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Sound wave channelling in near-critical sulfur hexafluoride (SF$_6$)

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Strong density and speed of sound gradients exist in fluids near their liquid-vapor critical point under gravity. The speed of sound has an increasingly sharp minimum and acoustic waves are channelled within a layer of fluid. Geometrical acoustic calculations are presented for different isothermal fluid columns of sulfur hexafluoride (SF$_6$) under gravity using a semiempirical crossover equation of state. More than 40% of the emitted acoustic energy is channelled within a 20 mm high duct at 1 mK above the critical temperature. It is shown how, by changes in temperature, frequency, and gravitational strength, the governing length scales (wavelength, radius of ray curvature, and correlation length of the critical density fluctuations) can be varied. Near-critical fluids allow table-top sound channel experiments. © 2004 Acoustical Society of America.

NOMENCLATURE

Fluid and equation of state parameters

- $a$: speed of sound
- $A$: Helmholtz free energy
- $A_j$: parameters for analytic background of Helmholtz free energy ($j=0,...,4$); see Table I
- $c, c_r, c_t, d_i$: scaling field coefficients; see Table I
- $C_v, C_p$: specific heats at constant volume and pressure
- $M$: densitylike order parameter; defined by Eq. (6)
- $p$: pressure
- $t$: temperaturelike order parameter; defined by Eq. (5)
- $T$: Temperature
- $\tilde{u}$: crossover parameter; see Table I
- $u^*$: universal fixed-point coupling constant; see Table I
- $V$: volume
- $Y$: crossover function; defined by Eqs. (9) and (10)
- $T_c, \rho_c, p_c$: temperature, density, and pressure at liquid-vapor critical point; see Table I
- $\chi$: susceptibility
- $\kappa$: proportional to fluctuation-induced portion of the inverse correlation length; defined by Eq. (10)
- $\mu$: specific chemical potential
- $\xi$: correlation length of critical density fluctuations
- $\rho$: density
- $\Lambda$: dimensionless cutoff wave number; see Table I
- $\alpha_c, \nu_c, \gamma_c, \eta_c$: critical exponents; see Table I
- $a_0, a_6, a_{14}, a_{52}$: parameters from classical mean-field theory; see Table I
- $\Delta_S, \Delta_A$: critical exponents of symmetric and asymmetric correction terms; see Table I
- $\tilde{\mu}_j$: parameters for analytic background of chemical potential ($j=0,...,4$); see Table I
- $\bar{T}, \bar{D}, \bar{U}, \bar{V}, \bar{K}$: rescaling functions, defined by Eq. (8)

\textbf{Acoustics parameters}

- $f$: frequency of acoustic source
- $g$: constant of gravity ($=9.81$ m/s$^2$)
- $h$: height of duct ($=20$ mm)
- $\hat{n}$: unit vector perpendicular to wavefront
- $R, R^+, R^-$: range of loop, range of upper/lower cycle section
- $r$: radius of curvature of rays
- $r_{\text{min}}$: defined by Eq. (16)
- $s=(s_x,s_y,s_z)$: wave slowness vector ($=\hat{n}/a$ for fluid at rest)
- $t$: time
- $x=(x,y,z)$: coordinate vector
- $Y$: crossover function; defined by Eqs. (9) and (10)
- $\eta$: waveguide efficiency
- $\lambda$: wavelength of acoustic waves ($=a/f$)
- $\tau, \tau^+, \tau^-$: propagation times associated with $R, R^+$, and $R^-$

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I. INTRODUCTION

Bending of waves occurs when the gradient of the propagation speed in the direction perpendicular to the direction of propagation is nonzero. In this case, the wave bends in the direction of smaller propagation speeds. This is observed at interfaces as well as for smooth gradients. Consider, for example, optical lenses made from glass of smoothly varying index of refraction or the phenomenon of sound shadows after big explosions. Assuming that the speed of wave propagation only varies in one direction and that it has a local minimum, rays can be channelled within a finite material layer. If no such minimum exists, but if the propagation speed decreases towards an interface (e.g., water surface) then the waves are reflected at the interface and channelling is possible, where the interface represents one boundary of the wave channel. Wave channelling purely by means of reflection (e.g., in an optical fiber) is also possible. Waveguides involving the reflection from an interface are not considered as wave channelling devices for the purpose of this work. Interest in sound wave channelling has mostly focused on underwater sound propagation in the context of long-range communication, submarine detection and detection avoidance, and global temperature sounding. Peder sen et al. examine a range of sound speed profiles, both generic and from measured data in the Pacific.

Critical phenomena in fluids, i.e., the behavior of fluids in the vicinity of the vapor-liquid critical point, have gained a lot of interest in physics and thermodynamics. Near the critical point, many thermodynamic properties, such as the isothermal compressibility, diverge. At the same time, the correlation length of the density fluctuations, which normally is microscopic, becomes macroscopic, causing the phenomenon of critical opalescence when the correlation length becomes comparable to the wavelength of visible light. Since the isothermal compressibility tends to infinity when approaching the critical point, the fluid collapses under its own weight in the presence of gravity. Very steep density gradients over short vertical distances (10% over 1 mm; also see Fig. 1) result. Along with the density profile goes a variation of the speed of sound. An increasingly sharp minimum is observed near the point where the density equals the critical density as one approaches the critical temperature [Fig. 2(a)].

In the present work, numerical results are presented for SF₆. This choice is motivated by several factors: First, by the availability of a suitable equation of state, second, by the experimentally convenient location of the critical point (see Table I), and last by the availability of SF₆ in good purities due to its applications in the semiconductor industry. Xenon and CO₂ are similarly popular for experiments with near-critical fluids, but adequate equations of state for these fluids are not available to date.

II. SETUP AND PROCEDURE

A. Setup

A duct of height \( h = 20 \text{ mm} \) (\( z = -10 \ldots +10 \text{ mm} \)) is considered, which is filled with near-critical, isothermal, pure sulfur hexafluoride (SF₆). Due to gravity and the large compressibility, a density and consequently a speed of sound profile develops in the duct. By choosing the average density in the duct such that \( a(+10 \text{ mm}) = a(-10 \text{ mm}) \) and by placing the acoustic point source at the sound speed minimum, the waveguide efficiency is maximized. The walls of the test duct are assumed to be perfectly absorbing, i.e., wave reflections are neglected.

B. Equation of state

Critical phenomena are not captured by analytical equations of state. Wyczalkowska et al. propose a semiempirical equation of state for SF₆, which shows the correct singular behavior near the critical point (including the correct critical exponents) and crosses over smoothly to regular thermodynamics.
The Helmholtz free energy and the chemical potential are obtained from a fit to experimental data. They are given by

\[ \Delta A = \Delta A_0 + \rho \mu_0 (\Delta T) + \sum_{j=0}^{4} \Delta A_j (\Delta T)^j, \]

where \( \Delta \tilde{\rho} = \tilde{\rho} - 1 \) and \( \Delta \tilde{T} = \tilde{T} + 1 \). The constants \( \Delta A_j \) and \( \mu_j \) are obtained from a fit to experimental data. They are given in Table I, which also contains the parameters which will be introduced subsequently.

The critical part of the Helmholtz free energy is given by

\[ \Delta \tilde{A} = \Delta \tilde{A}_0 - c \tilde{\rho} \frac{\partial \Delta \tilde{A}}{\partial \tilde{\rho}} \bigg|_{M}, \]

where

\[ t = c_1 \Delta \tilde{T} + c \frac{\partial \Delta \tilde{A}}{\partial \tilde{T}} \bigg|_{M}, \]

are temperaturlike and densitylike order parameters and

\[ M = c_\rho (\Delta \tilde{\rho} - d_1 \Delta \tilde{T}) + c_\Delta \frac{\partial \Delta \tilde{A}}{\partial \tilde{T}} \bigg|_{M}, \]

are relevant for the present work are summarized here. For a more detailed derivation, the reader is referred to Ref. 9.

### Table I. Parameters for equation of state

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>( T_c )</td>
<td>982 J</td>
</tr>
<tr>
<td>( p_c )</td>
<td>742 kg/m³</td>
</tr>
<tr>
<td>( \rho_c )</td>
<td>3.7545 MPa</td>
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### Critical point

<table>
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<td>( p_c )</td>
<td>742 kg/m³</td>
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<tr>
<td>( \rho_c )</td>
<td>3.7545 MPa</td>
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### Cross-over parameters

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<td>( \Lambda )</td>
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### Scaling field parameters

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### Classical parameters

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### Critical exponents

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<td>( \Delta_A)</td>
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<td>( u^* )</td>
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### Equation of state and caloric background parameters

<table>
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<td>( j )</td>
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<tr>
<td>( \tilde{\rho}_0 )</td>
<td>N/A</td>
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<tr>
<td>( \tilde{A}_0 )</td>
<td>N/A</td>
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</table>

The pressure and the speed of sound are related to the chemical potential and the Helmholtz free energy by

\[ \tilde{p} = \tilde{\rho} \tilde{\mu} - \tilde{\rho}_0, \]

\[ \tilde{a} = \left( \frac{\tilde{p}}{\tilde{C}_v} \right)^{\frac{1}{2}}, \]

with

\[ \tilde{C}_v = \frac{\tilde{C}_v}{T^2} \left( \tilde{p} - T \frac{\partial \tilde{\rho}}{\partial T} \right)^2. \]
of the acoustic waves, this length scale has to be much larger than the wavelength gradient. In order for the geometrical limit to be applicable, which is observed for a ray perpendicular to the sound speed gradient. For reference, the minimum vertical distance over which the speed of sound changes by 1% is shown.

C. Geometrical acoustics

Geometrical acoustics assumes that the radius of curvature of rays is much larger than the wavelength and that the amplitude does not change significantly over the same length scale. These assumptions simplify the general solution of the wave equation. For rays in an inhomogeneous medium at rest, one finds
\[
\frac{ds}{dt} = -\frac{1}{a} \nabla a \quad \text{and} \quad \frac{dx}{dt} = a^2 s,
\]
where \( s = (s_x, s_y, s_z) = \hat{a}/a \) denotes the wave slowness and \( a \) is the local speed of sound.

For a given temperature, the smallest possible radius of curvature of a ray is
\[
r_{\min} = \min_{|z| \leq 10 \text{ mm}} \left\{ \frac{a}{da/dz} \right\},
\]
which is observed for a ray perpendicular to the sound speed gradient. In order for the geometrical limit to be applicable, this length scale has to be much larger than the wavelength of the acoustic waves, \( r_{\min} \gg \lambda \). The correlation length of the critical density fluctuations on the critical isochore is
\[
\xi = \xi_0 \left| \frac{T}{T_c} - 1 \right|^{-\nu}, \quad \rho = \rho_c, \quad T > T_c
\]
with \( \xi_0 = 0.19 \text{ nm} \) and \( \nu_c = 0.630 \). This neglects the limiting effect of gravity. When \( \lambda \gg \xi \), then the diffraction of the acoustic waves at the critical fluctuations is negligible. The wavelength can be adjusted by varying the driving frequency of the transducer. Figure 3 shows the characteristic length scales for the case \( f = 1 \text{ MHz} \). The wavelength satisfies both conditions, namely \( \lambda \gg \xi \) and \( \lambda > r_{\min} \). Mueller et al. and examine ultrasonic attenuation in near-critical xenon. Kogan et al. present experimental results on critical attenuation

and dispersion in He-3 and He-4. No such data exists for sulfur hexafluoride. Onuki reviews some theoretical concepts of critical sound attenuation. It is assumed that attenuation does not invalidate the assumption of ray acoustics.

D. Numerical integration of the ray equations

Density profiles are calculated iteratively for a range of temperatures. Initially, they span a range of \( z \) values, which is much larger than the duct height. A uniform density is used as starting value, from which a vertical pressure distribution is obtained by integration in \( z \) direction. An improved density profile then follows from the equation of state. Finally, a 20 mm section of the profile is extracted, for which \( a(-10 \text{ mm}) = a(+10 \text{ mm}) \). Integrating the densities over this section yields the average density \( \bar{\rho} \).

Given speed of sound profiles, the ray equations (15) are integrated numerically using a fifth order Runge–Kutta scheme (Dormand–Prince pair). Initial conditions
\[
(x_0, 0, z_0) \quad \text{and} \quad (\cos \alpha_0/a(z_0), 0, \sin \alpha_0/a(z_0))
\]
are used to calculate rays originating at different initial ray angles \( \alpha_0 \) from a source at \( z_0 \), the location of the sound speed minimum. Figure 4 shows a few representative rays for the case \( T - T_c = 10 \text{ mK} \).

III. RESULTS

FIG. 3. Relevant characteristic length scales for an acoustic source with \( f = 1 \text{ MHz} \) located in an isothermal fluid column (height \( h = 20 \text{ mm} \)) of near-critical SF\(_6\) at the sound speed minimum. The acoustic wavelength is at least two orders of magnitude larger than the correlation length of the critical fluctuations and at least one order smaller than the minimum ray bending radius. For reference, the minimum vertical distance over which the speed of sound changes by 1% is shown.

FIG. 4. Rays emanating with different initial ray angles from an acoustic point source located at the sound speed minimum in isothermal, near-critical SF\(_6\) at \( T - T_c = 10 \text{ mK} \) under gravity. Reflections from the duct boundaries are not considered.

total density variation is limited to an increasingly narrow region. For $T - T_c = 1 \text{ mK}$, for example, the density varies by 10% over 1 mm.

Given a temperature, the vertical shift of the density profiles in Fig. 1 is controlled by the average density $\bar{\rho}$ in the duct. It is found from the condition that $a(10 \text{ mm}) = a(10 + 10 \text{ mm})$. The symbols in Fig. 1 mark the results for $\bar{\rho}$ and the location where $\bar{\rho} = \rho$. In an experiment one would fill the test section with the appropriate average density and then equilibrate the duct at the desired temperature, which can take hours or even days, depending on the temperature and the size of the fluid volume.

The sound speed profiles, which provide the vertical reference for the density profiles, are shown in Fig. 2(a) for a selection of temperatures. The sound speeds generally increase with increasing temperature and an increasingly sharp minimum develops as one approaches the critical temperature from above. As required, the speeds of sound at the top and bottom of the duct are identical. Due to the local properties of the sound speed profile (no local maxima), this places the local sound speed minimum within the duct. The dashed line connects the location of the sound speed minima. Since the acoustic point source is located at the sound speed minimum, its location is used as one of the initial conditions for Eqs. (15) and is therefore denoted by $z_0$. The sound speed profiles are not symmetric with respect to the minima, which are thus off center. For $T - T_c = 1 \text{ mK}$, for example, the sound speed minimum is located at $z = +7 \text{ mm}$. For larger reduced temperatures, the location of the minimum approaches the center line. The inset in Fig. 2(a) shows a magnification of the sound speed minimum for $T - T_c = 1 \text{ mK}$.

The minimum is not a cusp, but smooth and numerically well resolved. Figure 2(b) shows the speed of sound variation vs depth below MSL at a point in the Pacific Ocean for comparison. The horizontal scales and panel sizes in Figs. 2(a) and (b) are chosen such that the relative variation of the speed of sound is preserved. The total variation is approximately 4% over 4700 m. The same variation is achieved over 20 mm in near-critical SF$_6$ at a temperature of $T - T_c = 31 \text{ mK}$.

Figure 3 shows plots of the relevant length scales. The acoustic wavelength (assuming a frequency of 1 MHz) increases by 40% between $T - T_c = 1 \text{ K}$ and 1 mK. The correlation length of the critical density fluctuation $\xi$ and the minimum ray bending radius $r_{\text{min}}$ depend more strongly on the temperature. $\xi$ increases by almost two orders of magnitude as one approaches $T_c$. Over the same range of temperatures, $r_{\text{min}}$ decreases by more than six orders of magnitude. For all temperatures under consideration, the requirements for geometrical acoustics to be applicable, $\xi<\lambda$ and $r_{\text{min}}>\lambda$, is satisfied. Also plotted in Fig. 3 is the minimum vertical distance over which the speed of sound varies by 1%.

Some example results of the numerically integrated ray equations are shown in Fig. 4. The temperature is $T - T_c = 10 \text{ mK}$. For initial angles $\alpha_{\text{0,min}} \leq \alpha_0 \leq \alpha_{\text{0,max}}$, rays can propagate within $|z| \leq 10 \text{ mm}$. Because $a(10 \text{ mm}) = a(-10 \text{ mm})$, $\alpha_{\text{0,max}} = -\alpha_{\text{0,min}}$ by construction. Rays with $|\alpha_0| > \alpha_{\text{0,max}}$ hit the upper or lower duct boundary as shown in Fig. 4 for the ray with $\alpha_0 = -30^\circ$. For channelled rays, the length of a ray loop is referred to as range $R = R^+ + R^-$, where $R^+$ and $R^-$ are the ranges of the ray loop above and below $z_0$, respectively. The propagation times over one loop is denoted by $\tau$. Like the sound speed profiles, the waves are not symmetric with respect to $z = z_0$. By construction, however, the range is independent of the sign of $\alpha_0$.

Snell’s law applied to the current example is

$$\cos \alpha_{\text{0,max}} = \frac{a_{\text{min}}}{a_{\text{max}}} = \frac{a(z_0)}{a(10 \text{ mm})}.$$  

The maximum initial ray angles as function of the temperature are plotted in Fig. 5. The fraction of acoustic energy channelled within the duct out of the total emitted energy is the waveguide efficiency $\eta$. It is

$$\eta = \frac{2\alpha_{\text{0,max}}}{180^\circ}.$$

The scale for the waveguide efficiency is plotted in the secondary vertical axis on the right of Fig. 5. $\alpha_{\text{0,max}}$ does not seem to level off as one approaches $T_c$. At a reduced temperature of 1 mK, $\alpha_{\text{0,max}} = 36.8^\circ$. This value drops to 25.5° and 4.55° for $T - T_c = 10 \text{ mK}$ and 100 mK, respectively. Corresponding to $\alpha_{\text{0,max}}(T)$ is a range $R_{\text{max}}$ and a run time of the acoustic waves over one loop $\tau_{\text{max}}$. Some typical values are given in Fig. 5. Initially the range $R_{\text{max}}$ increases very slowly with increasing reduced temperature. It only doubles (from 245 mm to 500 mm) over almost two orders of magnitude in $T - T_c$ (1 mK to 70 mK), but doubles again between 70 mK and 110 mK.

IV. CONCLUSIONS

The effect of dispersion, which is observed near the critical point, has been neglected in the present analysis. The definition of the speed of sound is the limit for zero frequency, which is the speed of sound given by the equation of state. The sound speed profiles for higher frequencies might therefore be different from those shown in Fig. 2. Dy-
namic critical phenomena are an active area of research and an equation of state providing the speed of sound as function of the thermodynamic variables as well as frequency is not yet available. Likewise, and for the same reason, attenuation has not been considered. The results presented should therefore only be taken as qualitative rather than quantitative. The form of the variations in density and the sound speed along isotherms near the critical point is universal. Other fluids will show the same qualitative behavior. Intramolecular vibrations strongly influence the dispersion relationship such that the speed of sound profiles at a given frequency is fluid dependent.

From Fig. 3 one sees that the three characteristic length scales (wavelength, correlation length, and ray bending radius) become comparable for even smaller reduced temperatures. Interactions between acoustic waves and the critical density fluctuation become significant for $\lambda/\xi = O(1)$. A smooth transition away from geometrical acoustics can be observed for $r/\lambda = O(1)$. The length scales can be controlled by the temperature, gravity, and frequency. These effects are summarized qualitatively in Table II. Increasing the temperature, for example, and leaving all other parameters unchanged results (a) in a larger wavelength, because the speed of sound increases with increasing temperature, (b) in a larger radius of curvature through smaller speed of sound gradients, and (c) in a reduced correlation length by being further away from the critical point. The frequency, on the other hand, primarily only impacts the wavelength. Its influence on $r$ by means of dispersion (frequency-dependent sound speed profiles) is not clear. The formation of the density gradients is driven by gravity. In a reduced-gravity environment, these profiles are more uniform and the radius of curvature of the rays is thus larger. Furthermore, very close to the critical point gravity limits the correlation length to approximately 2 $\mu$m on earth, but much larger values can be achieved in low-$g$ experiments.

The combination of the two areas of research, wave channelling and critical phenomena, makes it possible to study the former using table-top facilities. Acoustics, on the other hand, can be used to study critical phenomena. While not discussed here, it can be shown that caustics exist for the sound speed profiles shown in Fig. 2. Acoustics could thus be used to introduce local energy disturbances into near-critical fluids. Another application is to use acoustic wave propagation to study the statistics of the critical density and sound speed fluctuations, e.g., as outlined by Ostashev for fluids with random inhomogeneities. Analogous to other tomographic techniques, an experimental setup with several ultrasonic transducers and receivers could yield the sound speed profile within a test section by means of an appropriate reconstruction algorithm.

**TABLE II.** The three characteristic length scales (wavelength $\lambda$, radius of curvature $r$, and correlation length $\xi$) are influenced by the reduced temperature $T-T_\text{c}$, the frequency $f$, and the level of gravity $g$.

<table>
<thead>
<tr>
<th>Reduced temperature $T-T_\text{c}$</th>
<th>Wavelength $\lambda$</th>
<th>Radius of curvature $r$</th>
<th>Correlation length $\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency $f$</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
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<tr>
<td>Gravity $g$</td>
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