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Finite-size effects in thermodynamics: Negative compressibility and global instability in two-phase systems

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Abstract...

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1. INTRODUCTION

Positivity of the compressibility, i.e., an increase of the internal pressure of a body as a result of a decrease of its volume, is intuitively obvious and is proved in the first chapters of textbooks on thermodynamics [1]. The classical proof of the positivity of the compressibility, however, does not account for energy of interfaces which are present if the system consists of more than one phase. The importance of the surface energy becomes nonetheless obvious if one considers a phase of smaller and smaller size $R$ in which the energy density (that is the internal pressure) $\alpha/R$ diverges ($\alpha$ is the surface tension). We will show below that the presence of a piece of surface, e.g., solid, merged in the bulk of another phase, e.g., liquid, results in several unusual effects such as negative compressibility of the whole system and global instability of such two-phase system.

The experimental observation of the finite-size effects in usual systems is quite problematic because of an extremely long relaxation time needed for thermodynamic equilibrium to settle down. To exemplify, the relaxation time of a cubic long relaxation time needed for thermodynamic equilibrium with finite surface energy and weak interactions is quite problematic because of an extremely large enough size, which is proven by the experiment. Crystal seeds that are too small spontaneously either melt completely or grow to a large enough size.

II. COMPRESSIBILITY OF TWO-PHASE SYSTEM

Without loss of generality, we may consider a small seed of solid merged into liquid. For simplicity, we neglect the anisotropy of solid as well as the gravity (the latter assumption is always valid if the size $R$ of the seed is smaller than the capillary length which is about 1 mm for the solid-liquid interface of helium). In equilibrium, the solid forms a sphere with radius $R$ surrounded by the liquid. For the finite curvature of the solid surface, the pressure in the liquid, $P_L$, and in the solid, $P_S$, are shifted up with respect to the equilibrium melting pressure for a flat surface, $P_0$, to satisfy the conditions of force balance at the interface, $P_S = P_L + 2\alpha/R$, and the thermodynamic equilibrium, $\mu_S(P_S) = \mu_L(P_L) = \mu_S(P_0) + (P_S - P_0)/\rho_S = \mu_L(P_0) = \mu_L(P_L) = \mu_L(P_0) + (P_L - P_0)/\rho_L$ ($\mu$ is the chemical potential per unit mass) [3].

The internal pressure of a body as a result of a decrease of its volume, is intuitively obvious and is proved in the first chapters of textbooks on thermodynamics [1]. The classical proof of the positivity of the compressibility, i.e., an increase of the internal pressure of a body as a result of a decrease of its volume, is intuitively obvious and is proved in the first chapters of textbooks on thermodynamics [1].

We have measured the equilibrium melting pressure of helium-4 as a function of the crystal size. Negative compressibility of a liquid with an inclusion of solid seed is predicted theoretically and verified experimentally with helium-4 crystal-superfluid system at 0.15 K. This two-phase system is shown to be stable if the crystal size is large enough, which is proven by the experiment. Crystal seeds that are too small spontaneously either melt completely or grow to a large enough size.
TABLE I. Comparison of the product of the surface tension and the compressibility, \( \alpha \beta \), in different systems with the theoretical estimation, \( a/6 \) (see text). \( \beta \) is given for denser phase.

<table>
<thead>
<tr>
<th>System</th>
<th>( \alpha ) [erg/cm(^2)]</th>
<th>( \beta ) [cm(^3)/erg]</th>
<th>( \alpha \times \beta ) [(\AA)]</th>
<th>( a/6 ) [(\AA)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water liquid-vapour, NC</td>
<td>70</td>
<td>(4.4 \times 10^{-11})</td>
<td>0.31</td>
<td>0.52</td>
</tr>
<tr>
<td>Methanol liquid-vapour, NC</td>
<td>20</td>
<td>(1.0 \times 10^{-10})</td>
<td>0.20</td>
<td>0.68</td>
</tr>
<tr>
<td>Mercury liquid-vapour, NC</td>
<td>500</td>
<td>(3.2 \times 10^{-12})</td>
<td>0.16</td>
<td>0.48</td>
</tr>
<tr>
<td>Helium-4 solid-liquid ( T &lt; 2 ) K</td>
<td>0.2</td>
<td>(5.5 \times 10^{-9})</td>
<td>0.11</td>
<td>0.52</td>
</tr>
</tbody>
</table>

III. STABILITY OF TWO-PHASE SYSTEM

In the following we consider a stability of the two-phase system, i.e., sustainability with respect to a small change of the radius \( R \) of the solid. The change \( \delta R \) of the radius results in the change of pressures \( \delta P_L \) in the solid and \( \delta P_S \) in the liquid which are connected by the mechanical force balance, \( \delta P_L = - (2\alpha/\rho L^2) \delta R \). The condition of the conservation of mass \( \Delta \rho_S \delta V_L = V_L \delta P_S + (V - V_L) \delta P_L \) gives

\[
\delta P_L = - \frac{4\pi R \Delta \rho_S}{[V \beta_L + V_S (\beta_S - \beta_L \rho_L)]} \delta R,
\]

and the corresponding change of chemical potential difference between the phases is

\[
\delta \mu_L - \delta \mu_S = \frac{\delta P_L}{\rho_L} - \frac{\delta P_S}{\rho_S} = \frac{\Delta \rho_S}{\rho_S \rho_L} + \frac{2\alpha}{\rho_S R^2} \delta R = \left( -4\pi R \frac{\Delta \rho_S}{V} - \frac{(2/3) \alpha \beta S}{\Delta \rho_S} \right) \frac{\delta R}{[V \beta_L + V_S (\beta_S - \beta_L \rho_L)]} + \frac{2\alpha}{\rho_S R^2} \delta R. \tag{9}
\]

As shown in Sec. I, the ratio \( \alpha \beta / R \) is always much smaller than unity, and, with the assumption \( V_S \ll V \), the exact Eq. (10) simplifies to

\[
R^2 \frac{\partial \Delta \mu_{LS}}{\partial R} = \frac{2\alpha}{\rho_S} - \frac{3\Delta \rho_S V_S}{\beta_L \rho_L} \frac{\delta R}{V}. \tag{11}
\]

The derivative \( \partial \Delta \mu_{LS} / \partial R \) is positive if the volume \( V_S \) of the solid is relatively small. This means global instability of the solid seed: a random decrease of its size results in the undersaturation \( \Delta \mu_{LS} < 0 \), and the crystal will continue melting and disappears completely. In the opposite case of small increase of the size, \( \Delta \mu_{LS} > 0 \), and the crystal will continue growing until its size reaches the critical value \( R_c = (\rho_L / \Delta \rho_S)^{1/2} (\alpha \beta V / \pi^2)^{1/4} \) at which the derivative Eq. (11) changes sign to negative, and the system becomes stable. For the solid-liquid helium-4 sample of 1 cm size, the critical radius \( R_c \) is about 0.1 mm.

Finally, let us consider the conditions for homogeneous nucleation of a solid in the case of a finite-size sample. In the infinite liquid the critical radius for 3D-nucleation is determined by the competition between the surface energy \( 4\pi R^2 \alpha \) and the oversaturation \((4/3)\pi R^3 (\Delta \mu_L - \Delta \mu_S)\):

\[
R_{3D} = \left( \frac{2\alpha}{\rho_L} / \Delta \rho_S \right)^{1/2} (\alpha \beta V / 2\pi)^{1/4} \tag{12}
\]

If the volume \( V \) of the liquid is finite, one should account for the compressibility of the liquid. After the nucleation of a solid seed with radius \( R \), the chemical potential difference between liquid and solid phases becomes

\[
\mu_L - \mu_S = \frac{\Delta \rho_S}{\rho_S \rho_L} \Delta P_L + \frac{\Delta \rho_S}{\rho_S \rho_L} \delta P_L - \frac{2\alpha}{\rho_S R^2}. \tag{12}
\]
where \( \Delta P_L = P_L^0 - P_0 \) is the initial oversaturation of the liquid, and \( \delta P_L = P_L(R) - P_L^0 \) is the change of the pressure in the liquid due to the formation of the solid seed. The change \( \delta P_L = P_L(R) - P_L^0 \) is found from the mass conservation relation, \( \rho_L \delta V_l + V_l \delta \rho_L + \rho_S \delta V_S = 0: \)

\[
\delta P_L = -\frac{4\pi R^3 \Delta \rho_{SL}}{\rho_B \rho_L}. \tag{13}
\]

By substituting Eq. (13) into Eq. (12) we find the chemical potential difference between phases after the nucleation,

\[
\mu_L - \mu_S = \frac{\Delta \rho_{SL}}{\rho_S \rho_L} \Delta P_L = \frac{4\pi R^3}{3} \frac{\Delta \rho_{SL}^2}{\rho_B \rho_L \rho_S^2} R - \frac{2\alpha}{\rho_S} R. \tag{14}
\]

Figure 1 displays a sketch of the dependence in Eq. (14). The finiteness of the volume \( V \) shifts the critical radius \( R_{3D} \) to a larger value \( R_1 \). This radius, \( R_1 \), however, corresponds to unstable configuration: it will either melt or grow further; but in contrast to the infinite liquid where the seed grows infinitely large (upper curve), there is finite radius \( R_2 \) at which the configuration is stable. The decrease of the initial oversaturation \( \Delta P_L \) brings \( R_1 \) and \( R_2 \) closer together, and at \( \Delta P_{L,c} = (8/3)(2\pi^3 \rho_L^2 / \beta_L \Delta \rho_{SL}^2 V) \) both radii coincide with the critical radius of global instability \( R_c \) derived above, \( R_{1,\text{max}} = R_{2,\text{min}} = R_c = (\rho_L^2 \alpha / V / 2\pi \Delta \rho_{SL}^2)^{1/3} \approx 0.1 \text{ mm} \) for \( V \sim 1 \text{ cm}^3 \). The corresponding shift of the equilibrium melting pressure amounts to \( \approx 0.5 \text{ mbar} \), and no crystal can be created at lower overpressures. This conclusion agrees very well with all available measurements data of the overpressure needed to nucleate a crystal. For example, in the experiments by Ruutu et al. in Helsinki [4,5] the nucleation occurred at overpressures 2.8...3.5 mbar, while in the \(^4\text{He} \) crystal experiments by Tspelein et al. [6] at 2.5 mbar, and in the experiments in Lancaster at 2...3 mbar [7]; in this work, we have observed 3...15 mbar.

IV. THERMAL EFFECTS AND RELAXATION TIME

Growing or melting of a solid is associated with the release of the latent heat \( \mathcal{L} \) on the interface. Due to the finite thermal conductivity \( \kappa \) and due to the Kapitza thermal boundary resistance \( R_K \), there will be thermal gradients in the system, \( \delta T_k = v L \rho_S \kappa / \delta T_K \) and \( \delta T_K = v L \rho_S R_K \), respectively. A typical velocity \( v \) of the helium solid-liquid interface in our experiments was about \( 10^{-5} \text{ m/s} \), and the latent heat at the temperature of the experiment, of \( 0.15 \text{ K} \), is \( \mathcal{L} = 3.6 \text{ ml/kg} \) [8]. Using \( \kappa = 3 \times 10^3 \text{ W/(m K)} \) [9] we find \( \delta T_k = 2 \times 10^{-11} \text{ K} \), which is negligible. The Kapitza resistance \( R_K = 0.78 \text{ J/(m}^2\text{K}) \) [10] gives \( \delta T_K \approx 5 \times 10^{-5} \text{ K} \). The temperature change \( \delta T_K \) contributes a term \( \delta \mathcal{S} T_K \) to the variation \( \Delta \mu \) of the chemical potential, which should be compared to the term \( \delta P / \rho \) due to the variation of the pressure. Thus, we find thermal corrections to the pressure in our experiments \( \delta P_T = \rho \delta T K \approx 4 \times 10^{-3} \mu \text{bar} \), which are negligible.

The relaxation time of the system can be estimated as \( \tau = R^2 \rho_S / (\alpha k) \) [2], where \( k \equiv v / \Delta \mu \) is the growth coefficient of the solid-liquid interface. In the absence of thermal effects the growth coefficient is limited by scattering of phonons on the interface, \( k = 33/T^4 \text{ sK}^4/\text{m} \) [11–13], and \( \tau \) is 0.1 s for a helium sample of radius \( R \approx 1 \text{ cm} \) at 0.15 K. We note again that helium at low temperatures presents a unique system where the relaxation is fast enough to carry out measurements on equilibrium crystal shapes [14].

V. EXPERIMENT

We have measured the pressure in superfluid \(^4\text{He} \) in contact with solid helium during slow melting at 0.15 K. The experimental cell is described elsewhere [15]. The capacitive mechanical pressure gauge of Straty-Adams type [16] had a sensitivity of 44 pF/bar allowing measurements with the accuracy of a few micr bars in a second using an Andeen-Hagerling 2700A capacitance bridge. Figure 2 shows the pressure during slow melting of the solid sample with the constant extraction rate \( V = -2.9 \mu \text{mol/s} \). Zero pressure corresponds to the equilibrium melting pressure \( P_0 \) for the flat interface. The solid curve represents \( P_L(R) = P_0 = 2\mu \rho_L / (\mathcal{L}(1) \Delta \rho_{SL}) \) assuming spherical shape of the solid with the contact angle of 135° [17–20] at the bottom of the cell and with the initial radius of 3.9 mm. Here we neglect the gravity which has two effects on the measured pressure in the liquid. First, gravity flattens crystals that are larger than the capillary length \( \lambda \approx 1 \text{ mm} \). Second, when the crystal becomes smaller, the hydrostatic pressure difference between the crystal surface and the pressure gauge increases. However, these effects are small: when the crystal is large, \( R \gg \lambda \), its height almost does not change with its volume, and the curvature on top is nearly zero; while the crystal is small, \( R \lesssim \lambda \), gravity effects are weak compared to the Laplace pressure. Indeed, one can see from Fig. 2 that the simple model of spherical crystal fits our experimental data very well.

The observed system of superfluid-solid helium-4 shows thus negative compressibility: its pressure increases when the number of particles decreases. No spontaneous instability shows up: the pressure increases smoothly without any unusual noise or jumps. In Sec. II we have predicted that the minimum
FIG. 2. Pressure in the cell containing superfluid and solid helium-4 during slow unloading with the rate $\dot{V} = -2.9 \, \mu\text{mol}/\text{s}$. The unloading begins at $t = 0$ and stops at $t = 410$ s. During the melting process the size of the crystal decreases which leads to the increase of the melting pressure. The system thus shows negative compressibility. Solid curve represents the theoretical dependence $P_L(R) - P_0 = 2\alpha \rho_L/|R(t)|\Delta \rho_{SL}$, assuming there is no gravity. See text for more details.

stable radius of the solid $R_c = 0.1$ mm and that corresponding shift of the melting pressure $P_L(R_c) - P_0 = 500 \, \mu\text{bar}$. In the experiment, however, we could not stabilize radii smaller than 0.5 mm with pressure shifts higher than 80 \, \mu\text{bar} because pressure changes became too fast and we had to stop the melting process in order not to lose the crystal. After the helium extraction was stopped, the pressure in the cell dropped because cold helium gas in the filling line warmed, and the crystal grew back slightly due to backflow of helium from the filling line to the cell. After this process the crystal and the pressure in the cell were stable.

VI. CONCLUSIONS

We have shown theoretically that any two-phase system of finite size has negative compressibility, i.e., its internal pressure increases when its volume increases. This effect is inherently originates with the surface tension of the interface between phases, which shifts the co-existence pressure. Moreover, if the size of one of the phases is too small, the phase is unstable and spontaneously melts completely or grows to a large enough size. We have demonstrated the negative compressibility in the system consisting of solid and liquid helium at 0.15 K where the relaxation time is short enough. We have observed the shift of the equilibrium melting pressure up to 80 \, \mu\text{bar} due to the melting of solid.

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[7] M. Poole (private communication).