Surface phenomena and phase change in nanoparticles and nanodroplets, a molecular dynamics study

Author(s):
Arcidiacono, Salvatore

Publication Date:
2004

Permanent Link:
https://doi.org/10.3929/ethz-a-004941023

Rights / License:
In Copyright - Non-Commercial Use Permitted
Surface Phenomena and Phase Change in Nanoparticles and Nanodroplets
a Molecular Dynamics Study

A dissertation submitted to the
EIGENÖSSISCHE TECHNISCHE HOCHSCHULE ZÜRICH
for the degree of
Doctor of Technical Sciences

Presented by
SALVATORE ARCIDIACONO
Dipl. Ing., Università degli Studi di Palermo, Italy

Born on July 9th, 1974
Citizen of Italy

Accepted on the recommendation of
Prof. Dr. D. Poulakakos, examiner
Prof. Dr. P. Koumoutsakos, co-examiner

Zurich, 2004
Seite Leer / Blank leaf
Acknowledgments

Above all I would thank Prof. D. Poulikakos for giving me the possibility to start a Ph.D. at ETH Zurich, for his supervision, and his ideas.

Thanks to all the people I worked with during my Ph.D. that strongly contributed to enrich the present work: Prof. P. Koumoutsakos, who was also the co-advisor of this thesis; Dr. Y. Ventikos, Dr. N. Bieri, Dr. J. H. Walther, and Dr. D. Passerone.

This work was supported by the Research Commission of ETHZ

Thanks to Prof. M. Ciofalo that taught me the scientific attitude and the love for research.

I would like to thank also all the people with whom I spent the last four years for their friendship and the fruitful exchange of ideas. The friends here in Zurich: Dr. A. Chaniotis, Dr. L. Demiryaidin, Dr. C. da Pieve, Dr. C. Del Taglia, M. Dietzel, S. De Gruttola, I. Chatsiprodromo, G. Romera. The friends in Palermo: A. Riggio, F. Incarbona, and all the people of the “Comparato”.

Last but not least, I would like to thank my family (my mother, Moira, Maria Piera, and Gianfranco “Armai”) for their constant support.
# Table of Contents

AWKNOLEDGMENTS ............................................................................................................... III
SUMMARY .............................................................................................................................. VII
SOMMARIO ............................................................................................................................. IX

1  MOLECULAR DYNAMICS SIMULATION IN NANOSCALE HEAT TRANSFER .............. 1
   ABSTRACT ............................................................................................................................. 1
   1.1 INTRODUCTORY COMMENTS ..................................................................................... 1
   1.2 THE BASIC PRINCIPLE OF THE MOLECULAR DYNAMICS SIMULATION METHOD ....... 2
   1.3 MOLECULAR DYNAMICS IN HEAT TRANSFER .......................................................... 4
       1.3.1 Liquid-Vapor Interface ......................................................................................... 5
       1.3.2 Solid-Liquid-Vapor Interactions ......................................................................... 8
       1.3.3 Nucleation and Phase Change .......................................................................... 13
       1.3.4 Coalescence ........................................................................................................ 18
       1.3.5 Other Topics Related to Nanotechnology Systems ........................................... 20
   SUMMARY .......................................................................................................................... 25
   REFERENCES ....................................................................................................................... 25

2  OSCILLATORY BEHAVIOR OF NANODROPLETS ...................................................... 30
   ABSTRACT ............................................................................................................................. 30
   2.1 INTRODUCTION ............................................................................................................ 30
   2.2 MOLECULAR DYNAMICS SIMULATIONS ................................................................... 32
   2.3 RESULTS ....................................................................................................................... 33
       2.3.1 Liquid-Vapor Interface ......................................................................................... 33
       2.3.2 Surface Tension .................................................................................................... 37
       2.3.3 Droplet oscillation ............................................................................................... 38
   CONCLUSIONS .................................................................................................................... 44
   REFERENCES ....................................................................................................................... 45

3  ON THE COALESCENCE OF GOLD NANOPARTICLES ........................................... 47
   ABSTRACT ............................................................................................................................. 47
   3.1 INTRODUCTION ............................................................................................................ 47
   3.2 MODEL ............................................................................................................................ 49
       3.2.1 Molecular Dynamics Simulation .......................................................................... 49
       3.2.2 Analytical Model .................................................................................................. 50
   3.3 RESULTS ....................................................................................................................... 53
       3.3.1 Single Particles ...................................................................................................... 53
       3.3.2 Two Particle Coalescence ................................................................................... 55
   CONCLUSION ....................................................................................................................... 62
   REFERENCES ....................................................................................................................... 63
4 ON THE SOLIDIFICATION OF GOLD NANOPARTICLES IN CARBON NANOTUBES

ABSTRACT

4.1 INTRODUCTION

4.2 MOLECULAR DYNAMICS SIMULATION

4.3 RESULTS

4.3.1 Particle Structure

4.3.2 Melting

CONCLUSIONS

REFERENCES

5 THERMAL DIFFUSION OF GOLD NANOPARTICLES INSIDE NANOTUBES:

A PRELIMINARY STUDY

5.1 INTRODUCTION

5.2 MOLECULAR DYNAMIC SIMULATION

5.3 RESULTS

5.3.1 "Intrinsic" thermal diffusion

5.3.2 Thermally driven diffusion

CONCLUSIONS

REFERENCES

APPENDIX

CURRICULUM VITAE
Summary

Surface phenomena are dominant in nanosystems and nanotechnologies because at such scales the surface to volume ratio is very high and surface forces, surface tension and surface energy in general greatly affect the behavior of the system. In addition, continuity is lost at the nanoscale and other approaches need to be implemented, accounting for the discrete nature of the system. Developing a knowledge base for phenomena at these scales is a necessary pre-condition for the development technologies at the nanoscale. Molecular dynamics (MD) simulations are used herein to investigate such phenomena where the continuum approach breaks down. The present study is a fundamental work applied to important topics in nanoscience such as the behavior nanodroplets and nanoparticles. Thermal equilibrium as well as non-equilibrium are both considered.

The knowledge of the intrinsic oscillation frequency of a droplet is important for many applications directly related to phase change phenomena and coalescence (for example the solidification of a liquid particle impinging on a surface and the coalescence of two liquid droplets). The first part of this work (Chapter 2) is focused on the oscillatory behavior of a droplet in order to understand how the nanoscale dimensions of the droplet are affecting the predictions of the macroscopic theories. The second part (Chapters 3-5) focuses on gold nanoparticles. The phenomena of interest here are phase change (melting), coalescence through sintering and the effect of the particle surroundings (the particle is embedded in a single wall carbon nanotube) on the melting behavior.

Chapter I is a general introduction and literature survey on the use of MD simulations in nanoscale heat transfer. Recent literature on the simulation of liquid-vapor and solid-liquid-vapor interfaces, phase change, coalescence, and other relevant topics in nanosystems is reviewed and discussed.

The oscillatory behavior of nanodroplets is presented in Chapter II. Key thermodynamic parameters of Argon nanodroplets such as surface tension, density and pressure profiles are calculated for three different temperatures. It is shown that with a proper choice of the cutoff distance it is possible to obtain with a good calculation of the corresponding experimental values of Argon. The liquid-vapor interface thickness of the droplet is also characterized. The two contributions, one “intrinsic” related to the atomic interaction and one due to capillary waves, are
calculated and compared with the corresponding analytical predictions and experiments in the literature. Finally the free oscillations of the above mentioned nanodroplets and the limit of the applicability of continuum theory for such oscillations are studied. Although the simulated system cannot be considered strictly as a continuum, a good overall behavioral agreement is found.

The melting and the coalescence process of two gold nanoparticles for a host of initial temperatures and starting radii in vacuum are discussed in Chapter III. The MD simulations are initially tested comparing the findings for single particle melting with experiments in the literature and a theoretical analysis. The coalescence process is investigated and described in detail in its diverse mechanisms and phases. The results of the simulations are compared with a simple phenomenological macroscopic model of others based on an energy balance and supplemented by a model for the surface variation of the nanosystem under consideration. Accounting for the findings of the MD simulations for the growth rate of the neck formed between two particles, the validity range of the analytical model with the initial temperature and radius of the particle is determined.

In Chapter IV the solidification and structure of gold nanoparticles with different number of atoms inside single wall carbon nanotubes (SWCNT) are studied and compared with previous findings obtained for particles in vacuum. A cylindrical layered structure is discovered for all the studied cases, while the solidification transition is delayed by the presence of the CNT. A comparison with a phenomenological model also developed in the present work indicates that the solidification temperature depends mostly on the length of the particle, while only a minor dependence on the radius $R_c$ of the CNT is found at least in the studied range $0.5 < R_c < 1.6$ nm.

The dissertation is concluded (Chapter V) with recommendations for future work, including preliminary findings on the thermally driven motion of discrete amounts of matter (gold nanoparticles) inside a carbon nanotube.
Sommario

I fenomeni superficiali rivestono un ruolo molto importante nei nanosistemi e nelle nanotecnologie, in quanto su scala nanoscopica il rapporto superficie/volume è molto elevato e, di norma, le forze di superficie, come la tensione o l'energia superficiale, influiscono in misura significativa sulla dinamica del sistema. Inoltre, l'ipotesi di continuità non è più valida su nanoscala ed è pertanto necessario implementare altri approcci che tengano conto della natura discreta di tali sistemi. Lo sviluppo di una conoscenza di base sui fenomeni a queste scale è una precondizione necessaria per lo sviluppo delle nanotecnologie. Simulazioni di dinamica molecolare (Molecular Dynamics) sono utilizzate in questa tesi per studiare tali fenomeni in cui l'approccio continuo fallisce. Il presente lavoro è uno studio di base applicato ad alcuni importanti campi della nanoscienza, come il comportamento di nanogocce e nanoparticelle. Sono presi in considerazione sia l'equilibrio che il non-equilibrio termico.

La conoscenza della frequenza d'oscillazione intrinseca di una goccia è importante per molte applicazioni direttamente connesse ai fenomeni legati al cambiamento di fase e alla coalescenza (ad es. la solidificazione di una particella liquida che collide con la superficie e la coalescenza di due gocce liquide). La prima parte di questo lavoro (Capitolo 2) è incentrata sul comportamento oscillatorio di una goccia al fine di capire come le dimensioni di tale goccia influenzino il fenomeno rispetto alle previsioni delle teorie macroscopiche. La seconda parte (Capitoli 3-5) verte sulle nanoparticelle d'oro. I fenomeni trattati sono: il cambiamento di fase (fusione), la coalescenza attraverso la sinterizzazione e l'effetto sulla solidificazione da parte dell'ambiente circostante (la particella è posta all'interno di un nanotubo di carbonio).

Il Capitolo 1 è un'introduzione generale all'uso delle simulazioni di MD nella termodinamica dei nanosistemi. Viene riportata e discussa un'ampia rassegna di letteratura scientifica di recente pubblicazione riguardante la simulazione delle interfacce liquido-vapore e/o solido-liquido-vapore, il cambiamento di fase, la coalescenza e altri aspetti rilevanti nei nanosistemi.

L'oscillazione delle nanogocce è descritta nel Capitolo 2. I parametri termodinamici chiave di una nanogoccia di argon, quali la tensione superficiale, la densità e i profili di pressione, sono calcolati a tre diverse temperature. Viene dimostrato che con una scelta
ad hoc della distanza cutoff nelle simulazioni è possibile ottenere una buona approssimazione dei valori sperimentali corrispondenti dell’argon. Lo spessore dell’interfaccia liquido-vapore della goccia viene anche caratterizzato. I due contributi, uno intrinseco correlato alle interazioni atomiche e uno dovuto alle onde capillari, sono calcolati e raffrontati a previsioni analitiche ed esperimenti. Infine, sono studiate le oscillazioni libere delle suddette nanogocce e i limiti d’applicabilità della teoria continua per tali oscillazioni. Nonostante il sistema di simulazione non può essere considerato come strettamente continuo, i due risultati sono in buon accordo.

La fusione e il processo di coalescenza di due nanoparticelle d’oro nel vuoto a partire da diversi raggi e temperature iniziali sono discusse nel Capitolo 3. Le simulazioni di MD sono testate inizialmente paragonando i risultati ottenuti per la fusione di una singola particella a quelli di esperimenti e analisi teoriche. Il processo di coalescenza è studiato e descritto in dettaglio nei sui diversi meccanismi e fasi. I risultati delle simulazioni sono confrontati con un semplice modello fenomenologico su scala macroscopica basato su di un bilancio energetico e integrato da un modello per il cambiamento della superficie del nanosistema in oggetto. Tenendo in considerazione i risultati delle simulazioni di MD per la crescita del “neck” che si forma tra le due particelle, è determinato l’intervallo di validità del modello analitico in funzione della temperatura e del raggio iniziali.

Nel Capitolo 4 la solidificazione e la struttura di nanoparticelle d’oro costituite da un diverso numero di atomi all’interno di un nanotubo di carbonio a parete singola (Single Wall Carbon Nanotube) sono studiate e confrontate con i risultati precedentemente ottenuti per le particelle nel vuoto. Una struttura a strati cilindrici è presente in tutti i casi studiati, mentre la transizione verso la solidificazione è ritardata dalla presenza del CNT. Un ulteriore raffronto con un modello fenomenologico, sviluppato nell’ambito di questa tesi, indica che la temperatura di solidificazione dipende soprattutto dalla lunghezza delle particelle piuttosto che dal raggio del CNT \( R_c \) almeno nell’intervallo studiato 0.5<\( R_c <1.6 \text{nm} \).

La parte finale della tesi (Capitolo 5) è dedicata alle raccomandazioni per ulteriori ricerche in questo ambito e include alcuni risultati preliminari sul trasporto di piccole quantità di materia (nanoparticelle d’oro) all’interno di un CNT.
1 Molecular Dynamics Simulation in Nanoscale Heat Transfer*

Abstract
The exponential growth of research activities in nanotechnologies, as well the rapidly increasing utilization of microscale technologies in societal applications is affecting directly the development and implementation of corresponding numerical methodologies in many scientific and technological areas, including heat transfer. Of particular interest are length scales at which the continuum approach ceases to be valid. Molecular Dynamics (MD) simulation is a very promising, general method to study such scales allowing for the direct simulation of the motion and interaction of particles (atoms or molecules). This paper reviews recent works on molecular dynamics in heat transfer, focusing on, but not limited to, challenging interfacial and phase change phenomena, to demonstrate the advantages, potential, as well as the current limitations of this methodology.

1.1 Introductory comments
A promising approach to investigate nanoscale phenomena (including nanoscale heat transfer) is Molecular Dynamics simulation. In this approach, one works directly at the molecular (resp. atomic) level. By solving Newton's equation of motion of every molecule in the system of interest numerically, detailed information on the entire nanoscopic (hopefully in the not too distant future also microscopic) system can be obtained. Although this idea is not new (it dates back to the 1950s and 1960s, when pioneering investigations were performed in the field of theoretical physics), it is not until recently that its employment in relatively “large” systems (involving several thousand particles or more) has begun. To exemplify, early studies, in 1957, Alder and Wainwright [1] focused on the dynamics of particles moving at constant velocity between perfectly elastic collisions and in 1964, Rahman [2] successfully solved the equations of motion for a set of Lennard-Jones particles. In selected engineering systems, the MD method can provide information that allows the revision or verification of ad hoc assumptions of continuum theory. However, there are two formidable difficulties that need to be overcome: first, all relevant intermolecular interactions should be correctly accounted for, and second, a large number of molecules need to be simulated in order to bridge the gap between the molecular and the

continuum levels and provide needed information for macroscopic models, or aid the understanding of the physics of the phenomena of interest. With the reference to the first difficulty mentioned above, physically correct potentials for the intermolecular interactions need to be available. Here one often relies on "ab-initio" calculations. Hence, although the molecular dynamics method deals with classical forces, the potentials necessary to determine these forces are often the result of quantum mechanical calculations. With reference to the second difficulty, it is hoped that the continuously and rapidly increasing computer speed, combined with constant improvements in the development of efficient computational algorithms, will allow for the realization of engineering computations that bridge the gap between the nano- and microscales, in other words, reach sizes after which continuum theory is applicable.

1.2 The Basic Principle of the Molecular Dynamics Simulation Method

The main premise of Molecular Dynamics simulation can be described as follows: considering the fact that at the primitive level every substance is made from elementary particles (atoms or molecules), if the basic dynamics parameters of these molecules, i.e. position, velocity, and interaction force, can be determined, the macroscopic physical properties of the substance, like volume, temperature, pressure, etc. can subsequently be obtained with a "bottom up" approach, via statistical methods. Based on this idea, the starting point of MD is Newton's second law. For the translational motion of a spherically symmetric molecule, this law has the simple form:

\[ F = m \frac{d^2 r}{dt^2} \]  

(1.1)

where \( F \) is the sum of the forces exerted on the molecule by the other molecules in the system,

\( r \) is the position vector of the molecule,

\( t \) is the time, and

\( m \) is the mass of the molecule

Integrating equation (1.1) once in time yields the velocity of the molecule. Integrating once more results in its displacement. If one integrates equation (1.1) for every molecule in the simulation domain step by step from some initial state, then detailed information of the movement of every molecule is obtained. This information can be further processed by time averaging, space averaging or both to provide the macroscopic physical properties over the entire simulation domain.

For molecules that have internal complex geometry, the original simple Newton equation of
motion is no longer sufficient. Depending on the type of molecular model used, a generalized form of the original Newton equation is adopted in the simulations. For example, using a rigid-body model, one has to consider the rotation of the molecule around its mass center; therefore the so-called "Euler Equation" should be used. However, no matter how complex the form of the equation of motion, the basic simulation procedure is always the same: first, integrating the equation of motion of every molecule to acquire its dynamical parameters; then performing an averaging of these dynamical parameters to obtain the values of macroscopic physical properties. As discussed earlier, one of the core problems (resp. difficulties) in Molecular Dynamics is the form and magnitude of the force term in the left-hand side of eq. (1.1). To calculate the interaction force among molecules, since in nature this force is electric/electromagnetic, one needs to have available an appropriate corresponding intermolecular potential model. Usually, this model comes from experimental data or quantum mechanics calculations (as mentioned earlier) and accounts for the contribution from two-body and three-body potentials. For calculations in a group of molecules, a many-body potential needs to be used [3]. Due to their small contribution to the total potential (and their significant impact on computational speed) the effect of more than two or three bodies in the potential equation is either overlooked, when acceptable from an accuracy standpoint, or simply appears as a correction term in the potential equation that can be calculated easily [4]. In many practical simulations, researchers consider only two-body potential so as to shorten the computational time with acceptable accuracy. Normally this is done by defining an "effective pair potential" and incorporating the effect of a three-body potential into this effective pair potential [4].

When a two-body potential model is chosen, the interaction force between a pair of molecules can be derived from this potential by the following relation:

$$F_{ij} = -\nabla u_{ij} \tag{1.2}$$

where $F_{ij}$ is the force acting on the $i$-th molecule by the $j$-th molecule, $u_{ij}$ is two-body potential between the $i$-th molecule and the $j$-th molecule.

Summing up all the forces exerted on one molecule by other molecules yields the total force on this molecule. After the total force on every molecule in the simulation domain has been calculated, one can integrate eq. (1.1) in time for each molecule.

Examples of potential functions for a host of materials relevant to heat transfer calculations are discussed in detail in a review paper by Maruyama [5] and will not be presented here for brevity.
It will suffice to mention the popular for its simplicity but limited Lennard-Jones (LJ) 12-6 potential which assumes that the molecules are spherically symmetric

\[ u(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]  

where \( \sigma \) [\text{m}] and \( \varepsilon \) [\text{J}] are scales for length and energy, respectively. Depending on the type of molecules, appropriate values of the characteristic length and energy scales should be used in the LJ model. The variation of the potential with the molecular separation distance \( r \) implies that to bring two molecules from far apart into closer proximity, we must remove energy. Conversely, if two molecules are close enough to feel attractive forces, but not so close that repulsive forces come into play, then energy must be supplied to increase the spacing of the molecules.

A generalization and improvement of the Lennard Jones potential with similar limitations is the Stoddard & Ford potential [6], which features a shift for the continuous decay:

\[ u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r_c} \right)^{6} \right] + \left( \frac{\sigma}{r_c} \right)^{12} - 3 \left( \frac{\sigma}{r_c} \right)^{6} \left( \frac{r}{r_c} \right)^2 - \left( \frac{\sigma}{r_c} \right)^{12} - \left( \frac{\sigma}{r_c} \right)^{6} \]  

The cut-off distance from the center of a spherical molecule or atom beyond which the effect of this potential is practically negligible is denoted by \( r_c \). Again, more complex molecules are non-spherical in nature and require more complex potentials. One such molecule very relevant to many heat transfer applications is water. A review of potentials for water can be found in [5].

1.3 Molecular Dynamics in Heat Transfer

Molecular level phenomena and their investigation are becoming with a very high rate important in heat and mass transfer research, driven both by the need to understand certain fundamental phenomena as well as by a plethora of new and forthcoming applications in the areas of micro- and nanotechnologies.

More specifically, studies of basic mechanisms of heat transfer such as in phase change demand the understanding of liquid-solid contact phenomena (such as wetting and nucleation) at the nanoscale level. Heat transfer in three-phase lines (evaporation or condensation of liquid on a solid surface, or solidification of a molten droplet on a surface) is a singular problem at the macroscopic level. The nucleation theory of a liquid droplet in vapor or of a vapor bubble in a liquid sometimes needs to take into account nuclei of the size of molecular clusters. The effect of the surfactant on the heat and mass transfer through liquid-vapor interface is also an example of
the direct effect of molecular scale phenomena on the macroscopic problem. Even though much effort has been expended in extending macroscopic analyses to microscopic conditions in space (micrometer scale down to nanometer scale), time (microsecond, nanosecond and picosecond scales), and rate (extremely high heat fluxes of the order of Gigawatts), there is a clear limitation to these extrapolations. On the other hand, the development of the molecular dynamics (MD) computer simulation technique has demonstrated the possibility of tackling such phenomena from the opposite direction, by following a bottom up approach. The MD methods have long been used and are well developed as tools in statistical mechanics and chemistry [4, 7]. However, it is a new challenge to employ the method to the spatial and temporal scale of microscopic heat transfer phenomena and systems [5, 8]. At the same time, a host of novel technologies such as, the thin film manufacturing developed in the semiconductor industry, nanotube manufacturing and characterization, and the development of novel materials, demand the prediction of heat transfer characteristics at the nanometer scale [9].

Two areas generic to many engineering applications where marked advances in molecular dynamics have already been made are phase change processes (at both ends, vaporization/condensation and freezing/melting) and heat conduction (exemplified by the determination of thermophysical properties of thin films). In the following, representative studies published in the open literature particularly in these areas will be reviewed, focusing on recent studies beyond the ones discussed in a recent review chapter by Maruyama [5].

1.3.1 Liquid-Vapor Interface

Surface tension is one of the benchmark properties to examine the applicability of the molecular dynamics method to a liquid-vapor interface and to evaluate the potential function model [5]. The typical simulation system is the liquid slab between vapor regions. When the liquid layer is thick enough, the bulk property of liquid can be obtained at the central region, and two liquid-vapor interfaces can be realized. By taking a time average, the density profile, pressure tensor, and surface tension can be reasonably predicted. The quite accurate prediction of surface tension has been demonstrated for Lennard-Jones fluid [10] and water [11] by integrating the difference of normal and tangential components of pressure tensor across the surface. The other typical configuration is the liquid droplet surrounded by its vapor [5, 12, 13]. When the size of the droplet is large enough, the bulk property of liquid is expected at the central region. The well-known Young-Laplace equation relates the curvature of a liquid-vapor interface and surface
tension to the pressure difference. Thompson et al. [12] used the spherical extension of Irving-Kirkwood's formula to calculate the normal pressure profile. The definition of the radius of a droplet is not straightforward, since the size of the droplet is normally very small and the liquid-vapor interface has a certain width. The equimolar dividing radius is one of the choices but more elaborate discussions based on statistical mechanics are found in the literature (see references in [5]). Roughly a thousand molecules are enough to calculate a reasonable value for the bulk surface tension for argon. At the other extreme, the surface tension for very small clusters, which may be important in nucleation theory, requires a completely different approach, because such a small cluster does not have the well-defined central liquid part assumed in the statistical mechanical discussions.

With reference to droplet vaporization, Long et al. [14] and Little [15] studied the evaporation of a liquid argon droplet exposed to both subcritical and supercritical surroundings using 5600 atoms, 27000 atoms and 100,000 atoms. The evaporation rate obtained by molecular dynamics simulation agreed well with existing theoretical results.

In recent publications, Walther et al. [16] and Walther and Koumoutsakos [17] investigated further the problem of subcritical evaporation of a nanometer-size droplet at 300 K and 3 MPa. Classical molecular dynamics techniques were combined with an adaptive tree data structure for the construction of the neighbor lists, allowing efficient simulations using hundreds of thousands of molecules. These high resolution simulations compute values of the evaporation coefficient that are in excellent agreement with theoretical predictions.

The determination of the condensation coefficient by MD simulations is also a challenging task. The condensation coefficient is simply defined as the ratio of rates of the number of condensing molecules to incident molecules. Through the detailed studies of the liquid-vapor inter-phase phenomena of argon, water, and methanol, Matsumoto et al. [18, 19] pointed out that this macroscopic concept could not be directly converted to the molecular scale and that the 'molecular exchange' process must be considered. On the other hand, Tsuruta et al. [20] has reported a significant dependence of the trapping rate on the normal velocity of incident molecules.

Figure 1.1 shows the effect of surfactant in a liquid-vapor interface. Daiguji [21] simulated the effect of n-alcohols in the liquid-vapor interface of water or LiBr-water solution. Here, three n-alcohols with different hydro-carbon chain length (n-propanol, C₃H₇OH; n-heptanol, C₇H₁₅OH;
and n-undecanol, C_{11}H_{23}OH) were modeled with OPLS potential [22] and water was modeled with the popular SPC/E potential [23].

Figure 1.1. Snapshots of n-heptanol and water mixtures as the function of number of n-heptanol molecules, [21]. The number of water molecules N_2 is 400. The dark molecules in the middle are water. Note the instability of water-alcohol interface is observed only at the medium concentration in (b).

Only for the moderate length alcohol, n-heptanol, the instability of the interface was observed for certain concentration as shown in Figure 1.1. When the alcohol concentration was lower as in Figure 1.1 (a), a monolayer of alcohol molecules with its hydrophilic site heading to water was stable. On the other hand, the 2-layers of alcohol molecules could be stable with the hydrophilic and hydrophobic interaction of 2-layers as in Figure 1.1 (c). With the medium concentration in
Figure 1.1 (b), it seems that the alcohol molecules seek for more hydrophilic interaction with water molecules by creating the disturbance in the surface. Daiguji [21] further analyzed these phenomena from the thermodynamics standpoint and addressed the connection to the onset of Marangoni instability. Arcidiacono et al. [24] studied the behavior of oscillating nanodroplets with around 320,000 argon atoms. The equilibrated droplet was “squeezed” with an imposed velocity field and, subsequently, it was allowed to oscillate freely. The oscillation frequency and the damping constant describing the time transient of the oscillation were in agreement with the macroscopic theory within 20%.

1.3.2 Solid-Liquid-Vapor Interactions

Solid-liquid-vapor interaction phenomena play an important role in phase-change heat transfer. The importance of the liquid wettability to the surface is apparent in dropwise condensation, high-heat-flux boiling heat transfer and capillary liquid film evaporators. There are good reviews of the connection between microscopic and macroscopic views of the wetting phenomena by Dussan [25], and from a more microscopic point of view by Koplik and Banavar [26]. Furthermore, the MD treatment of a simple Lennard-Jones liquid droplet on a solid surface and a Lennard-Jones vapor bubble on a solid surface are discussed in [5]. In brief, except for a few layers of atoms near the surface, the averaged shape of the Lennard-Jones liquid droplet is close to semi-spherical. By fitting a circle to the density contour disregarding the two layers of liquid near the solid surface, a “contact angle” can be measured. Controversially enough, the cosine of the measured contact angle is linearly dependent on the strength of the surface potential. The controversial discussions whether Young’s equation can hold or not in such system has been historically discussed [5].

As the more practical example of solid-liquid-vapor interaction, a water droplet on a platinum solid surface is shown in Figure 1.2 [27]. Water molecules were modeled with the SPC/E potential [23] and the interaction potential between water and platinum molecules was expressed by the potential function developed by Zhu and Philpott [28], based on the extended Hückel calculations. The contact structure of the water droplet with a finite contact angle on the absorbed monolayer water film is realized for the first time with molecular dynamics simulation. The contact angle is determined by the surface energy between this monolayer water film and bulk liquid water. This monolayer film has quite high density due to the strong interaction to the platinum surface atoms. The interaction of this water film with normal water strongly depends on
the density of the film. Higher density of water monolayer results the lower interaction. Hence, the dependence of contact angle on the platinum crystal lattice structure is explained by the structure of this monolayer water film.

Figure 1.2. A snapshot and 2-dimensional density profile of an equilibrium water droplet on a platinum surface at 350K [27]. SPC/E water molecules were interacting with the harmonic platinum surface represented by 3 layers of (111) surface through the water-platinum potential proposed by Zhu-Philpott [28].

The behavior of carbon nanotubes (CNT) in a water environment is needed in order to understand the possibility of using CNT as nanofluidic devices. Some recent experimental works [29, 30] studied CNT synthesized by a hydrothermal method, in which some aqueous fluid was entrapped inside (Figure 1.3). As showed in the picture, the two menisci in the liquid-vapor interface indicate that the fluid wets the carbon nanotube wall. Another experimental work [31] suggest that liquids with a surface tension lower than 100-200 mNm\(^{-1}\) can wet CNT, i.e. is expected that water, with a surface tension of 73 mNm\(^{-1}\), should wet CNT. Walther et al. [32-34] studied extensively the phenomenon via classical molecular dynamics. The CNT was simulated by Morse stretch, harmonic bend, torsion and LJ potential, the water with the SPC model and the interaction water-CNT with LJ potential describing the van der Waals interaction between oxygen and carbon. A quadrupole interaction between the carbon and the partial charges on hydrogen and
oxygen atoms was also considered. In the mentioned works the authors investigated both CNT in water environment and water droplets inside a CNT. They found that pure water does not wet CNT.

Figure 1.3. Transmission Emission Microscope image of liquid inclusion inside a carbon nanotube [30].

On the contrary, the nanotube was strongly hydrophobic (Figure 1.4). The water molecules are almost oriented parallel to the CNT surface and stand off from the nanotube at a distance of a few angstroms. The number of hydrogen bonds decreases in the proximity of the nanotube. They evaluated the energy balance related to the insertion of a nanotube in water. The process results to be energetically unfavorable and the main contribution in energy to create a cavity is due to the water-water interaction. The evaluated contact angle was around 105° (near the macroscopic value of about 80°-90° for the contact angle water-graphite) and small variations were induced when the interaction constant between water and CNT was changed by ±20%. The large difference with the experimental results can be due (speculatively) to the different behavior of pure water compared with the aqueous solution present in the CTN studied in [29, 30]. The coating of a substrate with a thin film has important applications in new technologies. In these
processes the stability of the film, that is whether the film remains uniformly distributed or a dewetting phenomenon occurs, has a crucial role. The instability of the film is caused by a competition between the surface tension and van der Waals forces, acting between liquid and solid atoms, and is bigger in thinner films.

Figure 1.4. Water density distribution inside a carbon nanotube and contact angle evaluation [33].

Figure 1.5 shows the rupture of a thin film on a plate [35]. The rupture evolves with an approximate circular shape as predicted by the macroscopic three-dimensional rupture theory. The rupture time and rupture velocity propagation are strictly related with the liquid-liquid and solid-liquid interaction parameters used in the LJ potential [35]. Larger liquid-liquid interactions correspond to a shorter rupture time and, on the contrary, the resistance to rupture becomes larger as the solid-liquid interaction becomes bigger. Liu et al. [36] found that for polymers there is a limit dry area after which the instability grows and dewetting takes place. Moreover they showed, both with numerical and some theoretical considerations, that for a non volatile fluid the time growth of the length of the dry patch goes with $t^{1/4}$. On the contrary Koplik and Banavar [37] affirm that each dry patch leads to the instability and the growth rate, evaluated from their simulations, goes roughly with $t^{3/4}$. The difference is probably due to the fact that Liu et al. [36] used a pure repulsive and unstructured substrate on which the liquid “slides”. Figure 1.6 depicts the dewetting time evolution of the film [37]. The film forms a rim that grows as it moves, the contact angle is smaller than his static counterpart and there is no second contact angle where the rim meets the flat part of the film (on the left in the Figure). Moseler and Landman [38] performed molecular dynamics simulations revealing the formation and break up of nanojets with
velocities up to 400m/s. The jet generation was created with pressurization and injection of liquid propane from heated convergent gold nanonozzles.

Figure 1.5. Time evolution of rupture of a thin film on a substrate, [35].

Heating was necessary to control condensation and subsequent wetting of the nozzle region around the nozzle. The atomistic description is very interestingly connected to continuum modeling with the derivation of a stochastic lubrication equation accounting for thermally
triggered fluctuations. This paper has several unusual features for it combines phenomena having to do with droplet generation at the nanolevel, surface wetting and heat transfer, as well as theoretical explanations of the numerical findings by expanding on continuum concepts.

Figure 1.6. Time evolution of a dewetting film, [37]

1.3.3 Nucleation and Phase Change

Homogeneous nucleation is one of the typical macroscopically investigated phenomena directly affected by molecular scale physics. Recently, Yasuoka et al. have demonstrated direct MD simulations of the nucleation process for Lennard-Jones [39] and for water [40] molecules. The key technique for such a calculation is the temperature control as discussed by Ikeshoji et al. [41] by observing the magic number clusters of 13, 19 and 23, which are abundantly observed in experimental mass spectra. After quenching to the supersaturation condition, the condensation latent heat must be removed for the successive condensation. Yasuoka et al. [39] used 5,000 Lennard-Jones molecules for the simulation, mixed with 5,000 soft-core carrier gas molecules connected to the Nosé-Hoover thermostat for the cooling agent. This cooling method mimicked the carrier gas of supersonic jet experiments. Through the detailed study of growth and delay of nuclei size distribution, they have estimated the nucleation rate and the critical size of nucleus.
The nucleation rate was seven orders of magnitude larger than the prediction of classical nucleation theory. Their similar simulation [40] for water of TIP4P potential at 350 K, resulted in a nucleation rate two orders of magnitude smaller than the classical nucleation theory, in good agreement with the “pulse expansion chamber” experimental results.

Heterogeneous nucleation is also obviously important in many heat transfer problems. Figure 1.7 shows an example of heterogeneous nucleation of a liquid droplet on a solid surface [42]. Argon vapor consisting of 5760 Lennard-Jones molecules was suddenly cooled by the solid wall controlled with the phantom technique [5]. The phantom molecules modeled the infinitely wide bulk solid kept at a constant temperature with proper heat conduction characteristics. The potential between argon and solid molecules was also represented by the Lennard-Jones potential function, and the energy scale parameter was adjusted to reproduce various wettabilities. After the equilibrium condition at 160 K was obtained, the temperature of the solid surface was suddenly set to 100 K or 80 K by the phantom molecule method. Initially, small clusters appeared and disappeared randomly in space. Then larger clusters grew preferentially near the surface for wettable cases. On the other hand, for the less wettable condition, relatively large clusters grew without the help of surface just like in homogeneous nucleation. The nucleation rate and free energy needed for cluster formation were not much different than the prediction of the classical heterogeneous nucleation theory in the case of smaller cooling rate.

![Figure 1.7](image_url)

(a) 500 ps (b) 1000 ps (c) 1500 ps

Figure 1.7. Growth of liquid droplet clusters larger than 5 atoms by suddenly cooling the solid surface, [42].

An MD simulation of homogeneous [43] or heterogeneous [44] nucleation of a vapor bubble is much more difficult compared to the nucleation of a liquid droplet. Even though the formation of a vapor bubble can be reproduced by expanding the liquid to the negative pressure, qualitative comparison of the nucleation rate or critical radius is not easy.
The intermediate cluster structures are extremely important when some of them can be stably observed as end products, such as in the simulation of fullerene formation [45, 46] and endohedral metallofullerene formation [47]. To exemplify, Figure 1.8 shows the nucleated cluster distributions observed in a simulation related to the single-walled carbon nanotube generation. Using the simplified Brenner [48] potential for carbon-carbon interaction and the empirical metal-carbon potential functions [47], the growth of metal-carbon binary clusters from a completely random vapor mixture of 2500 carbon and 25 Ni atoms was simulated. As shown in the inserted expanded views in Figure 1.8, many relatively large clusters up to about 100 carbon atoms and a few metal atoms were observed. Even though careful annealing examinations are necessary for the compensation of the accelerated simulation, these cluster structures were qualitatively in good agreement with the FT-ICR experimental results [49].

Figure 1.8. A snapshot of the clustering molecular dynamics simulation at 6 ns from initial random gas phase configuration. Large solid circles, empty circles, and gray circles represent Ni atoms, threefold-coordinated carbon atoms, other carbon atoms, respectively.

Pan et al. [50] went beyond the nucleation problem and performed molecular dynamics simulations of the vaporization phenomenon of an ultra-thin layer (2 nm) of liquid argon on a
Platinum surface. The simulation started from a molecular system of three phases (liquid Argon, solid Platinum and Argon vapor) at equilibrium at 110 K. The Platinum wall was then suddenly heated to a higher temperature (a moderately higher temperature of 150 K and a much higher temperature of 300 K were investigated). The entire vaporization process was successfully simulated. The results reveal trends that agree with our knowledge of vaporization of a similar macroscopic system. For example, for the high surface temperature (Figure 1.9) the vaporization process is reminiscent of the Leidenfrost phenomenon and after the formation of a vapor region between the surface and the liquid mass, the latter deforms and tends to approximately acquire a spherical “droplet” shape. Contrary to this, a gradual evaporation process occurs at moderate wall temperatures. After complete evaporation and upon reduction of the wall temperature, condensation takes place leading to reconstruction of the initial liquid layer.

Koplik et al. [51] studied the solidification, evaporation and coalescence, described in the next paragraph, of nanodroplets with up to O(10^5) atoms. The fluid atoms were simulated using the LJ potential and a finitely extensible nonlinear elastic (FENE) force to link atoms into chain molecules. Molecules of 2, 10 and 100 atoms were studied during solidification. The droplets formed by longer chains showed an amorphous structure; on the contrary the dimer molecule system had a local crystalline structure. No orientation of the molecules was noticed in all the simulations except near the substrate where there is the tendency of molecules to orient parallel to it. Presumably the solidification time was too short compared with that required for a molecular rearrangement. The simulation of droplet evaporation was done adjusting the parameters in eqn. (3), describing the interaction between solid and liquid, so that at the equilibrium the contact angle was 45°. During the evaporation there was a thickening of the interface region and the contact angle decreased to about 30° as predicted by a recent analytical work.

The deposition of a molten droplet spreading on a cold substrate, with a temperature below the solidification point, is a process involved in many industrial applications. Standard macroscopic models have difficulties to simulate the contact line behaviour in which there is a singularity in shear stress, the no-slip boundary condition can not be applied and ad hoc assumptions are needed. Some works investigated the spreading process of LJ or chain molecules [26, 52-56], showing controversial results. Finally, Bekink et al. [55] reported the same time dependence of the radii of the spreading layers with \( t^\nu \), as expected from experiments.
Figure 1.9. Front view projection of a 3D simulation domain of an evaporating Argon layer heated from below at characteristic times — wall temperature at 300 K, [50] (continued).
Ge et al. [57] considered spreading of a Cu liquid droplet on a Cu surface with a temperature well below the melting point. The thermodynamic system was simulated using the embedded atom method (EAM), see [58] and references therein. The time dependence of the spreading index (defined as the ratio between the equivalent radius of the area of the first layer of atoms spreading and the initial radius of the droplet) agrees well with the experimental contact area radius as a function of time. They concluded that for a rapid solidification the no-slip boundary condition for the contact line can still hold.

1.3.4 Coalescence

In many industrial processes it is important to predict the behavior of small droplets in sprays and aerosols. Continuum models based on the Navier-Stokes equations can reproduce the evolution of the droplet shape but still boundary conditions coming from first principles are missing and approximations have to be adopted. Molecular dynamics allows for the study of droplet phenomena from a molecular point of view accounting non-empirically for complicated boundary conditions, e.g. the presence of surfactants on the surface of the droplet. A review on coalescence and break up phenomena related to atomization and spray applications can be found in [59]. Typical findings of MD simulations are presented below.
When the two droplets are sufficiently close to one another (Figure 1.10) [60], some molecules, due to thermal fluctuations, can leave one droplet and move within the interaction range of the molecules of the other. These molecules start attracting others creating a thin filament joining the two drops. The resulting droplet shape has a high-enough surface energy to reduce thickening the filament and finally give a spherical shape to the drop. Figure 1.11 depicts the coalescence of a cylinder falling under a gravity force into a tank of molecules of the same liquid, in presence of an immiscible liquid (not showed in the figure) [60].

The coalescence mechanism is quite similar to that described above. Koplic and Banavar [51] extended the cited work to bigger droplets with a more complex potential to mimic chain molecules. The time dependence of the radius of the neck of the coalescing droplets was compared with the continuum theory but no agreement was found. The dynamics of coalescence was the same with that found for monoatomic molecules. Lehtinen and Zachariah [61, 62] showed, with the support of MD simulations of Si droplets, that
the heat transfer and the initial boundary conditions in temperature play a crucial role in this phenomenon. When two particles coalesce new chemical bonds are formed with a resulting heat generation (Figure 1.12). Depending on the exchanged heat, the droplet temperature can increase leading a decrease in the coalescence time. They found that below a critical temperature of the surrounding gas, the heat generated is released to the gas and the temperature of the particle does not increase. Above the critical temperature, a sharp increase in the particle temperature is observed with a decrease in the coalescence time.

Figure 1.11. Coalescence of a falling liquid cylinder into a bath under gravity in an immiscible background fluid (not showed) at different instants. The side view is a cross section parallel to the cylinder axes, [60].

1.3.5 Other Topics Related to Nanotechnology Systems

As an example of a "nanotechnology system" investigated with molecular dynamics simulations, is hydrogen absorption by carbon nanotubes as shown in Figure 1.13 [63]. Assuming the physical adsorption of hydrogen to occur at the surface of carbon nanotubes, the potential forms between H₂-H₂ and C-H₂ were both expressed by Lennard-Jones (12-6) functions. Each nanotube was
regarded as rigid and the van der Waals potential between the nanotubes was derived as a Lennard-Jones (8-4) function by integrating the potential between carbon atoms. During 500 ps simulation at 12 MPa and 77 K, the adsorption was observed only inside the tubes and outside the bundles. It was needed to once reduce the van der Waals potential between nanotubes to observe the phase transformation from the close packed bundle to the structure accommodating a hydrogen layer between the tubes as in Figure 1.13 (a). The phase transformation in the opposite direction was simulated by reducing the hydrogen pressure step as needed down to 6 MPa as shown in Figure 1.13 (b) and Figure 1.13 (c).

Figure 1.12. Temporal behavior of particle morphology as a function of temperature for the collision of two 240-atom particles, [61]. The gray curve is temperature. The black curve is the reduced moment of inertia.

Since many direct heat transfer problems of nanotechnology are currently related with thermophysical properties of solid materials, the heat conduction behavior of micro- and nanodevices is of importance. For best design of micro and nanodevices the knowledge of the dependence of thermal properties with temperature and dimension of the device is of interest. Based on the phonon dynamics approach [64], the direct calculation of phonon relations, phonon
mean free path, and phonon scattering rates using the molecular dynamics simulations are modeled [65,66].

The thermal conductivity of a solid can be predicted by standard MD when the heat conduction is dominated by phonons. Both non-equilibrium MD (NEMD) and equilibrium MD (EMD) can be used (see [67] and reported references). The former uses a “direct method”, a temperature gradient is imposed across the simulation domain, realizing an analogy to the experimental situation, and the conductivity is simply evaluated as the ratio between the imposed heat flux and temperature gradient. In the second approach, the thermal conductivity is calculated through the heat flux fluctuations via the fluctuation-dissipation theorem using the Green-Kubo correlation.

The evaluation of bulk conductivity is possible when the dimensions of the computational domain are bigger than the mean free path of the phonons. This can result in simulations with several hundred millions atoms over $10^6$ time steps. To avoid this problem Volz and Chen [69], using the Green-Kubo correlation, found a correction that took into account the cut off to low frequency phonons induced by periodic boundary conditions. The obtained thermal conductivity for Si crystals was not size dependent. The same authors [70] studied the heat transfer and the thermal conductivity of Si/Ge superlattices showing that the MD approach can yield heat transfer properties overcoming the difficulties of the phonon transport theory.

It is experimentally known that the thermal conductivity of thin films is lower than its bulk counterpart. Lukes et al. [68] studied an argon-type thin film via NEMD. They confirmed this trend and found that the dependence on the film length can be more pronounced at lower
temperatures.

The result of a heat conduction MD simulation along a carbon nanotube is shown in Figure 1.14 [71, 72]. The potential function employed was the Tersoff-Brenner bond order potential [48]. The thermal conductivity of nanotubes, which was speculated to be higher than that of many conductive materials (including diamond) along the cylindrical axis, was obtained from simulations for nanotubes with several different chiralities and lengths. The temperature at each end of a nanotube was controlled by the phantom technique [5], and no periodic boundary condition was applied to minimize the boundary scattering of phonons.

![Graph](image)

Figure 1.14. Molecular dynamics simulation of heat conduction along a single-walled carbon nanotube (SWNT). (a) Temperature distribution along a nanotube with (5,5) chirality and 202 nm in length. (b) Phonon dispersion relation obtained from the time-space 2-D Fourier transform of the longitudinal displacement of each molecule.

The thermal conductivity was calculated from the calculated temperature gradient as shown in Figure 1.14 (a) and the heat flux was obtained by integration of the additional force by the phantom molecules. The preliminary results showed that the thermal conductivity was about 200 ~ 300 W/mK. The temperature jump near the heating and cooling region was explained by assuming a thermal boundary resistance due to the miss-match of the phantom technique and the structured phonon density distribution. The phonon dispersion relations were directly calculated...
as the time-space 2-D Fourier transform of the position of each molecule as shown in Figure 1.14 (b). The relation to the solid-solid thermal boundary resistance and more generally to the liquid-solid thermal boundary resistance [73] can be simulated. Ohara et al. have analyzed the possible explanation of this thermal boundary resistance [74] based on their “intermolecular energy transfer” concept developed by the detailed studies of heat conduction in liquid phase water [75] and a Lennard-Jones fluid [76].

Another interesting field in new industrial processes is the irradiation with short pulse lasers for the manufacture of surfaces. The final chemical and physical properties, due to the short pulse time, are difficult to investigate experimentally. Computer simulations can help to understand the underlying physical phenomena related to the changing of the structure of the material and the laser pulse characteristics. Häkkinen and Landman [77] simulated the irradiation of fcc (100), (110) and (111) Cu atoms coupling the electron phonon absorption with the heating of the lattice. The EAM [58] potential was used to describe the metallic bond. For the same laser pulse, the (100) and (110) surfaces melt while the (111) lattice maintained the crystalline order and showed a superheating over the melting point. The high stability of the (111) was observed also for highly defective surfaces. In this case the superheating was coupled with the annealing of the surface structure through a non diffusive process that restored the crystalline structure.

Herrmann et al. [78] studied the ablation of silicon and compared the final structure obtained irradiating the surface with different energies and length of the laser pulse. They concluded that, using the same laser energy, shorter pulse lengths remove more material but this leads to a cylindrical ablation (the typical Gaussian shape is lost) and less deep holes. Surfaces irradiated with multishot lasers showed narrower and deeper holes compared with those done with only one shot of the same energy.

Wang and Xu [79] focused on heat transfer, melting and evaporation of argon during laser energy adsorption at different fluencies. The heat transfer during irradiation without phase change was compared to a finite difference simulation and good agreement was found, showing that even at this scale continuum approach is valid. The results of the simulation of the phase change predict some interesting phenomena. The solid-liquid interface is not sharp. A buffer zone is present, where liquid and solid coexist. The velocity of the liquid-solid interface is well below of the local sound speed. During the transient, superheating is observed both in the liquid-vapor interface and in the melting front. After the melting process stops, the temperature in the solid-liquid interface
drops below the melting point corresponding to the imposed system pressure.

**Summary**

With the constant emergence of micro- and nanoscale technologies, the research attention on heat transfer at corresponding length scales is continuously increasing. Wetting phenomena, discontinuities at solid-liquid-vapor interfaces, nucleation phenomena, wall velocity and temperature jump in microchannel flows, coalescence phenomena, as well as a great variety of entire nanoscale engineering systems, cannot be investigated with the continuum approach alone. Many such problems can be handled to a good extent with the Molecular Dynamics approach, once a correct potential mimicking molecule interaction is found and a representative number of molecules can be handled computationally. In the present paper, the recent progress in molecular dynamics heat transfer was reviewed, focusing primarily on interfacial and phase change phenomena, due to their special meaning and occurrence in small scale applications.

It is worth stressing that experiments are not always comparable with MD results and direct comparisons are still difficult. Despite this fact, the potential of the method is clearly demonstrated and it is believed that the future will bring a wide implementation of the method in thermal engineering applications.

**References**


2 Oscillatory behavior of nanodroplets

Abstract

Molecular dynamics (MD) simulations were performed in order to investigate the phenomenon of free oscillations of nanodroplets and the extent to which the continuum theory for such oscillations holds at nanoscales. The effect of temperature on these oscillations is also studied. The surface tension, a key property for the phenomenon of interest, was evaluated and compared with the experimental values of Argon, showing that with an appropriate choice of the cutoff distance in the MD simulations, it is possible to predict the surface tension with good approximation. Nanoscale capillary waves on the free surface of the droplet were observed and compared to continuum theoretical predictions of the same. The nanodroplet interface thickness calculated based on continuum theory for these waves agreed well with the molecular dynamics calculation of the interface thickness. The frequencies of the oscillation of the droplet were calculated for all the studied temperatures and compared with the classical continuum theory. Although the simulated system cannot be considered strictly as a continuum, a good overall agreement was found.

2.1 Introduction

The problem of oscillating liquid drops is relevant to several scientific fields and practical applications, such as, cloud physics, containerless processing in low gravity, collision, coalescence, and break up of droplets in sprays, chemical processes and measurement techniques of interfacial properties.

There is a rich literature on this subject for droplets described by continuum theory in all theoretical, numerical and experimental domains. We report briefly select key results directly relevant to the present work.

Lord Rayleigh [1] was the first to investigate mathematically the nature of oscillations of an inviscid liquid drop and assuming small deformations. Neglecting the effect of the surrounding gas, the natural frequency of a free droplet of radius \( R \), surface tension \( \gamma \), and liquid density \( \rho_l \), can be evaluated by:

\[
\omega_n^2 = \frac{\gamma}{\rho_l R^3} n(n-1)(n+2)
\] (2.1)

The fundamental oscillation mode in Eq (2.1) is corresponding to \( n = 2 \) whereas \( n = 1 \) relates to a rigid spheroid. Subsequently, Lamb [2] studied the effect of small viscosity, i.e.

\[
Re = \frac{1}{v} \left( \frac{R}{\rho} \right)^{1/2} \gg 1,
\]
where \( Re \) is the Reynolds number. With this hypothesis the frequency of the oscillation is the same as in Eq (2.1) while the amplitude is dumped exponentially:

\[
A = A_0 e^{-b_0 t}
\] (2.2)

where \( A \) is the amplitude of the droplet oscillation, \( A_0 \) is the same quantity, but in the inviscid limit, \( t \) is the dimensional time and \( b_0 \) is the dumping coefficient defined as:

\[
b_n = (n-1)(2n+1)v / R^2
\] (2.3)

The latter is a constant not depending on the restoring force, but only on the size of the droplet and its viscosity \( v \). Chandrasekhar [3] obtained later more general results for a viscous spheroid. Prosperetti [4] presented a theory for a viscous drop under infinitesimal amplitude oscillations. This analysis predicts that the system behaves as a dumped oscillator which, when viscous effects are small compared with the inertial ones, is characterized by a natural frequency: \( (\omega_n^2 - b_n^2)^{1/2} \).

The analysis predicted also a transition from a periodic to an aperiodic decay as the viscosity increases, while for certain ranges of the parameter \( 1/Re \) it is also possible to have an aperiodic oscillation that evolves into periodic.

Nonlinear effects due to moderate amplitude oscillations of an inviscid droplet were considered by Tsamopoulos and Brown [5] (TS) extending Rayleigh's analysis to second order for certain combinations of mode coupling. Their analysis predicted for the second oscillation mode a shift of the oscillation frequency with the increasing of the square of the initial amplitude of the oscillation \( A \):

\[
\omega_2 = \omega_1 \left[ 1 - 0.63876 A^2 + O(A^4) \right]
\] (2.4)

Becker [6] studied both theoretically and experimentally the oscillations of a free droplet generated from a break up of a liquid jet. They found that the frequency shift is decreasing with the square of the oscillation amplitude as predicted in [5], but with a larger rate and with variations for different generated droplets depending on the initial internal flow field inside the drop.

The study of a realistic configuration, including nonlinearities of viscosity and large oscillations,
requires solving the Navier-Stokes equations numerically. Basaran [7] performed a rigorous numerical study using a Galerkin/finite element technique for large oscillations of viscous drops and focusing on the oscillation of a drop released from the second spherical harmonic shape. The calculations showed a good agreement with the predictions of Prosperetti and TS analysis within their application limits. The influence on the oscillation period and decay factor due to initial internal circulations was investigated numerically by Mashayek and Ashgriz [8] showing that it can result in a significant change in the characteristics of the drop oscillation. Recently Pozrikidis [9] implemented a numerical method using a 3D generalized vortex formulation. The accuracy of the results obtained was dependent on the dominant droplet oscillation mode but was satisfactory overall.

On the experimental side, Trinh and Wang [10] studied the large amplitude oscillations of quasi-neutrally buoyant of silicon oil and carbon tetrachloride levitated in distilled water. They found that the frequency decreases with increasing the square of the oscillation amplitude and in an oscillation period the prolate phase lasts longer than the oblate phase, confirming the predictions of Tsamopoulos and Brown [5]. A study of the oscillation of a low viscosity droplet in a microgravity environment of a space shuttle flight was performed by Wang et al. [11]. The resulting frequency shift for the second mode oscillation was in agreement with the predictions of the theory [5] for $A<0.3$. Azuma and Yoshihara [12] employed electrical excitation to obtain three dimensional, large amplitude oscillations of a mercury drop. A relationship between drop oscillation modes and frequencies was found. Non linear interaction of waves resulted in polyhedral oscillations.

The novelty of the present work is to extend the previous findings for the second oscillation mode to nanoscales through the use of Molecular Dynamics, investigating whether the applicability of the continuous theories is still valid for atomic clusters. Another important issue is that the MD simulations are three dimensional thereby providing a complete view of the phenomena. In Section II the numerical method is described. Section III reports the results for the liquid-vapor interface, surface tension and droplet oscillation. Conclusions are presented in Section IV.

2.2 Molecular Dynamics Simulations

The studied argon nanodroplet consists of about 330,000 atoms interacting with the 12-6 Lennard-Jones pair potential:
The values for the parameters in Eq (2.5) were chosen such as to mimic the gas Argon ($\sigma = 3.405$ Å and $\epsilon = 1.67 \times 10^{-21}$ J). The simulation domain is a cubic box of side $L = 154.8\sigma$ with periodic boundary conditions in all the three directions.

The value of the cutoff distance is set to $4\sigma$. This particular choice was suggested by the results of Trokhymchuk and Alejandre [13] who compared previous findings with their calculations for the surface tension evaluation of a planar film via MD and Monte Carlo simulations. They showed that differences found by diverse authors in surface tension evaluation were due to the potential used, shifted or non-shifted, and mainly to the assumed cutoff radius. They concluded that different methods are giving the same results for a cutoff distance larger than $4.4\sigma$. A further comparison with experimental Argon data [14] showed that a cutoff distance of approx. $4\sigma$ could reproduce the experimental data for Argon, including the values of surface tension. The results are expressed in dimensionless form using the standard reference scales for a Lennard-Jones fluid ($\sigma$ as length scale, $\epsilon$ as energy scale and $\sigma \sqrt{m/\epsilon}$ as time scale, where $m$ is the mass).

We focus our attention on three different temperatures in this study: $T(\epsilon/k_B) = 0.81$, 0.9 and 0.97. The target temperature is reached by rescaling the particle velocities [15] every 250 time steps. The system is equilibrated until the average temperature is constant (this required up to 750,000 time steps for the case of $T(\epsilon/k_B) = 0.97$). The leap-frog algorithm is used to integrate the equation of motion with a dimensionless time step of 0.005 during the equilibration. The time step is halved during the droplet deformation-oscillation transient.

Each calculation required one/two months using a parallel algorithm, that employs simple spatial domain decomposition [16], on a 4 CPU DEC parallel machine.

2.3 Results

2.3.1 Liquid-Vapor Interface

In nanoscopic droplets one must define a radius since the liquid-vapor interface is not sharply identified. It is common to characterize the droplet size with the equimolar dividing radius $R_e$ as:

$$N = \rho_l \frac{4\pi}{3} R_e^3 + \rho_v \left( L^3 - \frac{4\pi}{3} R_e^3 \right)$$

(2.6)

where $N$ is the total number of atoms, $\rho_l$ and $\rho_v$ are respectively the liquid and vapor densities.
The non uniformity of the liquid-vapor interface is evident from observing the radial density profile in Figure 2.1 for all the studied cases. The value of the density is constant within the liquid and the vapor regions, while the interface region is characterized by a thin layer where the density profile is decreasing monotonically from the liquid to the vapor value. The reported curves in Figure 2.1 are relative to the equimolar dividing radius, so that the three curves are intercepting in the same point at \( R = R_e \). The two asymptotic values of the density \( \rho_l \) inside the liquid and \( \rho_v \) inside the vapor can be obtained by fitting the density profiles with the formula:

\[
\rho(r) = \frac{1}{2} (\rho_l + \rho_v) - \frac{1}{2} (\rho_l - \rho_v) \operatorname{erf}\left[\frac{\sqrt{\pi} (r - R_0)}{D}\right]
\]  

(2.7)

where \( D \) is a measure of the liquid-vapor interface thickness, \( R_0 \) is another path to estimate the droplet radius, defined as the radius at which the corresponding density is the average of the liquid-vapor asymptotic values. Numerically, \( R_0 \) is close to the quantity \( R_e \) defined in Eq. (2.6) (for the present calculations the discrepancy is less than 1%). The two parameters \( D \) and \( R_0 \) can also be obtained by fitting the density profile.

Figure 2.1: Density profiles relative to the equimolar dividing radius for the three different studied temperatures

The choice to fit the density profiles with the error function (Eq. (2.7)) rather than the usual hyperbolic tangent is supported by calculations of Sides et al. [17] stating a better prediction of
the interface thickness, as well as by the work of Toxvaed and Stecki [18].
Herein it is verified that the error in the fit of the density profile is smaller by around 10% compared to the fit performed with the hyperbolic tangent function. The prediction of interface thickness with the error function fit is by 5% larger compared to the hyperbolic tangent fit.
The thickness of the interface can be mostly explained by the presence of capillary waves excited by thermal energy. Capillary waves are nothing else than an expression of the internal Brownian motion that is randomly deforming the spherical shape of the droplet. This phenomenon is more evident in nanodroplets, since the amplitude of capillary waves is of the same order as the droplet radius. The thickness of the interface due to capillary waves can be evaluated analytically as a function of the mean square displacement $<\zeta_{cw}^2>$ of the radius.
A simplified theory for estimating $<\zeta_{cw}^2>$ was proposed by Bartell [19]. He found that the mean square displacement from the mean radius due to capillary waves of modes of energy $k_B T$, assuming it follows a Gaussian distribution, can be expressed as:
\[
<\zeta_{cw}^2> = \sum_l \sum_m \left( \frac{k_B T}{2\pi l \nu_{lm}} \right)^2
\]
where $K_B$ is the Boltzman constant, $\nu_{lm}$ is the integral over the surface harmonics (a detailed formulation can be found in [19, 20]), $m = l - 2n$ ($n$ is an integer including zero) and $l = 2, 3, ..., l_{\text{max}}$. An estimation of $l_{\text{max}}$ is obtained from the number of molecules in the periphery of a spherical cluster $N_e \equiv 2\pi \left( \frac{3N}{4\pi} \right)^{\frac{3}{2}}$ and can be assumed of the order of magnitude of $N_e/2$. Equation (2.8) shows that the mean displacement is larger at higher temperatures. Finally the thickness of the interface can be expressed as [19]:
\[
D_{cw} = <2\pi \zeta^2>^{1/2}
\]
Table 2.1 reports the values for $D$ obtained via MD with Eq. (2.7) and the analytical formulation with Eq. (2.9). The ratio between the thicknesses $D$ evaluated analytically and via MD is around 0.77 for the three cases considered. A similar result (value of 0.83) is reported by Bartell [19], where the prediction of Eq. (2.9) was compared with other previously performed MD simulations of smaller droplets [21, 22] (the hyperbolic tangent function was used to fit the density profiles in these references). The fact that the above mentioned ratio is smaller than unity is known [23]. There are two contributions to the liquid-vapor interface thickness: an intrinsic contribution due to the atomic structure of the fluid, and a contribution of the thermally excited capillary waves.
that become more important with increasing the total surface area.

<table>
<thead>
<tr>
<th>$T(\sigma/k_B)$</th>
<th>0.81</th>
<th>0.9</th>
<th>0.97</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{cw}(\sigma)$: Capillary Waves Theory, Eq. (2.9)</td>
<td>2.23</td>
<td>2.70</td>
<td>3.39</td>
</tr>
<tr>
<td>$D(\sigma)$: MD, Eq. (2.7)</td>
<td>2.87</td>
<td>3.34</td>
<td>4.38</td>
</tr>
<tr>
<td>Temperature oscillation period $t_f (\sigma \sqrt{m/\varepsilon})$</td>
<td>18.4</td>
<td>20</td>
<td>21.4</td>
</tr>
<tr>
<td>Temperature dumping constant $\tau (\sigma \sqrt{m/\varepsilon})$</td>
<td>88.5</td>
<td>74.8</td>
<td>61.3</td>
</tr>
</tbody>
</table>

Table 2.1: Interface thickness due to capillary waves ($D_{cw}$) and calculated via MD ($D$). The last two lines are the temperature oscillation period $t_f$ and the damping constant $\tau$ during the compression transient obtained by fitting the temperature profiles with Eq. (2.14) for all the studied cases.

![Figure 2.2](image.png)

Figure 2.2: Interface thickness $D$ and $D_{cw}$. Open symbols: present work. Lines and closed symbols: experiments [24]

The total mean square displacement can be written as the sum of the intrinsic and capillary wave contribution:

$$\langle \xi^2 \rangle = \langle \xi_{in}^2 \rangle + \langle \xi_{cw}^2 \rangle$$ (2.10)

and it can be calculated defining it as the variance of the derivative of the density profile (2.7), leading to the expression [17]:

...
\[ \langle \xi^2 \rangle = D^2 / 2\pi \]  

(2.11)

A comparison with the experimental predictions for the planar interface thickness \( D \) and \( D_{\text{ew}} \) for Argon \([24]\) is reported in Figure 2.2 as a function of \( 1-T/T_c \) where \( T_c \) is the critical temperature, showing good agreement. Discrepancies in \( D_{\text{ew}} \) are probably due to the different choice of the upper surface wave cutoff.

2.3.2 Surface Tension

The surface tension of a droplet can be evaluated using the well known Laplace formula:

\[ \gamma = \frac{\Delta p \cdot R}{2} \]  

(2.12)

where \( \Delta p \) is the difference between the pressure in the liquid \( p_l \) and the pressure in the vapor \( p_v \) phase and \( R \) is the radius of the droplet. In the present work, it will be assumed that the cluster is large enough to neglect the curvature effects and we will consider in Eq. (2.12) \( R = R_c \). This assumption is supported by the recent MD simulations of Bardouni \textit{et al.} \([25]\) conducted on smaller clusters \((5<R_c<10)\) showing that, within the error limit, the surface tension seems to be curvature independent.

The normal pressure profile is evaluated using the algorithm of Thomson \textit{et al.} \([22]\) to solve the spherical extension of Irving-Kirkwood’s formula:

\[ p_n(r) = k_B T p(r) - \frac{1}{4\pi r^2} \sum_k f_k \]  

(2.13)

where \( f_k \) is the normal component of forces acting across a control surface between a pair of atoms. The first term in the RHS of Eq. (2.13) represents the kinetic contribution (\( K_P \)) to the total pressure while the second is the contribution due to internal forces (\( I_F \)). In Figure 2.3 the two components \( I_F \) and \( K_P \) are shown for the three temperatures examined.

The pressure difference \( \Delta p \) in Eq. (2.12) is not obtained directly from Eq. (2.13), but by adding the asymptotic values of \( I_F \) and \( K_P \) (Figure 2.3) inside liquid and vapor where the required relative standard deviation was less than 0.5\% in order to minimize the error due to the compensation of the two terms in the RHS of Eq. (2.13).

Table 2.2 summarizes the values calculated for the densities \( \rho_l \) and \( \rho_v \), surface tension \( \gamma \), pressures \( p_v \) and \( p_l \), and the equimolar dividing radius \( R_e \) for the three cases studied. The corresponding experimental values of \( \rho_l \), \( \rho_v \) and \( \gamma \) for argon are also reported for comparison. The MD simulation results predict well the experimental values except for the surface tension of the case.
\[ T (\varepsilon / k_B) = 0.97 \] (the difference is around 10%). This is probably due to a non perfect thermal equilibrium despite the long time calculation required.

![Dimensionless pressure profiles in the radial direction for three different temperatures: K=Kinetic component, IF=Internal Forces component](image)

Figure 2.3: Dimensionless pressure profiles in the radial direction for three different temperatures: K=Kinetic component, IF=Internal Forces component

<table>
<thead>
<tr>
<th>( T (\varepsilon / k_B) )</th>
<th>( \rho_s (\sigma^3) )</th>
<th>( \rho_v (\sigma^3) )</th>
<th>( \gamma (\varepsilon / \sigma^3) )</th>
<th>( P_i (\varepsilon / \sigma^3) )</th>
<th>( P_v (\varepsilon / \sigma^3) )</th>
<th>( R_s (\sigma) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>0.008</td>
<td>0.794</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.81</td>
<td>0.010</td>
<td>0.781</td>
<td>0.67</td>
<td>3.73e-2</td>
<td>7.5e-3</td>
<td>44.85</td>
</tr>
<tr>
<td>0.9</td>
<td>0.017</td>
<td>0.749</td>
<td>0.52</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.9</td>
<td>0.020</td>
<td>0.737</td>
<td>0.51</td>
<td>3.95e-2</td>
<td>1.6e-2</td>
<td>43.87</td>
</tr>
<tr>
<td>0.97</td>
<td>0.030</td>
<td>0.709</td>
<td>0.39</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.97</td>
<td>0.033</td>
<td>0.698</td>
<td>0.36</td>
<td>4.38e-2</td>
<td>2.68e-2</td>
<td>41.89</td>
</tr>
</tbody>
</table>

Table 2.2: MD calculation and Argon experimental values [14]. Comparison for liquid/vapor densities \( \rho_s, \rho_v \) and pressures \( P_i, P_v \), equimolar radius \( R_s \) and surface tension \( \gamma \).

### 2.3.3 Droplet oscillation

In order to study the oscillation behavior of the droplet, after the thermal equilibrium was
reached, an impulsively imposed linear velocity field, $v_a = 2 \cdot \sqrt{\epsilon/m} \cdot \alpha \ (\alpha = y, z)$, is applied to each molecule of coordinates $x, y, z$ inside the liquid region to obtain an initially ellipsoid shape. Subsequently, the drop is allowed to oscillate freely. The temperature increase due to this energy input into the system can be considered negligible (less than 1%) so that it will be assumed that the thermodynamic parameters are the same as that of the equilibrated droplet.

Figure 2.4: Particle location inside the liquid region at four different time steps for the case $T(\epsilon/k_B) = 0.9$, time in $\sigma \sqrt{m/\epsilon}$ units

Figure 2.4 depicts the atomic positions inside the liquid region during the oscillation in four different time steps for the case $T(\epsilon/k_B) = 0.9$. The first picture reports the maximum deformation of the droplet along the $x$ direction. This instant will be considered as the initial stage of the temporal evolution. The maximum deformation along the $y$-$z$ direction is very small and difficult to capture (third picture). Finally, a spherical shape is reached (fourth picture) with no other visible oscillations.

To evaluate the magnitude of the droplet deformation, the computational domain is divided in
30x30x30 bins and a first order interpolation scheme is used to convert the Lagrangian description of the atom simulation to an Eulerian-type iso-surface of density. Subsequently, a least squares interpolation was used to fit the particles inside regions with a density $\rho(R_e) \pm 0.01\rho(R_e)$, (i.e. within a small range of density corresponding to that of the equimolar radius in the equilibrated configuration), onto an ellipsoid, in order to evaluate the three axes $a$, $b$, $c$ of the deformed droplet. This procedure gave the same qualitative results obtained by evaluating the gyration radius along the three axis defined as: $R_{\alpha} = \frac{1}{N} \sum_{i=1}^{N} a_i^2$, where $\alpha = x, y, z$.

Figure 2.5: Density field in a cross section in the middle plane during deformation

Figure 2.5 shows a typical density field in a cross section in the middle plane during the deformation. Due to the interpolation technique and the large number of atoms in each cell, a good spatial definition is achieved without time averaging.

The time behavior of $a/b$, is depicted in Figure 2.6 for the case $T(\varepsilon/k_B) = 0.81$. As observed
before, only one oscillation period can be seen, further oscillations are damped by viscosity and become indistinguishable from the noise due to capillary waves. Moreover, when the oscillation amplitude is comparable with the amplitude of capillary waves, the assumption of an ellipsoid shape is not anymore realistic.

![Graph showing the ratio between the two interpolated ellipsoid axes during the droplet oscillation for the case \( T(e/k_B) = 0.8 \)]

Figure 2.6: Ratio between the two interpolated ellipsoid axes during the droplet oscillation for the case \( T(e/k_B) = 0.8 \)

During the first deformation transient (negative time with respect to the curve reported in Figure 2.6), the mean temperature of the system exhibits also a harmonic damped behavior (Figure 2.7). The period and the dumping constant are small compared to those reported below for the droplet oscillation. This fluctuation is probably caused by the externally imposed velocity field that is perturbing the initially equilibrated configuration decreasing the distances among the atoms. This event is leading to a harmonic damped oscillation of the potential and kinetic energy (the total energy of the system is constant), hence the temperature, that is persisting until the droplet reaches its maximum deformation. The period \( t_\tau \) and the dumping constant \( \tau \) of the temperature oscillation are calculated by fitting the MD results with the function:

\[
T(t) = T_0 \sin \left( \frac{2\pi}{t_\tau} t + \phi \right) e^{-\tau t} + T_{\text{av}}
\]

(2.14)
where $T_0$ is the initial oscillation temperature amplitude, $T_a$, the average temperature and $\phi$ the phase. Results are reported in the last two lines of for all cases studied. It appears that both parameters are practically linear functions of the temperature.

![Figure 2.7: Time behavior of the system temperature during the deformation transient for the case $T(e/k_b) = 0.9$](image)

For the present study, the Reynolds number, which is a measure of the relative effect of viscosity compared to inertia, is $2.17 < Re < 2.52$. The values of $\nu$ were set equal to the experimental Argon values [14]. If the nonlinearities due to oscillation amplitude and viscosity are small, the second mode oscillation amplitude can be approximated [6, 26] as:

$$
\xi(t) = A \sin \left( \omega_2 \left[ 1 - \left( \frac{b_2}{\omega_2} \right)^2 + \alpha A^2 \right] t + \phi \right) + \beta A^2
$$

(2.15)

where $\alpha$ accounts for the oscillation amplitude influence on the frequency, $\beta$ for the asymmetry of the oscillation between the prolate and the oblate deformation and $\phi$ for the phase.

The amplitude dumping is evaluated as:

$$
A(t) = A_0 \exp(-b_2 t)
$$

(2.16)

The oscillation amplitudes of all cases were fitted with eqs. (2.15), (2.16) using as fitting parameters $A_0$, $\alpha$, $\beta$, $\phi$, $b_2$ and $\omega_2$ (Figure 2.8). The initial droplet deformations $A_0 = a/R - 1$.
achieved after the compression phase are 0.29, 0.34 and 0.34 for the temperatures $T(\varepsilon/k_B) = 0.81$, 0.9 and 0.97 respectively. The resulting values of $\omega_2$, $b_2$ and $\alpha$ are reported in Table 2.3 in dimensionless units. The values of $\omega_2$ obtained from Eq. (2.1) are also reported for comparison.

The asymptotic frequencies ($\omega_2$) obtained by Eqs. (2.15), (2.16) are quite close to that predicted by Rayleigh's linear analysis (the largest difference is approx. 8% for $T(\varepsilon/k_B) = 0.9$). The parameter $\alpha$ is ranging from -0.32 to -2.6. The latter value, corresponding to the case $T(\varepsilon/k_B) = 0.97$, is quite large and denotes a marked decrease in the oscillation frequency with the oscillation amplitude (Becker et al. [6] obtained with continuum theory $-0.6 < \alpha < -0.9$ for a droplet that had a maximum initial deformation $A = 0.65$ and $Re>>1$) so that the observed oscillation is quite close to that of the case $T(\varepsilon/k_B) = 0.9$. It has to be stressed that the fitting procedure is not entirely accurate due to the fact that only one oscillation is visible before the droplet becomes practically a sphere and for the higher temperature case the amplitude fluctuations due to capillary waves are large. The values obtained for $\beta$ are in the same range with those found by Becker et al. [6].

![Figure 2.8: Oscillation amplitude MD and fit with the Eqs. (2.15), (2.16)](image)

A direct comparison of the dumping constant $b_2$ with the corresponding value of Eq. (2.3) cannot be made, because this equation uses the shear viscosity, neglecting the effects of the bulk
viscosity. However, it is of interest to report that, possibly due to this viscosity inconsistency, the computed values for $b_2$ (reported in Table 2.3) are approximately 30% smaller than the $b_2$ values obtained from Eq. (3). This underlines the importance of bulk viscosity contribution in a compression and volume change process like the one we are studying here.

<table>
<thead>
<tr>
<th>$T(eV_{th})$</th>
<th>$\omega_2 (\sigma\sqrt{m/\varepsilon})$</th>
<th>$\omega_2 (\sigma\sqrt{m/\varepsilon})^{1} MD$</th>
<th>$\omega_2 (\sigma\sqrt{m/\varepsilon})^{1} Eq. (2.1)$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$b_2 (\sigma\sqrt{m/\varepsilon})^{1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>0.0090</td>
<td>0.0088</td>
<td>-0.91</td>
<td>0.32</td>
<td>0.0050</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>0.0075</td>
<td>0.0082</td>
<td>-0.32</td>
<td>0.32</td>
<td>0.0039</td>
<td></td>
</tr>
<tr>
<td>0.97</td>
<td>0.0077</td>
<td>0.0074</td>
<td>-2.72</td>
<td>0.29</td>
<td>0.0040</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3: Fitting parameters of Eqs. (2.15), (2.16) describing the droplet oscillation behavior for the three studied temperatures.

Conclusions

The oscillatory behavior and related thermophysical properties of nanodroplets were studied using molecular dynamics simulations. Using a proper cutoff distance it was possible to obtain the experimental values of density and surface tension for Argon with a good approximation. The surface thickness due to capillary waves based on continuum theory was quantified to be around 86% of the total surface thickness evaluated via MD. A linear interpolation scheme was used to obtain a Lagrangian formulation of the system in order to calculate the oscillation amplitude of the droplet. Although due to the viscosity effects only one oscillation period is visible, typical phenomena that are described in previous works both experimental and numerical/theoretical based on continuum theory were observed. The frequency of the oscillation decreases for the finite oscillation amplitude and the prolate phase lasts longer than the oblate. The values obtained for the asymptotic frequencies are in good agreement with that of Rayleigh’s linear theory. In all it was found that the continuum analysis can predict reasonably well the oscillation behavior of nanodroplets, although quantitative differences exist.
References

23. J. Lekner and J.R. Henderson, Theoretical Determination of Thickness of a Liquid-Vapor


3 On the Coalescence of Gold Nanoparticles*

Abstract
The present work investigates the coalescence process of two gold nanoparticles for a host of initial temperatures and starting radii in vacuum with the help of molecular dynamics (MD) simulations. Diverse mechanisms of the first sintering stage, characterized by a growing neck region, were found. The results are compared with a phenomenological macroscopic model based on an energy balance and supplemented by a model for the surface variation of the nanosystem under consideration. The model is also modified to account for the curvature dependence of the melting temperature of the nanoparticles. Accounting for the findings of the MD simulations for the neck growth rate, the validity of the analytical model with the initial temperature and radius of the particle is shown. The calculations were extended to particles having radii between 9.5 to 25 Angstroms.

3.1 Introduction
As the utilization of ultrafine particles is becoming increasingly important in industrial applications, including a host of novel manufacturing processes, there is a great interest to understand the basic phenomena, not only in the production, but also in the utilization of such particles under a host of thermodynamic conditions. To this end, there are different models developed for ceramics describing the evolution of sintering of equally sized particles based on the neck growth rate [1] valid in the early sintering stages and often used in numerical simulations [2-4]. Friedlander and Wu [5] derived a theory for solid-state diffusion valid for the coalescence stage (intended as the approach of a non spherical particle to a spherical shape). Zachariah and Carrier [6] showed, comparing their MD simulations with a phenomenological model, that the results obtained in Friedlander and Wu [5] could be applied also in the early stage of sintering of silicon nanoparticles. The same authors and Lehtinen and Zachariah [7] reported that during the sintering process of two particles the surface area reduction leads to an energy release with a consequent increase of temperature that accelerates the entire process. Several works compared the sintering process of nanoparticles of different materials both

experimentally and theoretically and found good agreement with the “neck” theory [1]. To exemplify, Kobata et al [3] investigated the sintering of TiO₂ during gas-phase reaction. Shimada et al. [4] investigated experimentally the size reduction of fine silver agglomerates by sintering in a heated gas flow. Nakaso et al. [8] reported that gold agglomerates with small primary particles will compact mainly by the subsequent coalescence of these primary particles.

Xing and Rosner [9] were able to predict some experimental results for alumina and titania nanoparticles assuming that coalescence occurs via surface diffusion and taking into account the curvature dependence of the surface melting temperature. Tsantilis et al. [10] suggested a similar approach for the coagulation of silica nanoparticles.

The sintering of two copper nanoparticles via MD was studied in Zhu and Averback [11]. The evaluated diffusion coefficient for the studied sintering event was by a factor of 10³ larger than the diffusion coefficient for grain boundary diffusion, the expected dominant mechanism. They observed during the early sintering stages an elastic deformation after which a relative rotation between the two particles begins until a low minimum energy grain boundary was reached. The simulation of Cu and Au nanoparticle arrays [12] showed a different sintering mechanism of nanosized particles compared to microsized. Large atomic potential gradients, present where the two surfaces form a cusp at the point of contact, are decreasing the expected temporal scales of the process. Lewis et al. [13] studied the coalescence of liquid-liquid, solid-liquid and solid-solid of gold nanoparticles via MD simulations using the Embedded Atom Method (EAM) potential [14]. They found no agreement between the sintering time obtained by their MD results and the classical macroscopic neck theories. The latter are assuming that the leading phenomenon is surface diffusion, but do not account for the energy release due to the surface area reduction and the relative temperature increase of the system. The simulations showed a rapid increase of the neck growth at the beginning, followed by a slow tendency to recover the spherical shape. The simulation of the melting and the coalescence of metallic clusters (Ag, Cu and Pb) of size from 50 to 300 was performed by Mazzone [15]. Size dependence of the melting temperature and significant differences in the coalescence stage compared with classical theories were reported.

The configuration of a single gold nanoparticle has been studied in the past and results have been reported in the literature. As demonstrated in previous numerical [13, 16-18] and experimental [19, 20] works the melting temperature and the latent heat of fusion are dependent on the particle size and are markedly lower than their bulk counterparts. This phenomenon has great significance
in technological applications, since partial or complete melting can be obtained at lower temperatures when ultrafine particles of matter are used [21], enabling the manufacturing of gold nanostructures on temperature sensitive surfaces. Furthermore, a thin liquid shell can be present in a stable configuration around the solid structure even though the particle temperature is below the melting point [22]. This morphology can also be predicted by MD simulations [13, 16] and can have an important effect especially in the early sintering/coalescence stage.

The motivation and main novelty of this work is to achieve a better understanding of the phenomenology and specifics of the coalescence process of gold nanoparticles with the help of MD, by employing a reliable model for the interatomic potentials, which we first test herein again experimental data. A simple macroscopic model is developed and presented in parallel and its predictions vis. a vis. those of the simulations are discussed. At the same time, contrary to previous MD works, we show that classical "neck" theories, modified to take into account the size dependence of the melting temperature, can predict the first stage of the sintering process also in nanoscales at least for particles that are larger than ca. 20Å and temperatures near the corresponding melting point.

3.2 Model

3.2.1 Molecular Dynamics Simulation

The molecular dynamics simulations employed herein to study a wide range of gold nanoclusters, 9.5-25.2Å (225-3805 atoms), is based on the glue potential [23]:

\[ V = \frac{1}{2} \sum_{ij} \Phi(r_{ij}) + \sum_{i} U(n_{i}) \]  

(3.1)

where \( r_{ij} \) is the distance between two atoms, \( \Phi(r_{ij}) \) is a standard two body potential, \( U(n_{i}) \) is the energy associated with the coordination \( n_{i} \) of the atom \( i \), \( n_{i} = \sum_{j} \rho(r_{ij}) \) is defined as the superposition of contribution from neighbor atoms and \( \rho(r) \) is a short-ranged monotonically decreasing function of distance. The parameter \( n_{i} \) can be interpreted as the electronic density and the parameter \( \rho \) as the electronic density of an isolated atom. The functions \( \Phi(r) \), \( U(n) \) and \( \rho(r) \) are reconstructed empirically in order to reproduce the experimental values of gold in a wide range of thermodynamic conditions.

The gold nanoparticles are constructed to have a spherical shape with a face centered cubic (fcc)
lattice and placed in vacuum. The target system temperature was obtained rescaling every 250 time steps the velocity of each particle with the factor \( \chi = \left( \frac{T_{\text{target}}}{T} \right)^{\frac{1}{2}} \), where \( T_{\text{target}} \) is the requested temperature and \( T \) is the average instantaneous temperature of the system. The velocity rescaling was applied for ca. \( 5 \cdot 10^4 \) time steps. After that, the system was equilibrated until no change in the average temperature was observed. Depending on the studied system the equilibration required up to \( 5 \cdot 10^6 \) time steps, for the particles with a temperature near the melting point. The simulation runs were performed for ca. \( 10^6 \) time steps to collect data to have a good statistics. The chosen time step was 2.86 fs, while the cutoff distance was 3.9 Å for \( \rho(r) \) and 3.7 Å for \( \Phi(r) \) (these are intrinsically defined in the glue potential which is considering only the first neighbor atoms). Some particles were melted and then frozen before the sintering simulation process to obtain a low energy configuration. In order to simulate the coalescence process, one equilibrated particle and a copy of it were entered into the simulation domain at a distance small enough to be within the interaction range of the intermolecular forces, ca. 3 Å. Some of the copied particles were also rotated by 45° to study the influence of the lattice arrangement.

### 3.2.2 Analytical Model

As a macroscopic alternative, the sintering process can be analyzed with a free energy balance [7]. Considering our system as two gold particles consisting of each \( N \) atoms in a vacuum, the total energy \( E \) of this system is the sum of the bulk energy \( E_{\text{bulk}} \) and the surface energy \( E_{\text{surf}} \). Any change in the total energy would result from gains or losses to the surrounding. In the present model this change is zero, neglecting radiation and convective losses, to make the comparison with the MD simulation as close as possible. As the two particles coalesce to form one larger particle, the surface of the system is changing. This reduction in the surface area results in an energy release which increases the particle temperature significantly. Since the dynamics of the coalescing process is dependent on temperature, this temperature increase will accelerate the entire process.

---

\[ \text{by Dr. N. Bieri, (Nicole Bieri, Transport Phenomena in the Microprinting and Laser Annealing of Gold Nanoparticle Inks, Ph.D. Thesis, Mechanical and Process Engineering Department, Swiss Federal Institute of Technology, Zurich), used herein for comparison} \]
The energy change of the system can be written as:

$$\frac{dE}{dt} = \frac{d}{dt}(E_{\text{bulk}} + E_{\text{surface}}) = 2NC_v \frac{dT}{dt} + \sigma_{sv} \frac{da}{dt} = 0 \tag{3.2}$$

where $C_v$ is the constant-volume heat capacity, $\sigma_{sv}$ is the solid-vapor surface tension, $T$ and $a$ are the temperature and the surface of the two coalescing particles at time $t$.

The surface area reduction by sintering can be described by the linear law of [24]:

$$\frac{da}{dt} = -\frac{1}{\tau}(a - a_s) \tag{3.3}$$

where $a_s$ is the surface area of the final sphere (assumed in the analytical solution) and $\tau$ the characteristic sintering time that will be defined later in this section. The relation above was initially derived assuming that the coalescence rate of an agglomerate in the initial state is directly proportional to its excess surface area $[(\text{actual surface area}) - (\text{equivalent spherical area})]$. This assumption was later shown to be representative also for the final stages of transformation to sphericity for an originally slightly nonspherical particle by Friedlander and Wu [5].

Finally, the derivative of the particle temperature can be expressed as:

$$\frac{dT}{dt} = -\frac{\sigma_{sv}}{2NC_v} \frac{da}{dt} \tag{3.4}$$

This system (3.3)-(3.4) of two dependent differential equations was solved with a Runge Kutta fourth order algorithm.

There exist different mechanisms which can drive the coalescence of two solid nanoparticles such as surface diffusion, grain boundary diffusion, evaporation-condensation, and lattice diffusion.

![Figure 3.1: Sketch of the sintering of two equally sized particles](image)

The modeling of the initial stage of sintering expresses the neck growth of two spheres of the same radius (Figure 3.1) with a center-to-center approach as:

$$\left(\frac{x}{r_p}\right)^n = \frac{Bt}{r_p^n} \tag{3.5}$$

where $r_p$ is the initial particle radius, $x$ the neck radius, $t$ the time and $B$ a constant depending on
the temperature.

If grain boundary diffusion or surface diffusion are dominant Eq (3.5) becomes [1]:

$$t = \frac{\left( \frac{x}{r^p} \right)^6 r^4 RT}{C_w D \sigma_{sw} \Omega}$$

(3.6)

where \( C \) is a constant, \( R \) is the universal gas constant, \( D \) is the grain boundary or surface diffusion coefficient, \( \Omega \) is the molar volume and \( w \) is the surface or grain boundary layer width, estimated as \( \Omega^\infty \) [2]. The previously introduced characteristic sintering time \( \tau \) is defined as the time in Eq.(3.6) at which the neck radius to particle radius ratio reaches 0.83. This value was found by Kobata et al. [3] and represents the largest possible neck to radius ratios of two coalescing spheres where no undercutting is visible and it is consistent with that numerically evaluated for an infinite line of spheres sintering into an infinite cylinder (\( x/a = 0.817 \)) and the one of a sphere sintering onto a plane (\( x/a = 0.84 \)) [25].

The diffusion coefficient was assumed to follow the Boltzmann-Arrhenius dependency:

$$D = D_0 \exp \left( - \frac{E_a}{RT} \right)$$

(3.7)

where \( D_0 \) is the pre-exponential diffusion coefficient and \( E_a \) the activation energy.

Assuming grain boundary diffusion as the driving phenomenon [8], the proper pre-exponential factor and the activation energy can be calculated with the empirical relationship deduced from experimental data of bulk material valid for fcc crystal structures [26]:

$$D_0 = 0.3 \text{ cm}^2/\text{s}$$

(3.8)

$$E_a = 47.5 \cdot T_M \text{ J/mol}$$

(3.9)

where \( T_M \) is the bulk melting temperature.

The surface tension is calculated using the relation of [27] for pure fcc metals:

$$\sigma_{sw} = 1.2(\sigma_{\nu})_M + 0.45(T_M - T)$$

(3.10)

where \( (\sigma_{\nu})_M \) is the surface tension of liquid bulk gold at the melting point.

As it will be discussed in detail in the next section, the melting temperature of a nanoparticle \( T^0 \) is curvature dependent. In both equations (3.9) and (3.10) the value of the bulk melting temperature \( T_M \) was replaced by \( T^0 \). Furthermore, to account for the changing size from the initial to the final configuration, it was assumed that the starting melting temperature is equal to that corresponding to the initial particle radius and it increases exponentially up to that corresponding to the final radius. The final melting temperature is reached when the curvature is
approximately equal to unity.

3.3 Results

3.3.1 Single Particles

To benchmark of the methodology, calculations were first conducted on single gold nanoparticles with different radii.

The most common approach to evaluate the melting temperature of a particle via molecular dynamics is to evaluate the point of discontinuity in the potential energy function when plotted as a function of the temperature (Figure 3.2).

![Figure 3.2: Single particle calculations: Potential energy as a function of the particle temperature for different particle radii.](image)

The jump in the potential energy is the latent heat of fusion and the corresponding temperature is the melting temperature. Figure 3.3 shows the melting temperatures as a function of the particle radius evaluated from the present calculations and the analytical formulation reported in \[19\]:

\[
\ln \frac{T^0}{T_M} = -\frac{2}{\rho_s L} \left( \frac{\rho_s}{\rho_l} \right)^{1/3} \frac{1}{r_s^*} \left\{ \sigma_l \left( 1 - \frac{\rho_s}{\rho_l} \right) + \sigma_{sl} \left[ 1 - \frac{\delta}{r_s^*} \left( \frac{\rho_s}{\rho_l} \right)^{1/3} \right]^{-1} \right\}^{1/3}
\]

(3.11)

where: \(\sigma_{sl}\) is the solid-liquid interfacial tension, \(\sigma_l\) is the surface tension of the liquid, \(\delta\) is the liquid-layer thickness, \(r_s^*\) is the radius of the particle at the melting point assuming that the particle is in the solid form, \(\rho_s\) and \(\rho_l\) are respectively the solid and liquid densities and \(L\) is the
latent heat of fusion.

![Graph of melting temperature vs. particle radius with comparison to Buffat and Borel results]

Figure 3.3: Single particle: Melting temperature as a function of the particle radius and comparison with the results of Buffat and Borel [19]

![Graph of latent heat of fusion vs. particle radius with MD results and fitting curve]

Figure 3.4: Single particle: Latent heat of fusion as a function of the particle radius. Circles: MD results. Solid line: fitting curve proposed in [20]

The parameters $\sigma_0$, $\sigma_1$, $\rho_s$, $\rho_i$ and $L$ used in Eq. (3.11) correspond to the experimental values of
bulk gold while $\delta$ and $\sigma_d$ are the same obtained in [19] fitting their experimental data. The calculated latent heat as a function of the particle radius is shown in Figure 3.4. The solid line is the proposed relation by Lai et al. [20]:

$$L_M = L\left(1 - \frac{\delta}{r}\right)^3$$

where $L_M$ is the latent heat of fusion for the particle of radius $r$ and $\delta$ is a fitting parameter that is a measure of the liquid shell. The obtained value was $\delta \approx 7$ Å that is in agreement with the value reported in [19] for the melting temperature, $\delta \approx 6.2$ Å.

3.3.2 Two Particle Coalescence

The time evolution of the gyration radii during the particle coalescence evaluated via MD, defined as $R_x = \frac{1}{N} \sum_{i=1}^{N} \alpha_i^2$, where $\alpha = x, y, z$ are the molecule coordinates and $N$ total number of the simulated molecules, is reported in Figure 3.5 for two particles of 20 Å radius and an initial temperature of 895 K. A typical transient can be characterized by two main stages. A very fast first phase can be distinguished where a neck forms between the two particles and its growth rate is following a power law in time (Figure 3.6) as given in Eq. (3.5). This behavior is neither dependent on the particle size nor on the initial temperature. This phase, in present case, is persisting until ca. 0.3 ns (Figure 3.5 and Figure 3.6). A similar order of magnitude for this time is reported by Lewis et al. [13] for $r = 16.37$ Å. The second phase starts when the neck disappears and only one particle is recognized. The gyration radii evolution in this case is much slower. For the present case shown in (Figure 3.5) an actual sphere shape is not reached within the simulation time although more than $2 \cdot 10^6$ time steps were performed. It is difficult to state whether the final configuration will approach to a perfect spherical shape for this would require a simulation of hundred nanoseconds. As discussed in [5, 28] the dominant mechanism in this phase can be solid state self diffusion driven by stress gradients resulting from a non perfect sphericity. In addition, unlike liquids, in solids it is possible to have a non-spherical final shape (non spherical particles abandon in nature), because the surface energy gradient driving toward the spherical shape (minimum surface energy), may not be enough to overcome the resistance imposed by the crystal structure of the solid. In this phase the rearrangement of the lattice structure appears to be stronger than in the first phase. In Figure 3.5 a sequence of atomic structure is also shown. The
initial shape of an Au nanoparticle before the melting transition is a truncated octahedron because of the asymmetric surface energy along the index surfaces (the (1 1 1) surface has the lowest surface energy) [18]. This leads to a non zero initial neck radius that will depend on the initial contact area between the two particles.

Figure 3.5: Time evolution of the gyration radii in the three directions x (continuous line), y; z (dashed lines) during the sintering of two nanoparticles: \( r=20\,\text{Å}, \, T=895\,\text{K} \)

This realistic situation is not covered by the assumption of two perfectly spherical particles used in the phenomenological model. During the initial transient of coalescence, the energy release due to the surface area reduction, in terms of molecular forces due to the new formed bonds, leads to an increase of the temperature of the system (Eq. (3.4) and Figure 3.7). This behavior continues until ca. 2 ns, i.e. until a pronounced surface area reduction is visible, as also reported in the MD simulations of silicon nanoparticles in [6].

Figure 3.7 shows also the results of the analytical model for the surface reduction and the temperature behavior for the same case. The model is predicting a faster transient for the surface
area reduction (ca. 0.3 ns) and, consequently, the maximum temperature is reached faster.

Figure 3.6: Time evolution of the neck during the sintering of two nanoparticles: $r=20\,\text{Å}$, $T=895\,\text{K}$

Moreover the maximum temperature is underestimated of ca. 40 K. Since this is approx. 4% of the maximum temperature in the MD simulations, the agreement of the two models, analytical
and numerical, is satisfactory. It has to be stressed that, as shown before, the “glue” potential is well reproducing quantitatively the properties of gold in a wide range of temperatures, so it can be taken comfortably as a reference to check the validity of the approximate macroscopic analytical formulation. The neck growth obtained via MD and the predictions of the phenomenological model for the same particle at four different initial temperatures are depicted in Figure 3.8. The results of the MD simulations are giving almost parallel curves, within the accuracy of the neck evaluation calculation, except for the lower temperature case.

![Figure 3.8](attachment:figure3_8.png)

Figure 3.8: Time evolution of neck growth evaluated via MD simulations and the analytical model for different temperatures and \( r = 20\text{Å} \)

This case exhibits an early transient phase for the neck growth, that is as fast as that of the higher temperatures. However, later, after the neck practically disappears, the growth of region where the neck was, slows down compared to higher temperatures. It seems that for the specific case under consideration, the initial temperature is not the dominant parameter for early coalescence. The phenomenon at this stage could also be influenced by the potential gradient due to the cusp at the contact point, as discussed in [12]. All the curves finally reach a plateau that has lower values for lower initial temperatures. This means that the final shape of the particle is more deformed at lower temperatures, because the solid diffusion time scales required bringing the particle to a spherical shape are larger at lower temperatures. As a comparison, the asymptotic value of \( x/r \) for a final spherical shape can be evaluated assuming that the total volume of the two initial particles
is equal to the volume of the final particle; finally \((x/r)_{\text{spherical}} = \sqrt{2}\).

a)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure39a.png}
\caption{Time evolution of neck growth evaluated via MD simulations and the analytical model for different temperatures:
a) \(r = 15.3\,\text{Å}\)
b) \(r = 13\,\text{Å}\)
}\end{figure}

b)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure39b.png}
\caption{Time evolution of neck growth evaluated via MD simulations and the analytical model for different temperatures:
a) \(r = 15.3\,\text{Å}\)
b) \(r = 13\,\text{Å}\)
}\end{figure}
The analytical model yields acceptable results for the three higher temperature cases and provides good approximations for the corresponding sintering time. Similar results were obtained for larger particles ($r = 22.3$ Å and $r = 25.2$ Å), not shown here for brevity.

On the other hand, it seems that the initial temperature does not play a crucial role for smaller particles for all the studied cases. Figure 3.9 a reports the neck growth for the sintering of two particles of 15.3 Å radius at different initial temperatures. All the MD results are packed within a small range while the analytical model is predicting a stronger temperature influence. The trend is
more distinct when going to even smaller particles (Figure 3.9 b). The agreement between the model and the MD simulation deteriorates in accuracy signifying that at these scales other mechanisms rather than grain boundary or surface diffusion, strongly dependent on the particle temperature, have to be taken into account in the formulation of the macroscopic problem.

The influence of initial lattice orientation is studied by simulating two cases of two particles of the same radius (22.3 Å) at a temperature of 938 K with different orientation. In one simulation the copied particle was only translated with respect to the original. In the other, it was also rotated anticlockwise by 45°. The two initial configurations are depicted in the first frames of Figure 3.10 a, b. Both sintering processes (Figure 3.10) are evolving in a similar manner as described above. However, the initial setting has an influence on the entire transient. The sintering case in which one particle was rotated presents a smaller initial contact area between the two particles. This is visible looking from the top onto the system shown in Figure 3.10 b, but it is not reported for brevity. The particles having initially a larger contact area and therefore a smaller potential gradient are evolving slower than the ones having a smaller contact area (Figure 3.11).

![Figure 3.11](image)

**Figure 3.11:** Comparison of the neck growth for the sintering of two nanoparticles \( (r=22.3\,\text{Å}, \ T=938\,\text{K}) \), between two different initial lattice orientations. Triangles: same lattice orientation, closed triangles: 45° rotation. Solid line phenomenological model.

The same figure reports the prediction of the phenomenological model that is providing the trend
of the neck growth. Figure 3.10 a shows the sintering of the two particles with the same lattice orientation. During neck formation, small lattice rearrangement begins and the two particles have a small relative rotation. This behavior was observed in previous works both experimental on Au nanoparticles [29] and numerical on Cu nanoparticles [30] and on Au/Cu nanoparticles [12] and seems to be another path for boundary elimination in nanoscales. The rotation is even stronger when the initial lattice arrangement of the particles is very different (Figure 3.10 b). After the neck is filled, the resulting particle starts slowly rotating in the simulation domain. Generally this occurrence of rotation was observed in other simulations in the present paper, especially when the temperature is well below the melting point, we speculate that the mechanical stresses within the particle due to the vivid atomic rearrangement are large enough to cause rotation of the particle as a whole.

**Conclusion**

In this paper we reported MD simulations of gold nanoparticle melting and coalescence phenomena. The obtained results for single particle calculation were compared with earlier empirical-theoretical formulations showing that the MD approach is a reliable method to study such nanoscale phenomena. As a second step the coalescence of two nanoparticles was studied. The MD calculations improved our understanding the basics of the process such as the driving mechanisms acting at different particle sizes. For larger particles, *i.e.* with a radius greater than 20 Å, it can be assumed that grain boundary diffusion is dominant as the correspondence between the analytical and MD calculations is indicating. For the cases with an initial temperature near the particle melting, a good agreement between MD results and the predictions of a macroscopic phenomenological model, that was modified to account for the curvature dependence of the particle melting temperature, was found. On the other hand, for smaller particles the model does not hold. The initial temperature seems not to play an important role and choosing between temperature dependent mechanisms, such as grain boundary or surface diffusion, does not improve the predictions of the phenomenological model. As also reported in previous works for other materials as well, the relative rotation of the particles could be another route to nanoscale boundary elimination during coalescence.
References


4 On the Solidification of Gold Nanoparticles in Carbon Nanotubes

Abstract
The structure and the solidification of gold nanoparticles in a carbon nanotube (CNT) are investigated using Molecular Dynamics (MD) simulations. The simulations indicate that the predicted solidification temperature of the enclosed particle is lower than its bulk counterpart, but higher than that observed for clusters placed in vacuum. Comparison with a phenomenological model indicates that the solidification temperature depends mostly on the length of the particle, while a minor dependence on the radius $R_c$ of the CNT is found in the studied range of $0.5 < R_c < 1.6 \text{ nm}$. A layered structure is found for all the particles both in the solid and in the liquid phase. The unfolded sheet of each layered structure in the solid phase consists of a triangular ordered structure that is lost after the solidification transition.

4.1 Introduction
The presence of enclosed nanoparticles alters the properties of CNTs making feasible several promising applications (catalysis, sensors, semiconductor devices, data storage, contrast agents in magneto resonance imaging, etc.) [1]. A number of works has addressed the practical process of filling of CNTs with different metals (see [2] and reference therein). As an example Chu et al. [3] obtained nanotubes filled with silver, gold and gold chloride. The observed particle sizes ranged from $35 \text{ Å}$ to $190 \text{ Å}$ for Ag particles and from $10 \text{ Å}$ to $50 \text{ Å}$ for Au particles. The structure and melting of nanowires of some metals ( Cs, Cu, K) inside zig-zag $(n,n)$ carbon nanotubes at different values of $n$ were studied using MD simulations [2, 4, 5]. A cylindrical shell structure was found for all the wires with smaller CNT radii, while at larger radii the predicted structure consisted of an fcc core for the Cu particles [2] and a bcc core for the K particles [5]. In the aforementioned works nanowires inside CNTs showed a higher melting temperature compared to isolated nanowires indicating that the CNT wall increases the stability of the encapsulated nanowires. The shell structure of isolated nanowires was also predicted computationally [6] and observed experimentally [7]. Two notations were defined to describe this structure: the so-called

KT index (Kondo and Takayanagi [7]) and the T index (Tosatti et al. [8]). These indices were also successfully used to describe nanowires encapsulated in CNTs [2, 4, 5]. A numerical study of Wang et al. [9] on gold nanowires with diameters \( D \) up to 3 nm predicted that the wire structure is helical for \( D<0.6 \text{nm} \), multiwalled cylindrical for \( 1.0< D<2.2 \text{nm} \) and an fcc for \( D>2.2 \text{nm} \). The problem of melting of these mesoscopic structures has attracted particular interest in the last years. For example, the stability of finite length gold nanowires [10] and the melting of infinite gold nanowires [11] were studied in the past with MD. The predicted melting temperature for infinite gold nanowires was found between 900-1100K [11]. These values are below the bulk melting temperature, but higher than the expected melting temperature of corresponding finite gold nanowires [10]. A cylindrical shell structure with a limited layer interdiffusion was observed in infinite nanowires also after the phase change. Guo et al. [12] studied the structural transition of copper nanowires in single walled carbon nanotubes. The authors hypothesized that the combined effect of pressure and cylindrical shape of CNT dominates the structural transition of the particle. Experimental results on the melting of nitrobenzene and carbon tetrachloride within CNTs were used in [13] for validating Monte Carlo simulations. Simulations confirmed the experimental results of no formation of common three dimensional crystalline structures, but concentric layered structures that solidify into quasi-two-dimensional hexagonal crystals. The melting was found to start in the inner layers. Recently Liu et al. [13] conducted experiments on gallium encapsulated in CNTs. A large hysteresis was found between crystallization and melting. The melting temperature of the \( \alpha \) and \( \beta \) phase was found to be of the same order as the bulk melting temperature, while the \( \gamma \) phase was melting at a higher temperature compared to the corresponding bulk value. No influence of the CNT radius \( R_c \) was found on the melting temperatures in the studied range of \( 100<R_c<200 \text{nm} \).

In spite of the relatively many attempts to describe this class of phenomena using computer simulations, a convincing theoretical interpretation of the size effects affecting the thermodynamical stability of these particular systems is still missing. This may be attributed to the reliability of the simulation itself and its dependence on the chosen interatomic interaction model. Most of the work done on confined systems is limited to describing the metals using a two-body Lennard-Jones potential for modeling the interactions within the atoms. Moreover, there is no satisfactory model for a phenomenological description of the carbon-metal interaction. An \textit{ab initio} approach appears prohibitive at this stage for studying extended systems and the
size-dependence of their properties.

In this work we implement an interatomic model for the metallic interactions that has been validated in the past (see for example [14, 15]) and we verify the influence of the particular parameters chosen for the description of the CNT-gold potential on the results.

### 4.2 Molecular Dynamics Simulation

The present work studies in detail the solidification and the structural properties of gold nanoparticles with different number of atoms inside CNTs of three different chirality vectors: \((n,m)=(20,0), (30,0)\) and \((40,0)\). We find a particular dependence of the solidification temperature on the geometrical shape, and propose a simple phenomenological model that describes the results of our simulations. In Table I we report the parameters of all cases that have been simulated. In discussing a case studied herein we will always specify the number of gold atoms \(N_{\text{Au}}\) and the chirality index \(n\) of the CNT. We consider a system composed of an infinitely long CNT simulated in a box of length \(l=21.72\text{nm}\) (replicated using periodic boundary conditions along the axis) and a cluster of gold inside the tube. The interactions are modeled by the force field introduced in [16] for the carbon-carbon interaction, the glue potential [15] for the gold-gold interaction, while the gold-CNT interaction is modeled with a Lennard-Jones (LJ) potential using the parameters given in [17] \((\varepsilon_{\text{C-Au}}=0.01273\text{eV}, \sigma_{\text{C-Au}}=2.9943\text{ Å})\). The assumption of using a graphite-gold interaction to mimic the gold-CNT system does not take into account curvature effects. However a number of studies have used interaction potentials pertaining to graphitic surfaces for describing interactions with CNTs [2, 4, 5, 16, 18]. Moreover, we performed some calculations with different LJ interaction parameters as suggested in [19] \((\varepsilon_{\text{C-Au}}=0.022\text{eV}, \sigma_{\text{C-Au}}=2.74\text{Å})\). We observed no significant change in the predicted solidification temperature compared to the simulations using the parameters reported in [17] (ca. 25K difference for the case \((N_{\text{Au}}=1316, n=30)\), which is within the uncertainty affecting our evaluation of the solidification temperature). Concerning the glue potential for gold, we are aware that the empirical “glue” potential has not been validated (and would probably fail) in the case of wires of nearly atomic thickness and we will therefore not extend our analysis to such systems [6].

For all simulations, we use the MD package FASTTUBE [16], and we sample the canonical ensemble using a Berendsen thermostat [20]. The gold particle is inserted into the CNT and melted by bringing it to a temperature above the bulk melting temperature (1400K). The system
is then successively cooled to different target temperatures. The cooling rate is set to 1K/ps [2] in order to reach the final equilibrated configuration while the time constant of the thermal bath is set to $\tau = 0.1\text{ps}$. Once a selected temperature is reached, the system is equilibrated until no significant oscillation of the potential energy is observed; averages are collected for 1ns.

<table>
<thead>
<tr>
<th>$N_{Au}$</th>
<th>CNT (n,0)</th>
<th>CNT Radius $R_c$ [nm]</th>
<th>Particle Radius $R$ [nm]</th>
<th>$L$ [nm]</th>
<th>Solidification Temperature $T_m$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>534</td>
<td>20</td>
<td>0.78</td>
<td>0.56</td>
<td>7.2</td>
<td>1237.5</td>
</tr>
<tr>
<td>211</td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>537.5</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>787.5</td>
</tr>
<tr>
<td>399</td>
<td></td>
<td></td>
<td></td>
<td>1.6</td>
<td>962.5</td>
</tr>
<tr>
<td>540</td>
<td>30</td>
<td>1.17</td>
<td>0.94</td>
<td>2.2</td>
<td>1037.5</td>
</tr>
<tr>
<td>755</td>
<td></td>
<td></td>
<td></td>
<td>3.5</td>
<td>1150</td>
</tr>
<tr>
<td>1316</td>
<td>20</td>
<td></td>
<td></td>
<td>6.4</td>
<td>1212.5</td>
</tr>
<tr>
<td>1762</td>
<td></td>
<td></td>
<td></td>
<td>8.8</td>
<td>1237.5</td>
</tr>
<tr>
<td>2181</td>
<td>20</td>
<td></td>
<td></td>
<td>11</td>
<td>1237.5</td>
</tr>
<tr>
<td>2608</td>
<td></td>
<td></td>
<td></td>
<td>13.3</td>
<td>1237.5</td>
</tr>
<tr>
<td>589</td>
<td>40</td>
<td>1.57</td>
<td>1.34</td>
<td>1</td>
<td>887.5</td>
</tr>
<tr>
<td>1072</td>
<td></td>
<td></td>
<td></td>
<td>2.1</td>
<td>1062.5</td>
</tr>
<tr>
<td>1932</td>
<td></td>
<td></td>
<td></td>
<td>4.6</td>
<td>1187.5</td>
</tr>
<tr>
<td>4983</td>
<td></td>
<td></td>
<td></td>
<td>13.5</td>
<td>1212.5</td>
</tr>
</tbody>
</table>

Table I: Studied configurations for diverse number of gold atoms and CNT chirality vector. The corresponding radius of the CNT $R_c$, the radius of the particle $R$, the particle length $L$, and the solidification temperature are also reported.

4.3 Results

4.3.1 Particle Structure

The atomic positions for the case ($N_{Au}=775$, $n=30$) (Table I) are represented in Figure 4.1(a). The particle is composed of a cylindrical core of length $L$ and radius $R$ (Figure 4.1) with two spherical end caps of height $h = r(1 - \sin \theta)$, where $\theta$ is the contact angle and $r = \left(-\frac{R}{\cos \theta}\right)$ the radius of curvature of the caps. An estimate of the contact angle between the gold nanoparticle and the
nanotube from MD simulations can be performed by evaluating the curvature radius $r$ of one cap by fitting a spherical surface on the atom positions at the cap surface. The resulting contact angle is found to increase with temperature. For the cases $(N_{Au}=1316, n=30)$ and $(N_{Au}=1931, n=40)$ it ranges from $132^\circ$ to $138^\circ$ within the studied temperature interval across the melting point (1000–1400K). These values are in good agreement with those found using the same potentials for a liquid gold drop at 1400K on graphite substrate $133^\circ$ (not shown) and the experimental value of graphite-solid gold contact angle $131^\circ$ at 850$^\circ$ [21].

![Diagram of nanotube with annotations](image)

**Figure 4.1:** a) Atom position for the case $(N_{Au}=775, n=30)$ and definition of the nanoparticles shape: $L$ length of the cylindrical core, $R$ radius of the particle, $\theta$ contact angle, $h$ height of one cap. b) View along the axis of the CNT for the system of $(N_{Au}=775, n=30)$ at four different temperatures (400K, 800K, 1200K, and 1400K). First two pictures are corresponding to the solid phase, while last two to solid phase.

A view along the axis of the CNT for the system $(N_{Au}=775, n=30)$ at four different temperatures is shown in Figure 4.1(b). A cylindrical layered structure, similar to that observed in nanowires, is present for all the cases. In Figure 4.2(a), the radial density profiles for the same particle at different temperatures are shown. As expected, the peaks are higher at lower temperatures denoting a stronger layering. All peaks, especially the outermost ones, are shifted toward the center as the temperature increases.
This is due to the shape and two-body character of the CNT-gold interaction inducing a thermal interlayer expansion. However, as shown in Figure 4.2(a), the layered structure is maintained at all temperatures, i.e. also in the molten state as it will be further verified below. A different behavior can be observed in particles enclosed in a CNT with \( n = 40 \) (Figure 4.2(b)). While peaks in the radial density distribution are also present both in the liquid and in the solid phase, the
radial position of the innermost layers in the liquid phase is shifted outwards, compared to the corresponding peaks of the solid phase. Moreover, unlike in the case of \( n=30 \), the magnitude of all peaks in the liquid phase is decreasing exponentially with the distance from the CNT walls featuring small values of the peak heights in the center.

A deeper understanding and quantification of the layered structure can be achieved evaluating for each layer the two-dimensional orientation order parameter \( Q_6 \). If a segment or bond is drawn between all nearest neighbors within the same layer, \( Q_6 \) is defined as [22]:

\[
Q_6 = \frac{1}{N_b} \frac{1}{\pi} \int_{-\pi}^{\pi} \left| \sum_{k=1}^{N_b} \exp(i \theta_k) \right| \, dr
\]

where \( N_b \) is the number of nearest neighbor bonds and \( \theta_k \) is the angle that the \( k \)th neighbor bond forms with the \( x \)-axis. For a perfect 2D hexagonal structure \( Q_6=1 \) and for an isotropic structure \( Q_6=0 \). The order parameters \( Q_6 \) for the cases \( (N_{Au}=1319, n=30) \) and \( (N_{Au}=1931, n=40) \) are plotted in Figure 4.3 for all the studied temperatures. A 2D hexagonal structure with defects is present at lower temperatures denoting the presence of solid phase. This structure persists until a phase transition occurs and the order is abruptly lost (1212.5K and 1187.5K for the cases \( (N_{Au}=1319, n=30) \) and \( (N_{Au}=1931, n=40) \) respectively). The outermost layer maintains an ordered structure for the longest times as the temperature increases for both cases. This result is in agreement with the work reported in [23] and it indicates that the presence of the CNT helps to stabilize the particle structure while melting is starting at the center of the particle. On the contrary, Bilalbegović [11] found that in infinite isolated gold nanowires the melting occurs simultaneously in all shells.

4.3.2 Melting

The results obtained for the crystal structure are in agreement with the predicted solidification temperature inferred from the potential energy \( (E_p) \) as a function of temperature \( T \). The solidification temperature \( T_s \) is the temperature corresponding to the discontinuity in the potential energy plot (not shown here for brevity). The obtained melting temperature \( T_s \) is lower than its bulk counterpart \( T_\theta=1336K \) and decreases with the number of gold atoms as reported in previous numerical and experimental works [14, 24-26]. However, \( T_s \) is higher compared to isolated clusters of the same mass in vacuum (Figure 4.4 inset).
The presence of the nanotube induces a partial recovery of the solidification temperature. It appears that two competing driving forces play a role: the finite size of the nanoparticle favoring disordering, and the solid wall of the CNT, inducing ordering and layering. Moreover, the softening of the transition as the size decreases (not shown herein), already observed for isolated...
particles [14, 25] signals the conversion of the phase transition from first order to second order. An understanding of the solidification behavior of a nanoparticle inside a nanotube can be achieved by performing a free energy balance on the particle. The Gibbs free energy for the solid and the liquid phase can be written:

\[ G_s = N \mu_s + 2\pi RL \gamma_{C-s} + 2A \gamma_s \]  

(4.2)

\[ G_l = N \mu_l + 2\pi RL \gamma_{C-l} + 2A \gamma_l \]  

(4.3)

where \( N \) is the number of atoms, \( \mu_i \) the chemical potential of the phase \( i \), (s-solid or l-liquid), \( A = 2\pi hr \) the approximate area of one spherical cap, \( \gamma_{C-i} \) the surface tension between the CNT and the phase \( i \), \( \gamma_i \) the surface tension of the phase \( i \). The Gibbs-Duhem relationship near the solidification point and for an incompressible particle yields:

\[ N (\mu_s - \mu_l) = V \rho_s H (T - T_0)/T_0 + V (p_s - p_l) \]  

(4.4)

where \( V \) is the volume of the particle, \( H \) the bulk latent heat of fusion, and \( p_s \) and \( p_l \) the pressures of the solid and liquid phases. Equating the Gibbs free energies of the two phases and accounting for Eq. (5) we obtain:

\[ (T_s - T_0)/T_0 = -\frac{2\pi RL \gamma_{C-Au}}{V \rho_s H} - \frac{2A \Delta \gamma_{Au}}{V \rho_s H} + \frac{p_s - p_l}{\rho_s H} \]  

(4.5)

where \( \Delta \gamma_{Au} = \gamma_s - \gamma_l \) and \( \Delta \gamma_{C-Au} = \gamma_{Cs} - \gamma_{Cl} \). Note that the exact numerical value of \( \Delta \gamma_{C-Au} \) is not known (to the best of our knowledge), hence, the first term of the RHS of Eq. (6) (specific for this confined geometry) cannot be directly evaluated.

All three terms in the right hand side of Eq. (4.5) contribute in decreasing the solidification temperature of the particle with respect to the bulk. The first term depends on the free energy difference between the solid and the liquid phase at the interface of CNT and nanoparticle. For long particles, \( i.e. \) when the total volume \( V \) is practically equal to the volume of the cylindrical core, \( V_c = \pi LR^2 \), this term is inversely proportional to the radius of the particle \( R \). The second term (called herein II) is the contribution of the surface energy change in the two caps due to solidification and can be estimated using the experimental bulk values of gold [24]. This term is proportional to \( (aL + bR)^{-1} \) (where \( a \) and \( b \) are two constants dependent on the details of the particle geometry) and, assuming that the particle is elongated \( (L \gg R) \), shows a weak dependence on the CNT radius. Finally, the last term is due to the pressure change between the two phases.
Figure 4.4: Solidification curve as a function of particle length for all the studied cases. Markers, MD simulations: triangle CNT (20,0), circles CNT (30,0), squares CNT(40,0). Continuous lines, corresponding predictions of the second term (II) in the RHS of Eq. (4.5): dash-dotted line CNT (20,0), continuous line CNT (30,0), dashed line CNT(40,0). Inset: Solidification curve vs. number of gold atoms in the particle. Closed Squares: particles in vacuum, triangles: particles enclosed in a CNT (20,0), circles: particles enclosed in a CNT (30,0), squares: particles enclosed in a CNT (40,0).

Figure 4.4 reports the ratio \((T_s-T_0)/T_0\) (the LHS of Eq. 6) obtained by MD calculations for all the studied cases as a function of the length of the particle \(L\). In the same figure the term II of the RHS of the same equation is plotted. From a comparison of the two curves it is clear that term II captures alone quite well the behavior of the solidification point. However, in the limit of long particles, term II tends to zero, and Eq. 6 reduces to previous analytical findings that predict for the crystallization of an infinite liquid medium inside a pore a mere dependence on the radius \([27]\) or the combined effect of radius and pressure \([28]\). In our case, the presence of the free caps allows the system to relax in the axial direction of the CNT. As a consequence, we expect the pressure difference \(p_s - p_l\) to be small, particularly in the case of short particles \((L<10\text{nm})\).

Limiting our analysis to the short particle cases (and neglecting term III), a fit to the MD data leads to \(\Delta \gamma_{C-Au} = 0.015 \text{ N/m}\) for all CNT studied. We attribute this small change in \(\Delta \gamma_{C-Au}\) to the nature of the gold-gold interactions. The collective character of the cohesive forces in the gold particle renders the tendency to increase packing at the surface particularly strong. For this reason, as it has been shown in several works \([29]\), both the solid and the liquid layers (both of the (100) and of the (111) reconstructed surfaces) show a high surface density. To quantify this tendency in our case, we computed the in-shell density for the different gold layers. Though we
do not report the complete results, we point out that the outermost layer (the closest to the CNT) shows a lateral density of 15 Atoms/Å² both for the solid and for the liquid phase across the solidification transition. Thus, the CNT interacts through a pairwise Lennard-Jones potential with a close packed layer of gold in both phases. Averaged on the entire interface, the effect of this interaction should not change much across the transition. This fact, together with the observed layering effect in the liquid phase, is at the origin of the small value of $\Delta Y_{C-Au}$.

The effect of the CNT on the solidification temperature can be particularly dramatic for particles with few atoms. An example is shown in Figure 4.4: the case ($N_{Au}=534$, $n=20$) has a length of 7.2nm that corresponds to a solidification temperature of 1225K, though the particle has only 534 atoms (the corresponding solidification temperature for a spherical cluster in vacuum and with the same number of atoms is about 750K).

For longer particles ($L>10$nm) the contribution of term II in Eq. 6 to the solidification temperature depression $(T_m-T_0)/T_0$ becomes of the same order as the other two terms in Eq. 6 and MD results deviate from the continuous lines reaching a plateau. The particles enclosed in a CNT with $n=40$ show a lower solidification temperature compared to the corresponding cases at $n=30$ (see Table I), although at constant length with increasing radius a higher solidification temperature would be expected. Moreover, in both cases, $T_m$ is lower than the value predicted by the sum of term II and term I in eq. 6 with $\Delta Y_{C-Au} = 0.015$ N/m. This further reduction could be attributed to the role of the radial layering in the liquid phase. As seen above for the case at $n=40$ (Figure 4.2(b)), the layering induced by the CNT walls in central region of the liquid particle decays exponentially but is present throughout all shells. It is particularly true for long particles (and even more for long and thick ones) that the layering orders the structure, thus lowering the internal energy of the liquid phase. Even taking into account entropic effects, the free energy of the layered liquid phase is thus lower (at any temperature) than the free energy of the disordered liquid phase. This is manifested in the reduction of the solidification temperature.

Conclusions

Summarizing, in this paper the solidification and the structure of gold nanoparticles inside nanotubes have been studied using MD simulations. The results indicate the confined particle shows a radial layered structure. The solid phase of the particle is characterized by analyzing the orientational order of each layer that consists of a 2D triangular structure, which is lost after the
phase transition. On the contrary, the layered structure persists in the liquid phase even at very high temperatures. It was discussed why this could contribute to the observed additional reduction of solidification temperature for long particles. A comparison of MD calculations with a simple model indicate that the higher (compared to isolated particles) solidification temperature found for the gold nanoparticles inside CNTs is due to the cylindrical shape imposed by the CNT and the small change across the solidification transition in the interfacial tension between CNT and gold. An explanation for the latter can be the typical layered structure of the gold nanoparticles that is almost the same in the radial direction at different temperatures and states, as is the close packing of the outermost gold layer. A CNT appears to have the capability to delay and at least partially, control the solidification transition and the solidification temperature of gold nanoparticles within it. Interestingly, within in the range of tube diameters considered, the solidification temperature depends practically only on the length of the nanoparticle. Thin and long nanoparticles (nanowires) although made out of a small number of atoms can have a high solidification temperature or, in other words, particles with the same number of atoms, but enclosed in a CNT with a smaller radius have a higher solidification temperature due to the elongation effect (Figure 4.4 inset). It would be interesting to further pursue the present findings with future investigations involving ab-initio calculations and experiments.

References
8. E. Tosatti, et al., String tension and stability of magic tip-suspended nanowires, Science,
5 Thermal Diffusion of Gold Nanoparticles inside Nanotubes: A Preliminary Study

5.1 Introduction

The present chapter presents preliminary results for the thermal diffusion of gold nanoparticles inside a CNT using MD simulations and suggests directions for future work on this subject. The motivation of studying the diffusion of particles in CNTs is given by the increasing interest in nanodevices in which it can be important to carry a small quantity of mass in defined regions or to keep the position of the enclosed particle fixed for a wide range of temperatures.

To the best of our knowledge only one published numerical work studied the diffusion of nanoparticles inside a CNT [1]. Though no pressure gradient was imposed and no initial velocity of the particle center of mass was set, the particle was diffusing inside the CNT with a preferential direction. The authors supposed that this directionality of the movement was the result of periodic energy barriers inside the CNT. The speed of diffusion of the cluster as a function of temperature was following the Arrhenius law.

Regan et al. [2] were able to obtain experimentally mass transport on a CNT bundle applying an electric potential. Indium particles on the CNT surface were melting, disappearing and appearing again in another section of the tube giving birth to a global unidirectional mass transport.

Some studies on the possibility of building micropumps without moving parts can be found in recent literature (see [3, 4] and references therein). Since in microsystems surface forces become dominant, the driven diffusion of liquid droplets or bubbles inside microchannels or flat planes is obtained by changing the surface tension at the two extremities of the droplet (bubble) inducing a force gradient that leads the particle to move with a preferential direction.

A macroscopic approach can be followed to quantify the diffusion of a droplet inside a cylindrical channel due to an induced surface tension gradient. The geometrical configuration is sketched in Figure 5.1. The capillary pressure acting on one meniscus is given by the Young-Laplace equation:

\[ P_c = -\frac{2}{R} \gamma \cos \theta \]

(5.1)

where \( \gamma \) is the surface tension of the droplet and \( \theta \) is the contact angle.
At equilibrium the capillary pressures at the two sides of the droplet are the same. A pressure difference can be created by modifying the surface tension in one side. There exist different approaches to create a surface tension gradient, for example: by inducing a thermal gradient \([3]\) or applying an electric potential \([4]\) since the surface tension is linearly depending by this two factors.

![Diagram of a droplet in a channel](image)

**Figure 5.1:** Sketch of a droplet of radius \(R\) and length \(L\) inside a channel. The surface tension \(\gamma\) and the contact angle \(\theta\) are also defined.

Adopting the usual assumption (valid for many liquids) that the surface tension has a linear dependence on the temperature:

\[
\gamma = a - bT
\]

where \(a\) and \(b\) are two positive constants depending on the considered fluid.

Now, assuming that the difference between the advancing and the receding contact angle is negligible, the pressure difference applied on the droplet reads:

\[
\Delta P = -2\frac{\Delta \gamma}{R} \cos \theta
\]

with \(\Delta \gamma = \gamma_r - \gamma_l\) the difference between the surface the right side, \(\gamma_r\) and the left sides, \(\gamma_l\).

Eq. (5.3) shows that the droplet moves to regions with a smaller surface tension when \(\cos \theta\) is negative (non wetting case).

In terms of temperature gradient Eq. (5.3) can be written:

\[
\Delta P = 2b\frac{\Delta T}{R} \cos \theta
\]

\(i.e.\) a non wetting droplet will move to the hot side \([3]\).
5.2 Molecular dynamic simulation

MD simulations are conducted as reported in chapter 4. The studied CNT has a fixed chirality vector $(30,0)$ that corresponds to a radius $R_c=1.17\text{nm}$. The gold nanoparticle is composed by 775 atoms. Two different investigations are conducted to describe the diffusion of the particle. The first is starting from an equilibrated configuration of the system particle-CNT applying a thermal bath to fix the system temperature (as described in chapter 4) to study the "intrinsic" diffusion of the particle inside the CNT without any imposed pressure gradient. The second is carried out by applying a temperature gradient along the CNT through a rescaling of the velocities of the carbon atoms near the ends. In this case, no thermal bath is applied and the two CNT ends are pinned in order to dump the propagation of waves along the nanotube due to the phonon generation induced by the temperature gradient that would strongly influence the eventual particle diffusion.

5.3 Results

5.3.1 "Intrinsic" thermal diffusion

During the simulation without imposed temperature gradient the gold particle shows a random diffusion characterized by a stick-slip motion as shown in Figure 5.2.

![Figure 5.2: Axial position of the center of mass $Z_{\text{CM}}$ as a function of time for the case at 1200K. Stick phases are evidenced.](image)
The particle motion is characterized by a sticking period in which the position of the center of mass $Z_{CM}$ is oscillating around an equilibrium position (circles in Figure 5.2) and a slip period where the particle has an acceleration and moves to another equilibrium point without any preferential direction contrary to what is reported in [1], but similar to what found by Celestini [5] for a gold particle of the same dimensions of that studied herein on a flat disordered surface. This could be due to the fact that the gold lattice and the chosen CNT structure (armchair structure, i.e. the CNT chirality vector can be expressed as (n,0)) are not matching in order to promote a directional motion of the particle. One simulation with a zig-zag CNT as in the study of Hwang et al [1] (in the present work we considered the chirality vector (16,16)) is also performed to assess the influence of the CNT structure on the diffusion, but again no directional motion is observed. Unfortunately it was not possible in this preliminary study to quantify the sticking period for the long simulation time required to observe one sticking event. The same problem appears when we tried to have an estimation of the global diffusion coefficient defined as:

$$D = \lim_{t \to \infty} \frac{\langle Z_{CM}(t) - Z_0 \rangle^2}{4t} \tag{5.5}$$

with $Z_0$ is the initial position of the center of mass. No convergence on the final value of $D$ is obtained as it can be evinced by observing the axial position of the center of mass of the cluster at different temperatures in Figure 5.3.

Figure 5.3: Axial position of the center of mass $Z_{CM}$ as a function of time for different studied temperatures.
As reported in [5] the evaluation of $D$ and the sticking period requires really long calculations (of the order of 10-100 nanoseconds, *i.e.* for the considered system CNT-nanoparticle thus would lead to an average calculation time of 1-2 months per case). This can be a topic of a future research.

5.3.2 *Thermally driven diffusion*

The atomic position of the system and the relative imposed temperature gradient are shown in Figure 5.4. The final temperature gradient inside the CNT, far away from the extremities, is linear, while a parabolic profile is predicted in the regions where the velocities of the carbon atoms are rescaled to supply heat (left side) or to remove it (right side). We can consider that, due to the high phonon conduction along the CNT, its thermal inertia can be considered negligible and the linear temperature profile is immediately defined along the nanotube.

![Figure 5.4: Atomic position of a nanoparticle inside a CNT and correspondi applied temperature gradient.](image)

The target temperature of the left side $T_L$ is chosen to be the same as that of the initial equilibrium temperature of the system, while the temperature of the right side is decreased to $T_R = T_L - \Delta T_g$. 
with $\Delta T_g = 100, 200, 300, 400, 500K$. Large temperature gradients are required in order to overcome the “intrinsic” diffusion and to observe a directional movement of the particle within the simulation time. It can be questionable whether such a large temperature difference applied over such a small distance is physical, but this work is a preliminary study in order to understand the underlying basic phenomena.

As soon as the temperature gradient is applied, the particle starts to diffuse to the cold region. This result is in contrast to the macroscopic theories that, as seen above for a non-wetting fluid, are predicting an opposite behavior. We are attributing this result to the fact that decreasing the system dimensions to nanoscales the kinetic pressure becomes dominant compared to surface tension forces. Atoms in the hot side have a higher pressure compared to atoms in the cold side, resulting in a directional movement to the cold region (a phenomenon quite similar to the thermophoresis). Waves induced by the thermal gradient on the CNT surface can be another important variable affecting the particle motion.

Figure 5.5.a reports the position of the particle center of mass as a function of time for five different temperature gradients starting from 1000K. The resulting diffusion velocity is proportional to the imposed temperature gradient. Similar conclusions can be drawn by changing the initial equilibration temperature to 800K as shown in Figure 5.5.b.

It was not possible to achieve a quantitative explanation of the phenomena, because the evaluated trajectories of the center of mass of the particle are strongly dependent on the initial boundary conditions such as the equilibration temperature and initial position of the particle. A model able to predict MD results should take into account several factors such as the imposed temperature gradient, the geometry of the system, an eventual friction coefficient between CNT and the particle (which, as shown above at least in the case of $\Delta T=0$, is not simply a constant), and state whether and how the CNT surface waves can affect the diffusion.

**Conclusions**

Preliminary results for the thermal diffusion of a nanoparticle inside a CNT are presented. Two different diffusion processes are described: an “intrinsic” characterized by a random stick and slip motion and a forced obtained imposing a thermal gradient that gives directionality to the motion.
Figure 5.5: Time evolution of the position of the particle center of mass at five different imposed temperature gradients. Initial temperature: a) 1000K, b) 800K.

The motion of the particle driven by the thermal gradient is always directed toward the cold region, contrary to the predictions of the macroscopic theories based on surface energy change. The velocity of the particle inside the tube is proportional to the applied temperature gradient. The present study although clearly not conclusive regarding the understanding of the physics problem, it is giving directions to be pursued in future works.
References

Appendix

The present work is a study of surface phenomena and phase change at the nanoscale extended to three different systems: argon nanodroplets, gold nanoparticles, and gold nanoparticles enclosed in CNTs. The simulation of each one of these systems requires the implementation of different appropriate potentials and, for the case of the of the argon nanodroplet, a fast parallel code is needed in order to simulate a large number of atoms. We decided to use three different programs, one for each topic of this work:

1. A parallel program for the simulation of Lennard-Jones fluids [1] (Chapter II),
2. A serial program in which the “glue” model is implemented for the simulation of gold [2, 3] (Chapter III), and
3. The program FASTTUBE [4] developed in the Institute of Computational Science (ICOS) at ETH Zurich for the simulation of CNTs.

The latter program was herein modified by implementing the “glue” model to be able to simulate gold nanoparticles enclosed in CNTs (Chapters IV and V).

Though these programs are widely used and tested (see for example [1, 3, 4]), we tested them again in the context of this dissertation by comparing the obtained thermodynamic properties with previous data (numerical, analytical and experimental) found in literature. The time steps are chosen for the different cases in order to ensure that the total energy of the system is conserved when no thermal bath is applied.

Some comments need to be given for the simulation of the Argon nanodroplet. Simulations are performed with the typical time step used for Lennard-Jones calculations ($\Delta t^*=0.05$ in Argon units, see for details chapter II) during the equilibration and the time period in which data are collected in order to obtain the average thermodynamic parameters. A time step independence test is performed for the non-equilibrium calculations. The deformation transient is studied with two different time steps: $\Delta t^*=0.025$ and $\Delta t^*=0.05$ (Figure 1). As shown in Figure 1 the two time steps are leading to the same behavior for the initial transient and the entire prolate phase, but some differences are evidenced during the oblate phase. Finally the deformation transient calculations are performed with the smaller time step for all the studied cases.
Figure 1: Droplet deformation transient for two different time step used for the MD simulation

Figure 2: Comparison between the experimental surface tension of Argon and prediction obtained with MD simulations at different cutoff distances and different potentials (ST=Spherically Truncated, STS=Spherically Truncated and Shifted) [5]. Open circles, present work. (NB: The values found in literature are obtained for a planar interface while the values reported in the present work are obtained for a spherical droplet)

Another peculiar characteristic of this study is the choice of the cutoff distance of $4\sigma$ (the typical values usually used in MD calculations are discrete: $2.5\sigma$, $4.4\sigma$, $5.5\sigma$ etc., see Figure 2) . This
value is suggested by the study of Trokhymchuk and Alejandre [5]. As they report (Chapter II) the surface tension is very sensitive to the choice of the cutoff distance. The values of the surface tension of a planar interface reported in [5] for different authors and different cutoff distances are summarized in Figure 2. In the same picture the corresponding experimental values for Argon are also reported. The surface tension is underestimated for the smallest cutoff distance (2.5\(\sigma\)) while is overestimated for higher cutoff distances. As the authors observe in [5], an appropriate choice of the cutoff distance could predict the experimental values of surface tension. The findings of the present work are also reported in Figure 2 showing that the choice of a value of 4 \(\sigma\) leads to a good estimate of the experimental surface tension of Argon.

References

CURRICULUM VITAE

Name: Salvatore Arcidiacono
Date of birth: 9 July 1974
Birthplace: Palermo, Italy
Nationality: Italian
Marital Status: Single
Private address: Elfenweg 7, 8038 Zurich Switzerland
Residence permit B
Phone number: +41 043 243 18 78 Mobile: +41 76 52 53 901
E-mail: salvatore.arcidiacono@psi.ch

Education

Diploma of Nuclear Engineering
University of Palermo, Palermo, Italy
Final exam grade: 110 summa cum laude (best 110 - sufficient 66)
Thesis title: Convezione Naturale in Metalli Liquidi con Generazione Interna di Potenza in Cavità Rettangolari (Natural Convection in Liquid Metals in Internally Heated Rectangular Enclosures)

1/2001 – present (expected end 09/2004)
Ph.D. Student in Institute of Energy Technology, ETH Zurich
Thesis title: Surface Phenomena and Phase Change in Nanoparticles and nanodroplets a Molecular Dynamics Study

Supervisor: - Prof. Dr. D. Poulikakos
Attended Courses at ETH: - Energy Conversion and Transport in Biosystems
- Thermodynamics and Energy Conversion in Micro- and Nanotechnologies
- Numerical Simulations Using Particles
- Bioinspired Computation and Optimization

Employment

3/2002 – 3/2003 Teaching Assistant Institute of Energy Technology, ETH Zurich
Task: Teaching and supervision of students in Thermodynamics I and II

Informatics

Known operating systems: Unix, Linux, Windows
Programming languages: Fortran 77/95, Visual Basic
Parallel programming using MPI libraries
Some Experience in setting up Linux Clusters

Languages

Italian: mother tongue
English: good spoken and written
German: basic knowledge
Publications


S. Arcidiacono, I. Di Piazza and M. Ciofalo, Convezione Naturale a Basso Numero di Prandtl in Cavità Rettangolari con Generazione Interna di Potenza: Risultati Computazionali per \( AR=4, 1 e 0.25 \), Dipartimento di Ingegneria Nucleare dell'Università di Palermo, Internal Report, 2001

Conferences


S. Arcidiacono, I. Di Piazza and M. Ciofalo, Heat Transfer in Low-Prandtl Number Free Convection from Internally Heated Rectangular Enclosures, 16th UIIT National Heat Transfer Conference, Cernobbio, Italy, 2000