phase. Our study offers a starting point for further investigations, and extensions of the concept of local equilibrium and gauge-transformations to interfaces with complex microstructures, where additional conformational effects must be considered. But it would also be desirable to understand how the gauge-variance and invariance of interfacial quantities emerges from purely nonequilibrium statistical mechanics arguments. The formulation of which should offer particular challenges, since the starting point of statistical mechanics are atomistic systems in 3 dimensions, but the coarse-graining should yield a model that describes the interface as a 2 dimensional object.

We expect our work to be a milestone and solid foundation towards more involved applications...
of the nucleation theory. In this respect it is worthwhile to incorporate more order parameters into the macroscale description – for many future technological applications and industrial processes of utmost importance the morphology of the nucleated material is of tremendous interest, and therefore it would be desirable to treat the shape of the nuclei as an additional independent variable. Under shear-flows for instance the shape of nuclei is ellipsoidal and preferably oriented in a specific direction dictated by the external velocity field [80, 81]. In this respect we expect also significant generalizations towards more involved rheological models to treat nucleation in complex fluids where confirmation tensors characterize the coarse-grained details of the microstructure. But our approach should also be made applicable to multi-component systems. Ignoring these complications, the performance of our coarse-graining scheme should be checked for different nucleation processes beyond the liquid-drop nucleation in metastable Lennard-Jones gas we investigated. In this respect, the large-scale brute-force MD simulations results for the nucleation of liquid drops in water [173], but also for bubble nucleation in Lennard-Jones liquid [174] could be used as an illuminating reference.

From a broader perspective we realized that nucleation is solely the startup of a phase transformation towards its ultimate completion where usually two macroscopic bulk phases coexist. A first step would be to go beyond the onset of nucleation when the nuclei can no more be regarded dilute. This would require to deal with hydrodynamic interaction of the nuclei resulting likely in nonlinear terms in the Fokker-Planck equation for the nuclei distribution function, where for a convenient solution procedure an extended form of the direct simulation MC algorithm [175] would have to be developed. This unifies different stages of phase-transformations in a universal approach and would potentially be superior to existing work [86] in this field, since additionally nonisothermal and Brownian effects are taken into account, where the latter offers nuclei directly to explore their surrounding, so that Ostwald ripening is taken into account. The relation of such a unified approach to the theory of gauge-transformations and local equilibrium for interfaces [89] would rise further questions. In particular, “how can the thermodynamically motivated nonequilibrium generalizations of Clapeyron relations [89] and boundary conditions [153] on the hydrodynamic fields of the environment at the interface of large nuclei emerge?” and “are the diffusion coefficients regulating in our approach the exchange of mass, momentum and energy of the nuclei with their ambient phase related to the analogous transport coefficients for macroscale interfaces, i.e., the phase conversion rate, slip length and Kapitza resistivity?” Following these lines of thought, for certain large-scale phenomena, including for instance weather prediction [176] or studies of cosmic dust [177], our mesoscale description of nucleation might not be suitable - in this case the mesoscopic model must be coarse-grained further to an entirely (fluctuating) hydrodynamic description similar to the Avrami-Kolmogorov model [178, 179]. This two step multi-scale modeling process would first obtain microstructure information from atomistic scale and translate it into the proper mesoscale model from which further static and dynamic material information is extracted that enters the final hydrodynamic picture in a coarse-grained way.

While nucleation within classical physics is more and more understood, nucleation in the quantum regime lacks still largely a conceptual basis. When the temperature of the metastable
phase becomes sufficiently low, nuclei no longer reach the critical size by thermal fluctuations, since these are exponentially suppressed, but by tunneling. Recently a generalization of the classical GENERIC to quantum systems has been developed [180] that might shed light on the nucleation mechanism in the quantum regime. This is for instance relevant in the study of liquid Helium at low temperature [181], or the onset of superconductivity where magnetic field lines slowly start penetrating the superconductor [182]. Such a quantum nucleation theory is particularly challenging since the mass and momentum of the nuclei cannot easily be chosen simultaneously as independent variables; in the conversion of the classical Hamiltonian to its quantum counterpart a spurious ordering problem would arise, known as the position dependent mass problem in super-symmetric quantum field theories [183].
Bibliography


Bibliography


Bibliography


Bibliography


A Nonequilibrium Thermodynamics of Interfaces

A.1 Numerical Methods

We simulated a fluid of particles interacting through the smoothed Lennard-Jones spline potential, expressed at a separating distance \( r \) by

\[
\phi(r) = \begin{cases} 
4\epsilon\left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] & \text{if } 0 < r < r_s, \\
\zeta_1(r - r_c)^3 + \zeta_2(r - r_c)^2 & \text{if } r_s \leq r \leq r_c, \\
0 & \text{otherwise.}
\end{cases}
\]

The cutoff radius is \( r_c = 2.5 \times \sigma \) to account for the long-range Lennard-Jones potential, while the spline cutoff \( r_s = \frac{48}{67} r_c \) and the spline coefficients \( \zeta_1 = 0.099194 \times \epsilon/\sigma^3 \) and \( \zeta_2 = -0.16346 \times \epsilon/\sigma^2 \) are chosen such that the potential and its first derivative are continuous. Typical values of \( \sigma \) and \( \epsilon \) for a monoatomic Lennard-Jones system, made of argon-like particles [184], are \( \sigma = 3.822 \times 10^{-10} \text{ m} \) and \( \epsilon = 1.654 \times 10^{-21} \text{ J} \), with a particle’s mass \( m = 6.690 \times 10^{-26} \text{ kg} \). In the main text of Chap. 3, we set \( \sigma = 1, m = 1, \tau = \left( \frac{m \sigma^2}{\epsilon} \right)^{1/2} = 1 \) and \( \theta = \frac{\epsilon}{k_B} = 1 \) to define the Lennard-Jones units of length, mass, time and temperature respectively.

We placed 16192 particles in a simulation box with dimensions \( L_x = 213 \sigma \) and \( L_y = L_z = 21 \sigma \) along the \( x \), \( y \) and \( z \)-axis. We used periodic boundary conditions in the \( y \) and \( z \) directions. At \( x = 0 \) (in the vapor) and \( x = L_x \) (in the liquid), we used thermostated reflecting boundary conditions: particles hitting those surfaces were reflected according to a Maxwell distribution to impose a specific temperature. The liquid thermostat was complemented by rescaling accordingly the velocities of the particles in the volume \( L_x - 6 \sigma < x < L_x \) (see Fig. 3.2A).

Newton’s evolution equations used to obtain the trajectories \( \{ \mathbf{r}_i(t) \} \) of the particles were integrated using the velocity Verlet algorithm with a time step of \( \delta t = 0.0005 \tau \). A small force of magnitude \( 0.005 \frac{\epsilon}{\sigma^2} \) in the \( x \) direction was further applied\(^1\) in the liquid thermostat to pin the

\(^1\)We did not study the influence of the time step size \( \delta t \) and the magnitude of the applied force on the simulation results. We have taken the choice of \( \delta t \) recommended in other work [124, 127].
Table A1 – Nonequilibrium simulation conditions (thermostats' temperatures and swapping probabilities) in Lennard-Jones units.

<table>
<thead>
<tr>
<th>Type</th>
<th>#</th>
<th>Vapor thermostat</th>
<th>Liquid thermostat</th>
<th>Swapping frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1.025</td>
<td>0.830</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.025</td>
<td>0.840</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.050</td>
<td>0.750</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.125</td>
<td>0.890</td>
<td>0</td>
</tr>
<tr>
<td>Heat flux</td>
<td>5</td>
<td>1.150</td>
<td>0.850</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.200</td>
<td>0.870</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1.250</td>
<td>0.850</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.300</td>
<td>0.920</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>1.300</td>
<td>0.980</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.350</td>
<td>0.900</td>
<td>0</td>
</tr>
<tr>
<td>Mass flux</td>
<td>11</td>
<td>0.740</td>
<td>0.740</td>
<td>0.00080</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.740</td>
<td>0.740</td>
<td>0.00135</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>0.790</td>
<td>0.790</td>
<td>0.00135</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>0.870</td>
<td>0.870</td>
<td>0.00080</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.890</td>
<td>0.890</td>
<td>0.00080</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>0.940</td>
<td>0.940</td>
<td>0.00080</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>0.970</td>
<td>0.970</td>
<td>0.00025</td>
</tr>
</tbody>
</table>
liquid phase at the surface $x = L_x$. The system was preconditioned for $3 \times 10^6 \delta t$, upon which a steady liquid film coexisting with its vapor formed (Fig. 3.1A).

To simulate a system with an imposed heat flux, we set the vapor thermostat to a higher temperature than the liquid one. To create a mass flux, a liquid particle $i$ located in $L_x - 6\sigma < x < L_x$ was instantaneously translated by $-(L_x - 6\sigma)$ in the $x$ direction with a tunable probability after each time step. The attempt to insert the particle was accepted with probability $\min\{1, \exp[-\Phi_i(t)/T]\}$, where, calling $r_{ij}(t) = |\mathbf{r}_{ij}(t)| = |\mathbf{r}_i(t) - \mathbf{r}_j(t)|$, $\Phi_i(t) = \sum_{j \neq i} \Phi(\mathbf{r}_{ij}(t))$ is the total interaction energy of the particle at its new location (this step was necessary to avoid singularities in case the particle was placed too close to another one; for this reason, simulating evaporation - requiring particles reinsertion in the liquid - is prohibitively more time-consuming). We evolved the system for another $6 \times 10^6 \delta t$ to generate the corresponding nonequilibrium stationary state. Table A1 gives the set of thermostats’ temperatures and swapping probabilities of the 17 nonequilibrium simulations performed here.

We binned the simulation box into 426 layers of thickness $\sigma/2$ in the $x$-direction. We calculated the instantaneous mass density in layer $k$, $\rho_k(t) = m n_k(t)/V_b$, where $V_b = \sigma L_y L_z/2$ is the volume of a bin and the instantaneous number of particles in layer $k$ at time $t$ is $n_k(t) = \sum_j 1_{\mathbf{r}_j(t) \in \text{layer } k}$, with $1_{\mathbf{r}_j(t) \in \text{layer } k}$ the following indicator function: $1_{\mathbf{r}_j(t) \in \text{layer } k} = 1$ if the particle $i$ is in layer $k$ at time $t$ and $1_{\mathbf{r}_j(t) \in \text{layer } k} = 0$ otherwise. The corresponding discrete mass density profile is then defined at the position $x_k$ of the layer $k$ by $\rho(x_k) = \bar{\rho}_k$, where $\bar{\rho}$ indicates the time average of the process $\rho(t)$ (calculated over $50 \times 10^6 \delta t$ in equilibrium, $80 \times 10^6 \delta t$ in nonequilibrium).

Similarly, the instantaneous internal energy density $u_k(t)$ in layer $k$ at time $t$ is given by $u_k(t) = \eta_k(t) + \frac{1}{\rho_k(t)} \sum_{j \neq i} 1_{\mathbf{r}_j(t) \in \text{layer } k} \Phi(\mathbf{r}_{ij}(t))$, where $\eta_k(t) = \frac{m}{\bar{\rho}_k} \sum_j 1_{\mathbf{r}_j(t) \in \text{layer } k} \mathbf{v}_i(t) - \bar{\mathbf{v}}_k)^2$ is the instantaneous, non-convected kinetic energy. Here, $\mathbf{v}_j(t) = \mathbf{v}_i(t)$ and $\mathbf{v}(x_k) = \bar{\mathbf{v}}_k$ indicates the mean speed of the fluid in layer $k$, obtained by time-averaging the instantaneous velocity $\mathbf{v}_k(t) = \frac{1}{n_k(t)} \sum_j 1_{\mathbf{r}_j(t) \in \text{layer } k} \mathbf{v}_j(t)$ of the particles in layer $k$. The final profile of the internal energy density is given by $u(x_k) = \bar{u}_k$. There is an ambiguity in defining the instantaneous value of the internal energy of a layer, due to the potential energy contribution: if two interacting particles are in different layers, there are various ways of distributing their potential energy between the two layers. Hence, the potential energy may be attributed to the layer in which the center of mass of the pair particles falls, it may be distributed proportionally between the layers, or each layer may be given one half of the potential energy. The latter choice corresponds to the formula given in the text. The variations associated with different choices in the definition of the local internal energy were orders of magnitude smaller than other sources of error.

The kinetic temperature profile is calculated as $T(x_k) = \frac{2m}{3k_B} \bar{\rho}_k$, and the pressure as $p(x_k) = \bar{p}_k$ with $p_k(t) = \frac{2}{3} \rho_k(t) + \frac{1}{6\bar{\rho}_k} \sum_{j \neq i} 1_{\mathbf{r}_j(t) \in \text{layer } k} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij}$, where $\mathbf{F}_{ij} = \left.\frac{\partial}{\partial r_{ij}} \frac{\partial}{\partial r_{ij}} \right|_{r=r_{ij}}$ is the force acting on particle $i$ due to particle $j$.

The surface tension $\gamma$ of the interface was calculated by summing the difference between the components of the pressure that are normal and parallel to the interface [113].
Appendix A. Nonequilibrium Thermodynamics of Interfaces

The chemical potential $\mu$ in the system has been obtained with the Widom insertion method [125, 126]. We first write the sum $\mu = \mu_{\text{id}} + \mu_{\text{ex}}$, where $\mu_{\text{id}} = -\frac{3}{2} k_B T \ln \frac{\rho_e}{\rho} + k_B T \ln \frac{\rho}{\rho_e}$ is the chemical potential of an ideal gas with mass density $\rho$, at temperature $T$, and $\mu_{\text{ex}}$ the additional term that takes intermolecular interactions into account and that is calculated with the insertion method. The latter consists in inserting a Lennard-Jones particle in the system, say at a position $r_k$ in the layer $k$ and calculating $\mu_{\text{ex},k}(t) = -\frac{k_B T}{\rho} \ln \exp \left( -\frac{\Phi_k(t)}{k_B T} \right)$, where $\langle \ldots \rangle$ indicates an average over all possible trial insertions at this location [126]. We attempted 12 randomly generated trial insertions in each bin every time-step, from which we calculated the instantaneous values $\mu_{\text{ex},k}(t)$. We then performed a time-average to get $\mu_{\text{ex}}(x_k) = \bar{\mu}_{\text{ex},k}$, and finally $\mu(x_k) = \mu_{\text{id}}(x_k) + \mu_{\text{ex}}(x_k)$, where $\mu_{\text{id}}$ inherits its $x$-dependency from the spatial variations of $T(x)$ and $\rho(x)$. At equilibrium, $\mu$ is uniform across the system.

Each simulation was run on 16 processors (2.5-GHz 4×quad-core AMD Opteron 8380) simultaneously on the Brutus cluster of the ETH Zurich (http://www.cluster.ethz.ch), and took approximately 3 weeks.

A.2 Additional Remarks on Gauge Transformations

We introduce in the main text the gauge transformation $x^s \to x^s + \ell$ resulting from offsetting the position $x^s$ of the dividing surface by a small displacement $\ell$. Invoking the gauge invariance of the interfacial Euler equation (Eq. (1a) in the main text) then imposes the condition $\Delta u = T^s \Delta s + \mu^s \Delta \rho$, as obtained from the definition of the excess densities. However, Öttinger and Venerus [132] recently suggested that the gauge invariance condition for the Euler equation is $\Delta u + \frac{1}{2} (\Delta v)^2 / (\Delta \rho) = T^s \Delta s + \mu^s \Delta \rho$, where $\Delta v = \mathbf{v}^\beta - \mathbf{v}^a$ is the difference between the velocity fields of each phase, and $\Delta \frac{1}{\rho} = \frac{1}{\rho^a} - \frac{1}{\rho^\beta}$. The additional term originates from possible flows in the bulk phases, which induce a transfer of kinetic energy between phases upon changing the gauge.

In the main text, Eq. (2a) is then modified to $\frac{d(\mu/\sqrt{T})}{dT} = \Delta u / \Delta \rho - \frac{1}{2} \mathbf{v}^a \cdot \mathbf{v}^\beta$, provided with the conservation of momentum at an immobile interface, $\rho^a \mathbf{v}^a = \rho^\beta \mathbf{v}^\beta$, which is the only scenario investigated here. In our study however, this correction is negligible. The negligibility of kinetic energy effects might also be required to obtain consistency of the gauge invariance condition of Ref. [132] with the momentum balance at the interface derived in that paper.

In general, only the fields of thermodynamic densities $a$ that are defined in a fixed reference (such as $a = \rho$, $s$, $u = \rho \mathbf{v}$ the momentum density or $e = u + \frac{1}{2} \rho \mathbf{v}^2$ the total energy density) have surface excess densities that strictly gauge-transform as $a^s \to a^s + \ell \Delta a$.

Along the same lines, Legendre transformations of these densities do not normally gauge-transform because their variations lead to forbidden changes of intensive, gauge-invariant variables. For example, with the static approximation $u^s \to u^s + \ell \Delta u$, the excess Helmholtz free energy $f^s = u^s - T^s s^s$ gauge-transforms according to $f^s \to f^s + \ell (\Delta u - T^s \Delta s)$, but not according to $f^s \to f^s + \ell \Delta f$. 

88
Nonequilibrium Thermodynamics of Nucleation

B.1 Poisson Structure

We introduce the effective bulk densities $\bar{\rho} = \rho (1 - \langle V \rangle)$, $\bar{u} = u (1 - \langle V \rangle)$ and $\bar{s} = s (1 - \langle V \rangle)$, where $s$ is the entropy of the metastable phase. These densities are convected by means of the standard Poisson structure for hydrodynamics [77]:

$$
\{A, B\} = -\int d^3r \bar{\rho} \left( \frac{\partial A}{\partial \bar{u}} \cdot \frac{\partial B}{\partial \bar{\rho}} - \frac{\partial B}{\partial \bar{u}} \cdot \frac{\partial A}{\partial \bar{\rho}} \right)
- \int d^3r \bar{u} \left( \frac{\partial A}{\partial \bar{u}} \cdot \frac{\partial B}{\partial \bar{\rho}} - \frac{\partial B}{\partial \bar{u}} \cdot \frac{\partial A}{\partial \bar{\rho}} \right)
- \int d^3r \bar{s} \left( \frac{\partial A}{\partial \bar{u}} \cdot \frac{\partial B}{\partial \bar{s}} - \frac{\partial B}{\partial \bar{u}} \cdot \frac{\partial A}{\partial \bar{s}} \right).
$$

(B.1)

The distribution $f$ is convected by $\{A, B\}_f$ in Eq. (4.6). Obviously, the bracket $\{A, B\}' = \{A, B\}_f + \{A, B\}_f$ defines successfully a Poisson structure, and in particular obeys the Jacobi identity. By means of the successive variable transformation $(\bar{\rho}, \bar{u}, \bar{s}, f) \rightarrow (\rho, u, s)$ for simplicity we assume $\xi_{v_r} = \xi I_{3 \times 3}$. For the mass density we obtain:

$$
\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial r} \left( \rho v \right) + \frac{\rho}{1 - \langle V \rangle} \left( v \cdot \frac{\partial \langle V \rangle}{\partial r} - \frac{\partial}{\partial r} \langle V \rangle \right)
- \frac{mk_B}{1 - \langle V \rangle} \left( 1 - \frac{\rho}{\rho_c} \right) \left( \frac{\partial D_{N_c,N_c}}{\partial N_c} - D_{N_c,N_c} \frac{\partial V_S}{\partial N_c} + D_{N_c} \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} \right) \right).
$$

(B.2)
Appendix B. Nonequilibrium Thermodynamics of Nucleation

While the first term on the right hand side describes the reversible convection of mass, the
second describes reversible changes due to spatial changes in the occupied volume of nuclei.
The remaining terms define source or sink terms due to the mass exchange with the nuclei.
We obtain for the momentum density

\[
\frac{\partial \mathbf{u}}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{u} \mathbf{v}) - \frac{\partial}{\partial \mathbf{r}} \cdot \pi - \frac{\langle V_c \rangle}{1 - \langle V_c \rangle} \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{r} + \mathbf{u} \cdot \frac{\partial \langle V_c \rangle}{\partial \mathbf{r}} - \frac{\partial}{\partial \mathbf{r}} \cdot \langle V_c \mathbf{v}_c \rangle \\
- \frac{mk_B}{1 - \langle V_c \rangle} \left\langle \left( \mathbf{v}_c - \frac{\mathbf{u}}{\rho_c} \right) \left[ \frac{\partial D_{N,N_c}}{\partial N_c} - D_{N,N_c} \frac{\partial V_S}{\partial N_c} + D_{N,U_c} \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} \right) \right] \right\rangle \\
- \frac{1}{1 - \langle V_c \rangle} \left\langle M_c^2 k_B \xi (\mathbf{v} - \mathbf{v}_c) \right\rangle, \tag{B.3}
\]

where \( \tau = 2n \kappa^4 + \xi \mathbf{tr} \) is the extra stress tensor of the metastable phase, \( \pi = \tau + pI_{3x3} \) is the
stress tensor. We obtain for the energy balance:

\[
\frac{\partial u}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{u} \mathbf{v}) - \pi \frac{\partial}{\partial \mathbf{r}} \mathbf{v} - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{j}_q - \frac{\langle V_c \rangle}{1 - \langle V_c \rangle} \mathbf{r} \cdot \frac{\partial}{\partial \mathbf{r}} \mathbf{r} - \frac{\langle V_c \rangle}{1 - \langle V_c \rangle} \frac{\partial}{\partial \mathbf{r}} \mathbf{r} \cdot \mathbf{j}_q \\
+ \frac{\langle u + p \rangle}{1 - \langle V_c \rangle} \left( \mathbf{v} \cdot \frac{\partial \langle V_c \rangle}{\partial \mathbf{r}} - \frac{\partial}{\partial \mathbf{r}} \cdot \langle \mathbf{v} \mathbf{v}_c \rangle \right) - \frac{mk_B}{1 - \langle V_c \rangle} \left\langle \frac{1}{2} (\mathbf{v} - \mathbf{v}_c)^2 - \frac{u}{\rho_c} \right\rangle \left[ \frac{\partial D_{N,N_c}}{\partial N_c} \\
- D_{N,N_c} \frac{\partial V_S}{\partial N_c} + D_{N,U_c} \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} \right) \right] \right\rangle + \frac{k_B}{1 - \langle V_c \rangle} \left\langle \frac{M_c}{2} (\mathbf{v} - \mathbf{v}_c)^2 - 1 \right\rangle \\
- \frac{k_B}{1 - \langle V_c \rangle} \left\langle D_{N,U_c} \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} \right) + \frac{\partial D_{U,N_c}}{\partial N_c} - D_{N,N_c} \frac{\partial V_S}{\partial N_c} \right\rangle, \tag{B.4}
\]

where \( \mathbf{j}_q = -\lambda \frac{\partial}{\partial \mathbf{r}} T \) is the diffusive heat flux.

B.3 Entropy Production

In order to study the entropy production in the nucleation process, it is useful to look at
thermodynamic forces and fluxes in the mass-, momentum- and internal energy exchange
mechanisms. To this extent we define the thermodynamic force,

\[
X_{N_c} = k_B \frac{\partial}{\partial N_c} \left( -V_S - \ln (f) \right), \tag{B.5}
\]

roughly interpreted as a generalized chemical potential difference between the metastable
phase and nuclei, the thermodynamic force

\[
X_{U_c} = \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} - k_B \frac{\partial \ln (f)}{\partial U_c} \right), \tag{B.6}
\]

associated with temperature differences of the metastable phase and nuclei, and finally

\[
X_{M,v_c} = \frac{1}{M_c} \left( \frac{1}{2} M_c \mathbf{v} - \mathbf{v}_c - k_B \frac{\partial \ln (f)}{\partial \mathbf{v}_c} \right), \tag{B.7}
\]
related to differences in velocities between the two phases. We introduce the thermodynamic fluxes from the metastable phase into the nucleating phase, corresponding to mass flux,

\[ J_{Nc} = D_{Nc,Nc} X_{Nc} + D_{Nc,Uc} X_{Uc}, \] (B.8)

and analogously the internal energy flux

\[ J_{Uc} = D_{Uc,Nc} X_{Nc} + D_{Uc,Uc} X_{Uc}, \] (B.9)

and momentum flux:

\[ J_{M_v} = M_c T \xi \cdot X_{M_v}. \] (B.10)

The Fokker-Planck equation for nonisothermal nucleation (4.19) can be cast into

\[ \frac{\partial f}{\partial t} = - \frac{\partial}{\partial r} \cdot v_c f + \frac{1}{M_c} \frac{\partial}{\partial v_c} : f \frac{\partial}{\partial r} V_c p - \frac{\partial}{\partial v_c} \cdot J_{M_v} f - \frac{\partial}{\partial N_c} J_{Nc} f - \frac{\partial}{\partial U_c} J_{Uc} f. \] (B.11)

The fluxes Eq. (B.8)-(B.10) are of irreversible origin, and in Eq. (B.11) we realize that there is an additional influx into the state-space variable \( v_c \) related to the pressure gradient, which however as discussed is of reversible origin. The total entropy production in the system,

\[ \frac{dS}{dt} = \int d^3r \left( \frac{2}{T} \kappa : \kappa \right) - \lambda T J_q \cdot \frac{\partial}{\partial r} f + \left\langle X_{Nc} J_{Nc} + X_{Uc} J_{Uc} + X_{M_v} \cdot J_{M_v} \right\rangle, \] (B.12)

separates into irreversible processes in the environment and contributions due to exchange of mass, momentum and energy between environment and nuclei. The latter is governed by differences in intensive quantities.

### B.4 Thermodynamic Model for Nuclei: Detailed Derivation

We introduce the equilibrium pressure \( p_{eq,Nc}^{eq,Nc}(T_c) \) and chemical potential \( \mu_{eq,Nc}^{eq,Nc}(T_c) \) corresponding to an equilibrium state of a nucleus of size \( N_c \) in coexistence with its vapor at temperature \( T_c \). The state of the latter is described by the gas pressure \( p_{eq,Uc}(T_c) \) and chemical potential \( \mu_{eq,Uc}(T_c) \) (we also use the corresponding internal energy \( u_{eq,Nc}^{eq,Nc} \)), and the equilibrium conditions are

\[ p_{eq,Nc}(T_c) - p_{eq,Uc}(T_c) = 2\gamma(T_c)/r_c(N_c) \] and \( \mu_{eq,Nc}(T_c) = \mu_{eq,Uc}(T_c) \),

where \( r_c(N_c) \) is the nucleus radius. We also introduce the nuclei quantities \( p_{eq,\infty}(T_c) \) and \( \mu_{eq,\infty}(T_c) \), and respective gas variables \( p_{eq,\infty}(T_c) \) and \( \mu_{eq,\infty}(T_c) \) corresponding to the equilibrium coexistence values of a nucleus with size \( N_c \rightarrow \infty \) for which the interface separating the nucleus from the ambient phase can be considered flat and therefore \( p_{eq,\infty}(T_c) = p_{eq,\infty}(T_c) \) and \( \mu_{eq,\infty}(T_c) = \mu_{eq,\infty}(T_c) \). The fact that the surface tension \( \gamma(T_c) \), considered as a property of the
nucleus, is solely a function of the $T_c$ and the incompressibility assumption leads to [152]

$$\mu_c^{eq,N_c}(T_c) - \mu_c^{eq,\infty}(T_c) = \frac{1}{\rho_c} \left( p_c^{eq,N_c}(T_c) - p_c^{eq,\infty}(T_c) \right). \tag{B.13}$$

We assume that $\rho_c^{eq,N_c}(T_c), \rho_c^{eq,\infty}(T_c) \ll \rho_c$ and that the latent heat of evaporation $L$ obeys $mL(T_c) = mL_0 + (c^p - c_c^p)T_c$, where $c^p$ and $c_c^p$ are the heat capacities at constant pressure of the vapor and cluster [65]. From the Clapeyron relation we then conclude

$$\ln \left( \frac{p_c^{eq,\infty}(T)}{p_c^{eq,\infty}(T_c)} \right) = \left( \frac{1}{T_c} - \frac{1}{T} \right) mL(T_c) - (c^p - c_c^p) \left[ \ln \left( \frac{T_c}{T} \right) + \left( 1 - \frac{T_c}{T} \right) \right]. \tag{B.14}$$

We also fix the equation of state for $U_c^b$ using the Clausius jump relationship [153, 123]

$$\frac{1}{V_c} \frac{U_c^b(N_c, T_c) - V_c u_c^{eq,N_c}(T_c)}{\rho_c - \rho_c^{eq,N_c}(T_c)} = \mu_c^{eq,N_c}(T_c) - T_c \frac{d\mu_c^{eq,N_c}(T_c)}{dT_c} - \frac{2}{r_c A_c} \frac{U_c^b(N_c, T_c)}{\rho_c - \rho_c^{eq,N_c}(T_c)}, \tag{B.15}$$

where the third term on the right hand side involves the curvature correction. Using the Clapeyron equation again the simple form $U_c^b(N_c, T_c) = 3/2N_c k_B T_c - N_c (mL(T_c) - k_B T_c)$ is implied, and using Eq. (B.13), Eq. (B.14) and Eq. (B.15) the nucleation landscape (4.22) results.

### B.5 Stochastic Process Behind Nucleation Process

We seek a numerical solution of the Fokker-Planck equation (4.19) in the absence of pressure gradients and with $\xi_{\nu_c} = \xi_{3x3}$. Given the Wiener Increments $dW_{\nu_c}^E$, $dW_{t}^{N_c}$ and $dW_{t}^{U_c}$ the appropriate stochastic processes for the position of the nuclei $r(t)$, the velocity $v_c(t)$, size $N_c(t)$ and energy $U_c(t)$ in the Ito sense are given by [141]:

$$dr = v_c dt,$$

$$dv_c = -M_c \xi (v_c - \nu) dt + \sqrt{2k_B T_c} dW_t^\nu,$$

$$dN_c = k_B \left[ \frac{\partial D_{N_c,N_c}}{\partial N_c} - \frac{\partial V_S}{\partial N_c} + \frac{\partial V_S}{\partial U_c} \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} \right) \right] dt + \sigma_{N_c,N_c}^D dW_t^{N_c} + \sigma_{N_c,U_c}^D dW_t^{U_c}, \tag{B.16}$$

$$dU_c = k_B \left[ \frac{\partial D_{N_c,U_c}}{\partial N_c} - \frac{\partial V_S}{\partial N_c} + \frac{\partial V_S}{\partial U_c} \left( \frac{\partial S_c}{\partial U_c} - \frac{1}{T} \right) \right] dt + \sigma_{U_c,U_c}^D dW_t^{U_c}.$$

Here, $\sigma = \sqrt{2k_B D}$. To calculate the stationary nucleation rate for homogeneous nucleation we set the initial conditions (the stationary nucleation rate is independent on the initial conditions) of stochastic trajectories to $N_c(t = 0) = N_c^{\text{min}}$, where $N_c^{\text{min}}$ is the smallest possible size of a nucleus. We set $v_c(t = 0)$ to a Maxwellian corresponding to the temperature $T$, and $U_c(t = 0)$ is set to the corresponding value of nuclei of size $N_c^{\text{min}}$ in equilibrium with their ambient phase. When nuclei shrink to sizes smaller than $N_c^{\text{min}}$, we reset solely their size to $N_c^{\text{min}}$. Roughly, the nucleation rate is evaluated by counting the number of nuclei per unit time that pass the size $N_c^{\text{max}}$ much larger than the critical size $N_c^{*}$ of the isothermal nucleation theory. When a nucleus surpasses $N_c^{\text{max}}$ it is reset to the aforementioned initial conditions.
C Nonequilibrium Statistical Mechanics of Nucleation

C.1 Details to Derivation of Coarse-Graining Procedure

We use the GENERIC coarse-graining technique, see Sec. 2.2, in order to find the fundamental time evolution of the distribution function $f(x_c)$ of the nucleus of interest. To this extent a projection operator $\mathcal{P}$ is introduced that separates the macroscopically relevant contribution of an arbitrary observable $\Pi_A$ on the phase space $\bar{\Gamma}$ from the irrelevant ones to be eliminated - this corresponds to the separation of macroscopically relevant from irrelevant degrees of freedom when switching from the finer-level of description involving all atoms to the coarse-grained level characterized by $(x_{\text{tot}}, f(x_c))$. Following the standard definition [98], we define the projection onto the slow variables

$$\mathcal{P} \Pi_A = \langle \Pi_A \rangle_{x_{\text{tot}}, x_c} + \langle \Pi_{x_{\text{tot}} - x_{\text{tot}}} \rangle_{x_{\text{tot}}, x_c} \frac{\delta}{\delta x_{\text{tot}}} \langle \Pi_A \rangle_{x_{\text{tot}}, x_c} + \int dx_c \langle \Pi f(x_c) - f(x_c) \rangle \frac{\delta}{\delta f(x_c)} \langle \Pi_A \rangle_{x_{\text{tot}}, x_c}. \quad (C.1)$$

Using $\rho_{x_{\text{tot}}, x_c} \Pi f(x_c) = f(x_c) \rho_{x_{\text{tot}}, x_c}$, where

$$\rho_{x_{\text{tot}}, x_c} \propto \delta(\Pi_{x_{\text{tot}}} - x_{\text{tot}}) \delta(\Pi_{x_c} - x_c), \quad (C.2)$$

is the microcanonical ensemble, the projection operator can be expressed alternatively through averages $\langle \ldots \rangle_{x_{\text{tot}}, x_c}$ over the ensemble $\rho_{x_{\text{tot}}, x_c}$ as

$$\mathcal{P} \Pi_A = \langle \Pi_A \rangle_{x_{\text{tot}}, x_c} + \langle \Pi_{x_{\text{tot}} - x_{\text{tot}}} \rangle_{x_{\text{tot}}, x_c} \frac{\delta}{\delta x_{\text{tot}}} \int dx_c f(x_c) \langle \Pi_A \rangle_{x_{\text{tot}}, x_c}. \quad (C.3)$$

The first part projects onto the nucleus variables $\Pi_x$, while the second part onto the system state $x_{\text{tot}}$. Complementary, we define $\mathcal{Q} = 1 - \mathcal{P}$ as the projection onto the fast variables. Denoting by $i\mathcal{L}$ the Liouville operator on $\hat{\Gamma}$, we notice that $i\mathcal{L} \Pi_{x_{\text{tot}}} = 0$. The fact that $x_{\text{tot}}$ are conserved quantities also implies on the macroscale $dx_{\text{tot}}/dt = 0$. The projection operator technique, see also Eq. (2.2), Eq. (2.6) and Eq. (2.8), then implies [77, 98] the time evolution for
Appendix C. Nonequilibrium Statistical Mechanics of Nucleation

\[
\frac{\partial f(x_c)}{\partial t} = (i \mathcal{L} \Pi_f(x_c)) \rho_{x_c} + \int dx'_c M_f(x_c, f(x'_c)) \frac{\delta S(x_{tot}, f)}{\delta f(x'_c)},
\]

(C.4)

where

\[
M_f(x_c, f(x'_c)) = \frac{1}{k_B} \int_0^{\tau_{GK}} du \langle \Pi_f(x'_c) G(u) \Pi_f(x_c) \rangle \rho_{x_c}.
\]

(C.5)

Here, \( \Pi_f(x_c) = \mathcal{D} i \mathcal{L} \Pi_f(x_c) \) is the fast time evolution of \( \Pi_f \) and \( G(u) = e^{2i \mathcal{L} \mathcal{D} u} \) is the time evolution operator. The time evolution equation for \( f \), Eq. (C.4), splits into a reversible part, see also Eq. (2.6), and an irreversible part involving the Green-Kubo coefficients \( M_f(x_c, f(x'_c)) \) and total entropy \( S(x_{tot}, f) \) of the system. The time-scale \( \tau_{GK} \) is an intermediate time-scale between microscopic collisions and the mesoscopic time-scale on which the nucleation process is described in a coarse-grained way.

Using the auxiliary properties

\[
i \mathcal{L} \Pi_f(x_c) = -\frac{\delta \Pi_f(x_c)}{\delta x_c} \cdot i \mathcal{L} \Pi_{x_c},
\]

(C.6)

and (C.2) the reversible part of the time evolution can be cast into

\[
\frac{\partial f(x_c)}{\partial t} \bigg|_{\text{rev}} = \langle i \mathcal{L} \Pi_f(x_c) \rangle \rho_{x_c} = -\frac{\delta}{\delta x_c} f(x_c) \langle i \mathcal{L} \Pi_{x_c} \rangle \langle x_{tot}, x_c \rangle.
\]

(C.7)

We now turn our attention back to the projection operator \( \mathcal{P} \). This operator, or its counterpart \( \mathcal{D} \) act on \( i \mathcal{L} \Pi_{x_c} \) in the evolution equation, see Eq. (C.4) and Eq. (C.7) - we must understand \( \langle i \mathcal{L} \Pi_{x_c} \rangle \langle x_{tot}, x_c \rangle \). For nucleation in homogeneous media this reversible part is known to vanish, so that we already expect

\[
\langle i \mathcal{L} \Pi_{x_c} \rangle \langle x_{tot}, x_c \rangle = 0
\]

(C.8)

This implies \( \mathcal{P} i \mathcal{L} \Pi_{x_c} = 0 \) and \( \mathcal{D} i \mathcal{L} \Pi_{x_c} = i \mathcal{L} \Pi_{x_c} \). The argument for Eq. (C.8) can be made more formal by recognizing that the average over \( i \mathcal{L} \Pi_{x_c} \) must be taken over all states compatible with the microcanonical ensemble \( \rho_{x_{tot}, x_c} \), that is over all states for which we encounter a nucleus with properties \( x_c \). But if a certain atomistic configuration \( C = (r_1, ..., r_N, p_1, ..., p_N) \) contains a nucleus with properties \( x_c \), then also the mirror image \( C' = (-r_1, ..., -r_N, p_1, ..., p_N) \) obeys this requirement. It is important that the momentum variables must not be mirror imaged, since otherwise the momentum \( \Pi_p \) of \( C \) and \( C' \) do not match and therefore \( C' \) would not fall into the class \( x_c \). In \( C \) all particles that would be about to join the nucleus would be about to leave it in \( C' \) and vice versa. In the same manner one can argue that in \( C \) a momentum influx is transformed to a momentum out-flux in \( C' \) and vice versa. The same argumentation holds with the energy flux and consequently we have \( i \mathcal{L} \Pi_{x_c}(C) = -i \mathcal{L} \Pi_{x_c}(C') \) which implies
C.2 Derivation of Law of McGraw and LaViolette

Eq. (C.8).

In general [77], the irreversible part of the evolution equation (C.4) can be cast into

$$\frac{\partial f(x_c)}{\partial t}_{t_{irr}} = \int dx'_c M(f(x_c), f(x'_c)) \frac{\delta S(x_{tot}, f)}{\delta f(x'_c)}$$

$$= -\delta \frac{\delta}{\delta x_c} f(x_c) \cdot M(x_c) \cdot \delta \frac{\delta S(x_{tot}, f)}{\delta f(x_c)},$$

where

$$M(x_c) = \frac{1}{k_B T_GK} \int_0^{T_GK} du \langle \mathcal{L} \Pi x_c G(u) \mathcal{L} \Pi x_c \rangle(x_{tot}, x_c)$$

$$= \frac{1}{2k_B T_GK} \langle \Delta T_GK \Pi x_c \Delta T_GK \Pi x_c \rangle(x_{tot}, x_c).$$

We hence derived the fundamental evolution equation for nucleation in homogeneous media based on microscopic considerations. Through Sec. 2.1 this implies the dissipative bracket (5.9).

C.2 Derivation of Law of McGraw and LaViolette

We show that in the reduced state space $x^{\text{red}}_c$, where only the size and total kinetic energy is measured, the temperature $T_c$ indeed obeys the equation of state $E_{kin, i}^{\text{c}} = C_V T_c$ with the fluctuation law by McGraw and LaViolette. To this extent, notice that the integrand in Eq. (5.19), denoted by $\phi(x_{tot}, x_c, E_{kin, i}^{\text{c}})$, represents the probability that we observe a nucleus with property $x_c$ and internal kinetic energy $E_{kin, i}^{\text{c}}$. Therefore

$$\phi(x_{tot}, x^{\text{red}}_c) = \int d^3 P_c dU_c \phi(x_{tot}, x_c, E_{kin, i}^{\text{c}}).$$

(C.11)

Employing the approximation (5.20) the probability $\phi(x_{tot}, x_c, E_{kin, i}^{\text{c}})$ has the form of the right hand side of Eq. (5.22), but without the integration over $E'_c$. Therefore the integrations in Eq. (C.11) can be performed. The temperature can then be defined analogously to App. B.II to obtain $E_{kin, i}^{\text{c}} = C_V T_c$, and by employing the Stirling approximation finally the suggested fluctuation law by McGraw and LaViolette emerges,

$$V_S(x_{tot}, x^{\text{red}}_c) = V_S(x_{tot}, N_c) + \frac{1}{2} \ln(N_c) - (C_V / k_B) \left[ \ln \left( \frac{T_c}{T} \right) + \left( 1 - \frac{T_c}{T} \right) \right].$$

(C.12)

This shows that the kinetic energy of the nucleus is indeed a valid measure to obtain the nucleus temperature if no information about its potential energy is available.
Appendix C. Nonequilibrium Statistical Mechanics of Nucleation

C.3 Kinetic Energy as a State Variable

In view of the various equivalent expressions for the nucleation landscape $V_S$, see Eq. (5.17) and Eq. (5.25) for instance, it is plausible to ask whether the kinetic energy of the nucleus $E_{\text{kin},s}^c = P_c^2/(2mN_c)$ can be used as a state variable instead of the momentum $P_c$, since the latter enters the entropic barrier only in the contribution $P_c^2/(2k_BTmN_c)$ being the “systematic” kinetic energy of the nucleus. Suppose for the further considerations that $P = 0$ by Galilean invariance. If we use the modified set of nucleus state variables $x_{\text{mod}}^c = (N_c, E_{\text{kin},s}^c, U_c)$ instead of $x_c = (N_c, P_c, U_c)$ we have to construct the entropic potential in terms of these new variables. The entropic potential $\phi(x_{\text{tot}}, x_c)$ is the probability that we encounter a nucleus with state $x_c$ and therefore we find the clarifying relationship

$$\phi(x_{\text{tot}}, x_{\text{mod}}) = \int d^3P_c \delta \left( E_{\text{kin},s}^c - \frac{P_c^2}{2mN_c} \right) \phi(x_{\text{tot}}, x_c).$$  (C.13)

This can be used to obtain the landscape $V_S(x_{\text{tot}}, x_{\text{mod}}) = -\ln(\phi(x_{\text{tot}}, x_{\text{mod}}))$ which as a result, see also Sec. 5.3.2 and Eq. (5.25), is given by

$$V_S(x_{\text{tot}}, x_{\text{mod}}) = V_S(x_{\text{tot}}, N_c) + \frac{E_{\text{kin},s}^c}{k_BT} + 2\ln(N_c) - \left( C_p/k_B \right) \left[ \ln \left( \frac{T_c}{T} \right) + \left( 1 - \frac{T_c}{T} \right) \right]$$

$$+ \frac{1}{2k_B^2} \left( \frac{1}{T} - \frac{1}{T_c} \right)^2 + \Theta \left( \frac{1}{N_c} \right) + \text{const}(T).$$  (C.14)

The modified set of state variables have the advantage that the state space is smaller upon catching the same relevant macro-physics. The intuition is that in a homogeneous medium it is irrelevant in which direction the momentum $P_c$ points and therefore the nucleation process can equally be described by $|P_c|$, $P_c^2$ or the kinetic energy $E_{\text{kin},s}^c$.

C.4 Saddle Point Approximation for Nucleation Rate of Extended MFKT

For the prediction of the standard isothermal MFKT nucleation rate $J_K$ we refer to the book [27] of Kalikmanov (Chapter 7.7 - Steady State Nucleation Rate).

The dynamics of the extended MFKT is governed by Eq. (5.16) with the coefficient matrix for Brownian motion being diagonal. The evolution equation (5.16) of a nucleus in a metastable phase at temperature $T$, pressure $P$ and corresponding mass density $\rho$ can be solved in the saddle point approximation [156, 66], see also Sec. 4.5.2, and gives the prediction $J_{K,\text{ext}}$ of our extended MFKT:

$$J_{K,\text{ext}} = \sqrt{-\frac{1}{2\pi} \frac{\partial^2 V_S(x_{\text{env}}, x_c)}{\partial N_c^2}} |\lambda_{\text{min}}| \rho m w \sqrt{\det G} e^{-\Delta V_S(x_{\text{env}}, x_c^*)},$$  (C.15)
C.5 Nucleation Rates of MFKT Evaluated for Argon

where the Hessian matrix of \( V_S(x_{\text{env}}, x_c) \) at the saddle point is

\[
G = \frac{\xi^2}{\sigma^2_{U_c}} \begin{pmatrix} 1 - \frac{\omega^2}{\xi^2} & \frac{1}{\xi} \\ \frac{1}{\xi} & \frac{1}{\xi^2} \end{pmatrix}.
\]  

(C.16)

The coefficients are given by

\[
\sigma^2_{U_c} = T^2 \left. \frac{\partial U_c(N_c, T)}{\partial T} \right|_{N_c^*},
\]

\[
\frac{1}{\sigma^2_{N_c}} = -\theta_{\text{micro}}(T) \left. \frac{\partial N_c(T, N_c)}{\partial N_c^2} \right|_{N_c^*},
\]

\[
\omega^2 = \left. \frac{\sigma^2_{U_c}}{\sigma^2_{N_c}} \right|_{N_c^*},
\]

\[
\frac{\xi}{k_B} = -\frac{3}{2} T + T^2 \left. \frac{\partial \ln(\rho^{eq,\infty}(T))}{\partial T} \right|_{N_c^*} + T^2 \left. \frac{\partial^2 N_c(T, n)}{\partial N_c \partial T} \right|_{N_c^*} \theta_{\text{micro}} + T^2 \left. \frac{\partial N_c(T, n)}{\partial N_c} \right|_{N_c^*} d\theta_{\text{micro}}(T),
\]

(C.17)

and

\[
\lambda_{\text{min}} = \frac{1}{2} \left[ \text{tr} R - \sqrt{\text{tr}(R)^2 - 4 \det R} \right].
\]  

(C.18)

identified as the smallest eigenvalue of \( R = \bar{D}(N_c^*) G \). All quantities in Eq. (C.17) and \( \lambda_{\text{min}} \) must be evaluated at the saddle point \( x_c^* = (N_c^*, P_c^* = 0, U_c^*) \) of the nucleation landscape \( V_S(x_{\text{env}}, x_c) \) as given by Eq. (5.17). For the internal energy this saddle point falls on \( U_c^* = U_c(N_c^*, T) \). Here, \( \Delta V_S(x_{\text{env}}, x_c^*) \) denotes the height of the nucleation landscape, and \( m \) is the mass of atoms. In the saddle point approximation (C.15) the effects of Brownian motion are seemingly irrelevant since the coefficients \( \xi_{P_c} \) are not involved. This is however not true since the logarithmic normalization factor \( 3/2 \ln(N_c^*) \) contained in \( \Delta V_S(x_{\text{env}}, x_c^*) \), see Eq. (5.17), enters the prediction.

C.5 Nucleation Rates of MFKT Evaluated for Argon

Specifically, we evaluated the MFKT nucleation rates \( J_K \) and \( J_{K, \text{ext}} \) by resampling to the following relationships for which precise MD thermo-physical data is available, see Table 5.1.

We shortly summarize the parameters appearing in the MFKT and closely follow the lines of its inventor [52, 27]. According to Kalikmanov, the microscopic surface tension is given by

\[
\theta_{\text{micro}}(T_c) = -\ln(-B_2(T_c) p^{eq,\infty}(T_c)/(k_B T_c)),
\]

where \( B_2 \) is the second virial coefficient of the gas. Introducing the macroscopic surface tension \( \gamma(T_c) \), we can define the ratio \( \bar{\omega}(T_c) = \gamma(T_c)/(k_B T_c \theta_{\text{micro}}(T_c)) \). We further define \( \xi = N_c^{-1/3} \) and the coefficient \( \lambda = \sqrt{N_1/\omega - 3/4 - 3/2} \), where \( N_1 \) is the number of neighbors of particles in the nucleus. The number of neighbors
in the nucleus is evaluated from the argon-liquid properties and can be approximated by
\[ N_1(T_c) = 5.5116\eta(T_c)^2 + 6.1383\eta(T_c) + 1.275, \]
where \( \eta(T_c) = \frac{\varrho_c(T_c)}{\varrho_c(T_c) d_{hs}^3} \). Here, \( d_{hs} \) is given by
the Barker-Henderson relation with the Weeks-Chandler-Anderson decomposition of the
intermolecular potential, and represents the effective hard sphere diameter in the theory
of liquids, \( d_{hs}(T_c) = a_1 T + b_1 / (a_2 T_c + a_3) \sigma \) with the Lennard-Jones parameters \( \sigma = 3.822 \times 10^{-10} \text{m} \) and \( \epsilon = 1.654 \times 10^{-21} \text{J} \). The coefficients are given by \( a_1 = 0.56165 \frac{k_B}{\epsilon}, \)
\( a_2 = 0.60899 \frac{k_B}{\epsilon} \), \( a_3 = 0.92868 \frac{k_B}{\epsilon} \), and \( b_1 = 0.9718 \frac{k_B}{\epsilon} \). The mass of argon particles is \( m = 6.690 \times 10^{-26} \text{kg} \).
The average number of particles \( N_c^s(N_c, T_c) = \tilde{a}(N_c, T_c) N_c \) located at the surface of the nucleus is
obtained by solving a cubic equation for the introduced coefficient \( \alpha(N_c, T_c) \). In particular,
\[ \tilde{a} = 3\omega \tilde{a} (1 - \alpha)^{2/3} + 3\tilde{a}^2\tilde{a}^2 (1 - \alpha)^{1/3} + \tilde{a}^3 \tilde{a}^3 \]
For the kinetic coefficient \( D_{N_c N_c} \), we used the form suggested by Kalikmanov
\[ k_B D_{N_c N_c} = \frac{S}{\sqrt{2\pi m k_B T}} A_c(N_c), \quad (C.19) \]
where \( A_c(N_c) = 4\pi r_c^2 \) is the surface area of the nucleus and \( r_c = (3m N_c / (4\varrho_c \pi))^{1/3} \) its ra-

dius. The remaining coefficients are given by predictions of Barret \[ 66, 185, \] i.e., \( D_{N_c U_c} =
2k_B T D_{N_c N_c} \) and \( D_{U_c U_c} = 6(k_B T)^2 D_{N_c N_c} \).

C.6 Additional Notes on Short-Time MD for Diffusion Coefficients

In evaluating the coefficients \( \langle \Delta r_{Gk} \Pi_{x_k} \Delta r_{Gk} \Pi_{x_k} \rangle_{x_{out}, x_k} \) we notice that the microscopic process
behind its contribution is the exchange of mass, momentum and energy of the nucleus with
the ambient phase. We adopted the tWF cluster criterion in our MC simulations, and within
this criterion there are always particles located at the surface of the nucleus which are not
part of the nucleus since they have less than 5 neighbors. These particles can however stay
at the surface of the nucleus for a considerable time-scale much larger than the collision
time-scale \( \tau_{Gk} \) and even rapidly oscillate between being part of the nucleus and part of the
ambient phase. These oscillations lead to significant noise effects that make it difficult to
evaluate the true diffusion coefficients, which by nature should only be affected by particles
that truly collide, are absorbed or emitted by the nucleus and do not fall in the undesirable
class of oscillating surface particles, an inherent drawback of the tWF cluster criterion. The
contribution to the diffusion coefficient from the oscillating particles should disappear if we
average over sufficiently many simulations. The resulting noise effects are understood by the
fact that the number of attempts with which the outer shell particles oscillate between being a
nucleus property and a gas property outnumbers the true collision attempts from the ambient
phase. We found that we can significantly improve the statistics of \( \langle \Delta r_{Gk} \Pi_{x_k} \Delta r_{Gk} \Pi_{x_k} \rangle_{x_{out}, x_k} \) by
using instead of the tWF cluster criterion, the Stillinger-cluster criterion only so that now the
oscillating particles in the tWF cluster definition belong to the nucleus as well and thereby,
the nucleus state \( x_k \) only changes through desirable collision processes. It is expected that
this procedure results in an error in the obtained diffusion coefficients since by deciding
that the outer layers of the nucleus is now also a nucleus property, the original nucleus state obtained from the tWF definition is modified. This error only affects the prefactor $D^0_{N_t,N_c}$ in Eq. (5.30). The Stillinger criterion gives typically nucleus sizes $N_{c,\text{Stillinger}}^*$ that are 3/2 larger than the ten-Wolde nucleus size $N_{c,tWF}^*$. In Eq. (5.30) we set $D^0 = D_{N_t,N_c}/N_{c,tWF}^{2/3}$. Suppose we obtained $D_{N_t,N_c}$ in our simulation around the critical size $N_{c,\text{Stillinger}}^* \approx 3/2 N_{c,tWF}^*$ with the Stillinger criterion, then $D^0 = D_{N_t,N_c}/(N_{c,\text{Stillinger}}^*)^{2/3}$ and if we use the ten-Wolde definition, we must get the same coefficient $D_{N_t,N_c}$, but $D^0 = D_{N_t,N_c}/(N_{c,tWF}^*)^{2/3}$. This means that the two values obtained for $D^0$ are distinct by a factor $(N_{c,\text{Stillinger}}^*/N_{c,tWF}^*)^{3/2} \approx 2$, so that the nucleation rate prediction that depends linearly on $D^0$ is affected by an error of a factor of two. In nucleation theory this error is negligible.
Marco Schweizer

Contact Information
Vladimir-Prelog-Weg 2
Department of Materials
Polymer Physics
ETH Zurich
Switzerland
Voice: +41 44 632 35 59
Fax: +41 44 632 10 76
E-mail: marco.schweizer@matl.ethz.ch
www.polyphys.mat.ethz.ch/people/phd_stud/schmarco

Research Interests
Nonequilibrium statistical mechanics, nonequilibrium thermodynamics, dissipative quantum mechanics, physics of interfaces, Brownian dynamics, molecular dynamics, Monte-Carlo simulations

Education
ETH Zurich, Zurich, Switzerland
Ph.D. Candidate, Polymer Physics, April 2011 (graduation date: September 2015)
- Advisors: Hans Christian Öttinger, Leonard Sagis, Thierry Savin

M.S., Physics, 2010
- Advisor: Hans Christian Öttinger

Awards
IBM Research Prize for master thesis, 2011

Academic Experience
ETH Zurich, Zurich, Switzerland
Teaching Assistant: Includes courses in transport phenomena (fluid dynamics), design and supervision of student projects in molecular dynamics and Brownian dynamics.

Publications


Papers in preparation

Conference Presentations

Local equilibrium for interfaces and gauge transformations verified by simulations, 6th International Workshop on Nonequilibrium Thermodynamics and 3rd Lars Onsager Symposium, Roros, Norway, August, 2012.