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On the Gibbs–Thomson equation for the crystallization of confined fluids

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ABSTRACT

The Gibbs–Thomson (GT) equation describes the shift of the crystallization temperature for a confined fluid with respect to the bulk as a function of pore size. While this century old relation is successfully used to analyze experiments, its derivations found in the literature often rely on nucleation theory arguments (i.e., kinetics instead of thermodynamics) or fail to state their assumptions, therefore leading to similar but different expressions. Here, we revisit the derivation of the GT equation to clarify the system definition, corresponding thermodynamic ensemble, and assumptions made along the way. We also discuss the role of the thermodynamic conditions in the external reservoir on the final result. We then turn to numerical simulations of a model system to compute independently the various terms entering in the GT equation and compare the predictions of the latter with the melting temperatures determined under confinement by means of hyper-parallel tempering grand canonical Monte Carlo simulations. We highlight some difficulties related to the sampling of crystallization under confinement in simulations. Overall, despite its limitations, the GT equation may provide an interesting alternative route to predict the melting temperature in large pores using molecular simulations to evaluate the relevant quantities entering in this equation. This approach could, for example, be used to investigate the nanoscale capillary freezing of ionic liquids recently observed experimentally between the tip of an atomic force microscope and a substrate.

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I. INTRODUCTION

Most fluid properties are modified under confinement due to the interactions with the confining surfaces. Of particular importance is the shift of phase transitions, which is more pronounced for small pore sizes (large surface to volume ratio). Such a shift depends on the excess free energies associated with the interface between the pore walls and both coexisting phases.1 For instance, the capillary condensation of vapor inside a pore occurs at a pressure lower than the saturation pressure corresponding to the bulk liquid–vapor equilibrium, with a shift described by the Kelvin equation.2 The crystallization of confined fluids, such as in freeze–thaw cycles or salt crystallization in porous rocks and stones, is also of great practical importance to understand weathering in the context of the durability of civil engineering constructions or the preservation of cultural heritage. The fact that the crystallization of a confined fluid occurs at a different temperature than in the bulk can be exploited to investigate the properties of “supercooled” water (even though the confinement also has an influence on these properties) or to estimate pore size distributions in complex porous materials, e.g., via nuclear magnetic resonance (NMR)-cryoporometry. Several reviews are available on the effect of confinement on freezing/melting as probed using experiments and molecular simulations.3,4

The shift of the melting temperature $T_m$ induced by the confinement of the liquid in a slit pore of width $H$ is traditionally described by the Gibbs–Thomson (GT) equation,

$$\frac{T_m - T_m^b}{T_m^b} = \frac{2(\gamma_{LW} - \gamma_{SW})}{H \rho \Delta_m h},$$

(1)

where $T_m^b$ is the bulk melting temperature, $\gamma_{LW}$ and $\gamma_{SW}$ are, respectively, the liquid-wall and solid-wall surface tensions, $\rho = N/V$ is density, and $\Delta_m h = h_L - h_S$ is the latent heat of melting per particle.
Since the latter is usually positive, for a given fluid, the sign of the shift is determined by that of the surface tension difference, i.e., the difference in the free energy cost to create an interface between each of the phases and the confining walls. This balance is often complex to predict as it is significantly system-dependent: for example, recent experiments on the capillary freezing of ionic liquids between the tip of an Atomic Force Microscope (AFM) and a solid substrate indicate that the switch to a mechanical response typical of a solid occurs at a distance which depends on the metallicity of the substrate.

Even though the GT equation has been used for more than a century, one finds in the literature a variety of expressions, which differ not only because they may correspond to different geometries but also in the use of the liquid or solid density in the denominator. In addition, its derivations do not always state explicitly the assumptions that are made at the different steps. We believe that some of the ambiguities that can be found in the literature are due to the similarity between the thermodynamic problem of phase equilibrium under confinement, where two phases are stable, and the kinetic problem of nucleation, where one phase is more stable than the other, but the growth of a nucleus is hindered by the free energy cost associated with the creation of an interface. Even if these two aspects have in common the presence of interfaces and associated surface free energies and lead to similar expressions, they correspond to different thermodynamic conditions and processes (so that the similar expressions correspond to different physical quantities).

From the nucleation point of view, one considers the kinetic barrier for the solid to grow from the liquid phase, when the former is thermodynamically more stable than the latter. Classical nucleation theory involves the free energy associated with the interface between the two phases and the chemical potential difference between them at the considered thermodynamic conditions—typically, fixed temperature \( T \) and pressure \( P \). The competition between the bulk driving force and the cost of creating the interface leads (a) to a critical nucleus size, which also reflects the curvature of the interface and satisfies a relation similar to the GT equation [Eq. (1)], and (b) to the corresponding free energy barrier. This barrier controls the kinetics of the phase transition and explains why the liquid may be cooled down below the bulk melting temperature without observing crystallization. One can note in passing that the standard assumption of a spherical nucleus, which is reasonable for the liquid–vapor transitions, is questionable for the nucleation of solids, which are faceted objects (leading, in addition, to facet-dependent interfacial free energies).

For crystallization under confinement, arguments borrowing from this nucleation picture have been proposed to derive the shift in melting temperature induced by confinement. However, the GT equation deals with the thermodynamic equilibrium between the two phases in the presence of confining walls (typically, slit or cylindrical pores). In that case, the relevant interfaces and associated free energies are not between the solid and liquid phases but between each of them and the walls. The interfacial free energies will, in general, differ for the confined liquid and the confined solid so that one of them is more stable than the other at the bulk melting temperature \( T_m^b \). Conversely, the melting temperature \( T_m \) under confinement is shifted with respect to \( T_m^b \). These considerations are not related to the formation of an interface between the two confined phases. As a result, several important simulation studies have performed free energy calculations using umbrella sampling to probe crystallization under confinement by estimating the free energy of the confined liquid and crystal phases without explicitly considering their interface.

In the present work, we propose a derivation of the GT equation for the crystallization of a liquid confined in a slit pore, based only on the phase equilibrium of the confined phases. We discuss,
in particular, the importance of the definition of the system and of the thermodynamic ensemble corresponding to an experimental situation. We then estimate independently the various terms entering in the GT equation for a model system and compare the prediction of this equation to the melting temperature under confinement determined in simulations. In Sec. II, we provide a derivation of the GT equation and discuss the assumptions leading to the final result. The rest of this article is then devoted to the numerical study of the phase behavior of a model system, introduced in Sec. III, in order to test the relevance of these assumptions and the GT equation to predict the shift of its melting temperature. This requires the computation of several quantities, using complementary strategies as schematized in Fig. 1. The bulk phase diagram and relevant properties of the bulk phases are investigated in Sec. IV. Section V presents the computation of differences in interfacial free energies under confinement using a thermodynamic integration approach. Finally, Sec. VI discusses crystallization under confinement by comparing results from Hyper-Parallel Tempering Grand Canonical Monte Carlo (HPT-GCMC) simulations with the prediction of the GT equation.

II. DERIVING THE GIBBS–THOMSON EQUATION UNDER CONFINEMENT

As mentioned in Sec. I, some derivations in the literature refer to metastable states using arguments related, e.g., to supersaturation or undercooling under given thermodynamic conditions. In contrast, in the following, we consider only the equilibrium phases at coexistence and determine the coexistence line in the space of relevant thermodynamic variables. The derivation, which largely borrows from that of Evans et al. for capillary condensation using a slightly different ensemble, allows us to focus on the effect of the confining walls (W) on the phase equilibrium. Even though we consider here the solid–liquid coexistence and a slit-like pore, it can be easily adapted to different confining geometries or conditions. The derivation proceeds in two steps. First, we identify the relevant thermodynamic ensemble and associated thermodynamic potential to derive a “confined Clapeyron” formula satisfied by the thermodynamic variables along the coexistence line. Second, integration along this line to connect the bulk conditions to the confined ones leads to the GT equation.

A. A “confined Clapeyron” approach in the $\mu A_{W}HT$ ensemble

Our system of interest corresponds to the experimental setup of Ref. 5, schematized in Fig. 2, where the tip of an AFM confines a room temperature ionic liquid that undergoes capillary freezing at a finite distance $H$ between the tip and the substrate. The height at which this transition occurs depends on the nature of the substrate. At the macroscopic level, the interactions of the substrate with the confined fluid/solid are reflected in the surface tensions, as discussed below. Because of the large radius of curvature of the tip, the region in which the phase transition occurs can be considered as a slit pore between two parallel walls. The slit pore has a surface area $A_{W}$, a width $H$, and hence a pore volume $V = A_{W}H$ (see the inset of Fig. 2). In contrast to the experiments in Ref. 5, we will assume that both confining walls are made of the same material so that their interactions with the confined fluid or solid are identical. The rest of the liquid in which the AFM tip is placed can be considered as a macroscopic reservoir so that the chemical potential $\mu$ is fixed and the number of particles $N$ is fixed and hence a pore volume $V = A_{W}H$ is set by the liquid–gas equilibrium in the reservoir.

FIG. 2. Illustration of a system confined between the tip of an atomic force microscope and a substrate, as in the experiments of Ref. 5. From the thermodynamic point of view, it forms an open system confined in a slit pore with lateral area $A_{W}$ and distance between walls $H$ at a fixed temperature $T$ and chemical potential $\mu$.
\[ d\Omega = -\frac{SdT}{T} - PdVdH + (2y - PH)dA + N\mu. \] (5)

We then follow the reasoning of the Clausius–Clapeyron equation, which gives the slope \(dP/dT\) of the coexistence line (in the \(P, T\) plane) for a bulk system, and consider an infinitesimal change in the control variables while staying at coexistence so that \(d\Omega = d\Omega_b = d\Omega_L + d\Omega_L\) along this path, giving \(d\Omega_b = d\Omega_L\). After simplification of the term in \(d\Omega\) using Eq. (4), we obtain

\[
(S_L - S_S)dT + \frac{2A_L(Y_LW - \gamma_{SW})}{H}dH + (N_L - N_S)d\mu = 0. \] (6)

Equation (6) relates the variations of \(T, H, \mu\) along the liquid–gas coexistence. We note that, as expected, Eq. (6) shows that the confinement effect does not depend on the variations of the surface area.

**B. Integration along a bulk-to-confined thermodynamic path**

In order to obtain the GT equation, we will integrate Eq. (6) from an unconfined, bulk system (\(H \rightarrow \infty\)) where the transition occurs at the bulk melting temperature \(T_m^b\) to another point along the coexistence line with a melting temperature \(T_m\) for a finite distance \(H\) between the confining surfaces. This requires introducing some additional setup-specific information on the thermodynamic conditions in the reservoir, allowing us to express the dependence of the chemical potential with the temperature \(d\mu/dT\). We thus rearrange Eq. (6) as

\[
\frac{dH}{H} = -\frac{dT}{2(Y_LW - \gamma_{SW})}\left[ (\rho_L s_L - \rho_S s_S) + (\rho_S - \rho_L) \frac{d\mu}{dT} \right]. \] (7)

where we used the densities \(\rho = N/V\) and entropies per particle \(s = S/N\). Equation (7) defines the L–S coexistence line under confinement by the joint variations of \(H\) and \(T\). In addition, unlike in the steps leading to Eq. (6), we will make some assumptions (discussed along the derivation and numerically in Secs. III–VI) on some physical quantities.

In the experiments of Ref. 5, the liquid is in equilibrium with its vapor, as shown in the right part of Fig. 2. The chemical potential of the reservoir in equilibrium with the confined system is fixed by the bulk liquid–gas coexistence, i.e., \(\mu_b(T) = \mu_b(T) = \mu_c(T)\), where the L and G subscripts refer to the liquid and gas phase, respectively. Its derivative with respect to temperature is given by (see Appendix A)

\[
\frac{d\mu}{dT} = -\rho_L^b \frac{s_L^b - s_S^b}{\rho_L^b - \rho_G^b} \approx \frac{s_L^b}{T}. \] (8)

where the superscript \(b\) refers to the bulk (unconfined) liquid and gas phases. In the case of an isobaric–isothermal liquid phase, the result would be exactly \(-s_L^b\). Introducing Eq. (8) into Eq. (7), we obtain

\[
\frac{dH}{H} = -\frac{\rho_L - \rho_S(s_L - s_S)}{2(Y_LW - \gamma_{SW})}dT. \] (9)

For sufficiently large confining distances (and corresponding small shift in the melting temperature \(T_m - T_m^b\)), one can approximate the densities and entropies per particle of the confined phases by their bulk counterparts. The first term in the numerator can safely be neglected (since, in addition, to this assumption, \(|\rho_L - \rho_S| \ll \rho_S\)), and we obtain

\[
\frac{dH}{H} = -\frac{\rho_S^b (\Delta s^b)}{2(Y_LW - \gamma_{SW})}dT, \] (10)

with \(\Delta s^b = s_L^b - s_S^b\) being the bulk entropy of melting per particle.

The final step to recover the GT equation is to integrate this equation along a thermodynamic path connecting the confined system for a finite \(H\) and corresponding one (\(H \rightarrow \infty\) and bulk melting temperature \(T_m^b\)). To this end, we assume that the ratio on the right-hand side is independent of temperature and confining distance over the considered range. This approximation should be accurate at least for sufficiently large \(H\) and corresponding small \(T_m - T_m^b\); it will be tested numerically and discussed in Sec. IV. Under these conditions, we can write

\[
\int_{T_m^b}^{T_m} \frac{dH}{H} = -\frac{\rho_S^b (\Delta s^b)}{2(Y_LW - \gamma_{SW})} \int_{T_m^b}^{T_m} dT, \] (11)

Noting that in the present case of a liquid–gas equilibrium in the reservoir, the melting temperature is, in fact, the (bulk) triple point \(T_m^b\), the final result can be written as

\[
T_m(H) = T_m^b + \frac{2(Y_LW - \gamma_{SW})}{H \rho_S^b (\Delta s^b)} \int_{T_m^b}^{T_m} dT. \] (12)

This derivation can be easily adapted to other geometries or external reservoir conditions. In the case where the reservoir is an isobaric liquid, the first term in the right-hand side is simply the bulk melting temperature at the corresponding pressure.

**III. MODEL SYSTEM**

To assert the validity of the assumptions in the above derivation (in particular, neglecting the temperature dependence of some quantities), we use molecular simulation to compute the various terms entering in the GT equation for a simple system of Lennard-Jones (LJ) particles confined between unstructured walls. More precisely, in order to avoid the difficulties associated with the long-range corrections (LRC) in the computation of physical properties under confinement, we consider the truncated shifted Lennard-Jones (TSLJ) potential for a pair of atoms \(i\) and \(j\) at a distance \(r_{ij}\),

\[
\phi_{ij}^{\text{TSLJ}}(r_{ij}) = \begin{cases} \phi_{ij}(r_{ij}) - \phi_{ij}(r_{\text{cut}}) & \text{if } r_{ij} < r_{\text{cut}} \\ 0 & \text{otherwise,} \end{cases} \]

(13)

where \(r_{\text{cut}}\) is the cutoff radius and

\[
\phi_{ij}(r_{ij}) = 4\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6, \]

(14)

with \(\epsilon\) and \(\sigma\) being the LJ energy and diameter, respectively. The total energy of the system is then given by...
where the sums run over all atoms in the system. Simulations are performed with typical values for argon: \( z = 119.8 \) K and \( \sigma = 3.405 \) Å. We employ a cutoff radius \( r_{\text{cut}} = 2.5\sigma \), for which some data on the phase diagram are available in the literature. In the following, most quantities will be given in reduced LJ units, indicated by a \( \ast \) superscript: \( r^* = r/\sigma \) for distances, \( E^* = E/\epsilon \) for energies, \( T^* = k_B T/\epsilon \) for temperatures (with \( k_B \) being the Boltzmann constant), \( P^* = \rho \epsilon/\sigma^3 \) for pressures, and \( \gamma^* = \gamma \sigma^2/\epsilon \) for surface tensions.

As for the confining medium, we use the unstructured Steele wall,\(^25,26\) with parameters corresponding to a mica surface, which is for an atom at a distance \( z \) from the surface,

\[
u_{\text{Steele}}(z) = 2n_\epsilon^{\nu_F} \epsilon^{\nu_F} \Delta \left[ \frac{2}{5} \left( \frac{\sigma^{\nu_F}}{z} \right)^{10} - \left( \frac{\sigma^{\nu_F}}{z} \right)^4 \right] - \frac{\sigma^{\nu_F}}{3\Delta(z + 0.61\Delta)^3},
\]

where \( \rho^{\nu_F} = 1.0 \) is the atomic density of the material, \( \epsilon^{\nu_F} = \sqrt{\epsilon^T} \) and \( \sigma^{\nu_F} = \left( 1 + \sigma^T / 2 \right) \) are obtained by combining LJ parameters with surface parameters \( \epsilon^{\nu_F} = 7.85 \) and \( \sigma^{\nu_F} = 1.28 \), respectively, and \( \Delta^* = 0.84 \) corresponds to the distance between atomic crystal planes. In practice, we use two walls separated by a distance \( H \), which controls the pore size (see Sec. VI).

The crystalline structure of the Lennard-Jones fluid is a face-centered cubic phase and the most stable face that crystallizes on the Steele wall is the (111) face, with which subsequent simulation boxes were initialized. Because crystallization is a phenomenon particularly sensitive to the box size, we worked on crystal configurations consistent between the different techniques. Care was taken to ensure the reversibility of calculations and to avoid polycrystalline recrystallization: boxes were initialized from a perfect crystal and liquid configurations were obtained by melting. Simulated systems considered in Sec. IV consisted of 4000 atoms per phase in a cubic box of variable volume, and those considered in Sec. V consisted of 4116 atoms with lateral dimensions \( L_x^* = 16.4, L_y^* = 14.2 \) and a pore size \( H^* \) between Steele walls fluctuating between 19.5 and 21.5. In Sec. VI, we use boxes with \( L_x^* = 21.1, L_y^* = 20.3 \), and different \( H^* \) values (8.7, 11.6, 14.5, 17.3, 20.2, 23.1, 26.0, and 28.8), covering a wider range than studies focusing on disjoining pressure effects, which typically consider pores up to \( \approx10 \) molecular diameters.

### IV. BULK PROPERTIES

The phase diagram of LJ particles has been extensively studied,\(^25,29,30\) mostly using LRC to correct for the use of a cutoff to compute the interactions. For the TSLJ potential, however, the choice of \( r_{\text{cut}} \) greatly influences the phase diagram.\(^32,36\) For example, the use of TSLJ with a cutoff of 2.5\( \sigma \) results in a critical temperature difference of about 35 K for an argon fluid with respect to the prediction with LRC.\(^32\) For this cutoff value, Vrabec et al.\(^37\) computed the liquid–vapor coexistence line and determined the critical point, whereas Ahmed and Sadus\(^25\) investigated the solid–liquid coexistence line at high pressure.

In order to accurately locate the triple point, we recompute both the liquid–vapor and the solid–liquid portions of the phase diagram using Gibbs–Duhem Integration (GDI).\(^38\) Starting from a known point on the coexistence line in the \((T, P)\) plane, a new point is found by integrating the Clausius–Clapeyron equation

\[
\frac{d\ln P}{d\beta} = -\frac{\Delta_h}{P\beta\Delta_v},
\]

where \( \beta = 1/k_B T \) and \( \Delta_h \) and \( \Delta_v \) are the transition enthalpy and volume per particle, respectively. The right-hand side is computed on-the-fly in simulations in the \(NPT\) ensemble of two systems corresponding to the two coexisting phases, (i.e., liquid and vapor, or liquid and solid). More details are given in Appendix B.

The starting point for the GDI method is crucial: one needs to accurately identify one point of the coexistence line because the integration of Eq. (17) allows us to stay on the latter but not to find it. For the liquid–vapor transition, we start from a coexistence point at high temperature \((T_m^* = 1.00, P_m^* = 0.0612 \pm 0.0005)\), determined using Gibbs-Ensemble Monte Carlo (GEMC) simulations.\(^39,40\) GEMC determines the coexistence between two phases by exchanging volume and particles between two systems until the chemical potential is equal in the two phases. While efficient for the liquid–vapor equilibrium, GEMC is insufficient for the liquid–solid one due to the low probability of particle exchange. Fortunately, at

![FIG. 3 Bulk phase diagram of the truncated shifted Lennard-Jones system with a cutoff of 2.5\( \sigma \): (a) in the \((T^*, P^*)\) plane and (b) in the \((\rho^*, T^*)\) plane. Our results obtained by Gibbs–Duhem integration for the liquid–vapor (light blue open circles) and solid–liquid (dark blue full circles) coexistence lines are compared to the results of Vrabec et al.\(^37\) (orange open squares) and Ahmed and Sadus\(^25\) (red full squares), respectively. All thermodynamic quantities are in LJ units.](https://example.com/figure3.png)
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using phases differs by 7%–15%, especially at lower temperatures, so that we can use the value for the bulk coexistence, $\rho_s^*$. The GT prediction relies on the assumption that one can use the bulk solid density $\rho_s^*$ instead of $\rho_s^b$ in the GT Eq. (12) to lead to a different estimate of the melting temperatures under confinement.

The quantity that enters in the denominator of Eq. (12) is, in fact, the product of the bulk solid density with the bulk melting entropy per particle. The latter can be determined from the GDI simulations, which provide the enthalpy of the coexisting solid and liquid phases; hence, $\Delta S = \Delta h/T_m$. Figure 3(b), in the ($\rho^*$, $T^*$) plane, further shows that the density of the liquid and solid phases differs by 7%–15%, especially at lower temperatures, so that the product $\rho_s^* \Delta S$ as a function of temperature along the liquid–vapor coexistence line (see Fig. 3). All thermodynamic quantities are in LJ units.

![Figure 4](image)

**Figure 4.** (a) Product of the bulk solid density $\rho_s^*$ with the bulk melting entropy per particle $\Delta S^*$ as a function of temperature along the liquid–vapor coexistence line (see Fig. 3). All thermodynamic quantities are in LJ units.

**V. CRYSTALLIZATION UNDER CONFINEMENT: SURFACE TENSION DIFFERENCE**

The last term in the GT equation that needs to be computed in order to predict the temperature shift induced by confinement is the surface tension difference $\gamma_{LW} - \gamma_{SW}$, which is positive if the walls favor the solid phase with respect to the liquid phase and negative otherwise. Computing surface tensions can be done following either a mechanical route through the stress tensor or a thermodynamical approach, which uses the definition of the surface tension as a (Gibbs) free energy per surface area,

$$y = \left( \frac{\partial F}{\partial A} \right)_{NVT} = \left( \frac{\partial G}{\partial A} \right)_{NPT}. \quad (18)$$

In order to avoid difficulties of the mechanical route for solid–solid interfaces, we use a thermodynamic integration procedure to obtain $\gamma_{LW} - \gamma_{SW}$ from the Gibbs free energy difference between the walls in contact with the liquid or the solid phase. To that end, a bias acting on the system is introduced, providing a handle to drive the phase transition, and the relevant thermodynamic quantities are computed to obtain the properties of the unbiased system. Here, we use the collective variable $Q_b$, derived from the sixth order Steinhardt parameters defined in Appendix C, which quantifies the average (over the system) local order: a large (respectively, low) value corresponds to an ordered solid (respectively, disordered fluid).

Such a procedure is computationally more demanding than the study of the bulk properties and cannot be performed systematically as a function of thermodynamic conditions. Therefore, we first identify suitable conditions in which both the confined liquid and solid phases are sufficiently metastable, i.e., close to the coexistence line under confinement, which is not known a priori (see also Sec. VI). For example, at the bulk coexistence temperature and pressure, the confined liquid tends to recrystallize, which points to an increase in the melting temperature under confinement. We fix the pressure to $P^* = 0.2036$ (which corresponds to a bulk melting temperature $T_m^* = 0.638$) and perform NPT simulations during which the temperature is slowly increased and then decreased. The evolution of the system density during these temperature ramps exhibits a pronounced hysteresis pointing to the metastability of both liquid and solid phases over a finite temperature range, which is then confirmed by long simulations (10 ns) of the two phases at the selected temperature $T^*_F = 0.659$. These unbiased simulations also allow to determine the characteristic values for the collective variable in the solid and liquid phases ($Q_b^s = 0.3632$ and $Q_b^l = 0.1425$ from 2 ns simulations at $T^*_m = 0.638$), which are then used in the definition of the bias.

The details of the thermodynamic integration are given in Appendix D. In a nutshell, it follows a three-step scheme,

1. introduce bias $\alpha_0 \rightarrow 1$
2. shift bias $\lambda_0 \rightarrow 1$
3. remove bias $\alpha_1 \rightarrow 0$

in which a bias on the $Q_b$ collective variable is introduced (via a parameter $\lambda$ rising from 0 to 1), shifted from the solid to the liquid (via a parameter $\alpha$ from 0 to 1), and removed (by decreasing $\alpha$ from 1 to 0). Along the way, one computes the relevant thermodynamic quantities, which are then integrated over the whole thermodynamic path [see Eq. (19)] to obtain the Gibbs free energy $\Delta G^{T_I}$ associated with this transformation between the non-biased confined solid and liquid phases,
The results of Fig. 5 show that with our choice of thermodynamic path, bias, and simulation parameters (see Appendix D 2 for more details), we achieve a good reversibility of the transformation. The final result for the Gibbs free energy difference at $T_I^*$ and $P^*$, taking into account the discretization error for the numerical integrations in Eq. (19), is $\Delta G_{TI}^* (T_I^*) = 50 \pm 28$ (in L/J units). This large uncertainty arises mainly from the numerical estimate of the integral due to the jump between $\lambda = 0.3$ and $0.4$.

The Gibbs free energy difference $\Delta G_{TI}^*$ obtained from the above thermodynamic integration can be decomposed into volume and surface contributions,

$$\Delta G_{TI}^* = (\Delta mH - T \Delta mS) + 2A_W (y_{LW} - y_{SW})$$

$$= \Gamma_{bulk} A_W \left(1 - \frac{T}{T_m}\right) \Delta m h^b + 2A_W (y_{LW} - y_{SW}),$$  

where we introduced $\Gamma_{bulk} = N/A_W - 2\Gamma$ the number of “bulk” atoms per unit surface, with $\Gamma$ being the excess number of atoms at each interface. The latter can be determined from the density profiles, as discussed in Appendix D 3. Equation (20) then leads to $\Delta y^* = y_{LW}^* - y_{SW}^* = 0.40 \pm 0.05$.

Before turning to the implications for the GT prediction, we note that for the present system, the strong attraction between the particles and the wall ($\epsilon_{gf}^W \approx 2.8$) results in a pronounced structuration in the vicinity of the surface, with several solid-like layers even between the wall and the liquid phase (see the snapshot for $\lambda = 1$ in Fig. 5 and the density profiles in Appendix D 3). This has two important consequences. First, this probably explains why the surface tension between the liquid and the wall (covered by a few solid-like layers) is larger than that between the solid and the wall, i.e., the positive sign of $\Delta y^*$. Second, the width of these solid-like films on both sides reduces the effective size of the bulk liquid and solid regions, assumed to be sufficiently large for the GT equation to apply.

VI. CRYSTALLIZATION UNDER CONFINEMENT: MELTING TEMPERATURE

In Secs. IV and V, we computed the terms entering in the GT equation (12) and investigated the temperature dependence of some of these terms. Here, we finally compare the resulting predictions of this equation to the melting temperature for our model system under confinement as a function of the pore size $H$ with results from Hyper-Parallel Tempering Grand Canonical Monte Carlo (HPT-GCMC) simulations. This technique, explained in detail in Appendix E, runs parallel replicas at different temperatures, regularly spaced in $\beta = 1/k_B T$, each replica being a GCMC simulation (in the $\mu_A W HT$ ensemble) in contact with a chemical reservoir. To model the setup described in Sec. II and Fig. 2, the imposed chemical potential $\mu$ is taken from the liquid–vapor coexistence at the replica’s temperature [see Fig. 4(b)]. The exchange between replicas improves the sampling of phase space. The confidence interval for the melting temperature $T_m$ is estimated for each pore size from the evolution of the average number of particles as a function of temperature, as explained in Appendix E, also supported by visual inspection of the equilibrated configurations.

In order to compare the results obtained by HPT-GCMC simulations to the prediction of the GT equation, one needs to consider the effective width of the pore occupied by the particles. From the position of the Gibbs dividing surfaces (GDSs) (see Appendix D 3)
located at \(\approx \sigma\) from the Steele walls, we define \(H_{\text{eff}}^* = H^* - 2\), with \(H\) being the distance between the positions of the walls (the difference between \(H_{\text{eff}}^*\) and \(H^*\) matters more in smaller pores but does not influence the conclusions below). Figure 6 shows the melting temperature \(T_m\) as a function of \(1/H_{\text{eff}}^*\), together with the prediction of the GT equation using the results of Secs. IV for \(T_f^*\) and \(\rho S_{\text{conf}}^b(T_f^*\) and Sec. V for \(\Delta \gamma(T_f^*)\).

One can first note that for large pores, despite the relatively large confidence interval due to the difficulties to converge the HPT-GCMC simulations, which does not allow us to identify a trend with temperature, the results are consistent with the bulk value \(T_f^*\) in the limit \(H_{\text{eff}} \rightarrow \infty\). In addition, the order of magnitude of the GT predictions is consistent with the HPT-GCMC results down to very narrow pores (a few molecular diameters). However, the agreement is not quantitative, even for the larger pores considered in the present work (\(\approx 20\) molecular diameters).

Importantly, though unsurprisingly, the GT equation fails to capture the transition from a regime dominated by the competition between volume and interfacial contributions to a different one for small pores, dominated by disjoining pressure effects, i.e., the mutual influence of the two interfaces. Even though this second regime is not the main focus of the present work and this is not visible with the considered pore sizes, the disjoining pressure oscillates due to the finite size of the particles and the formation of discrete layers at the interfaces so that non-trivial effects on the thermodynamic behavior can be observed.\(^{10,34-41}\)

Several reasons can be put forward to explain the somewhat disappointing comparison between the GT prediction and the HPT-GCMC simulations for large pores. First, there are uncertainties associated with the determination of the quantities entering the GT equation, but their combination does not seem too large in the large-pore regime. Second, the GT equation assumes that these quantities do not depend on the temperature or equivalently on the pore width.

The results on \(\rho_b^k \Delta m_s^b\) as a function of temperature in Sec. IV suggest that the effect would be limited to less than 10% in the temperature range corresponding to large pores. Unfortunately, the other contribution to the GT slope, \(\Delta \gamma\), could only be determined at a single temperature \(T_f^*\) (close to but different from \(T_f^*\) to avoid the liquid–vapor coexistence) so that we cannot assess the effect of \(T\) (or \(H\)) on the difference in surface tensions.

A further difficulty is that the chosen model system, with a dramatic ordering of the interfaces due to the strong attraction with the walls, leads to a small bulk region even for the larger pores considered here (see the density profiles in Appendix D 3). This makes it particularly difficult to converge the HPT-GCMC simulations (the exchange of two replicas is unfavorable when the difference in the number of molecules, which increases with system size, is large) and generally increases the computational cost—preventing, e.g., the systematic study of \(\Delta \gamma\) with \(T\) or \(H\). One possibility to mitigate this difficulty would be to consider a different system with a weaker interaction with the walls, leading to only two to three layers at the interface—more typical of simple liquids on flat walls than the seven to eight observed here. It is, however, not easy to predict the resulting effect on the magnitude of the temperature shift. Overall, the difficulties related to the sampling of crystallization under confinement suggest that evaluating the relevant quantities separately and using the GT equation may provide an interesting alternative route to predict the behavior in large pores from molecular simulations.

**VII. CONCLUSION**

We revisited the derivation of the Gibbs–Thomson equation for the crystallization of a liquid confined in a slit pore in order to clarify the definition of the system and corresponding thermodynamic ensemble, as well as the assumptions leading to the final result. We highlighted the importance of the thermodynamic conditions in the bulk reservoir in equilibrium with the confined system. We then tested the validity of the approximations by evaluating the physical quantities entering the GT equation (bulk density and melting entropy, and difference in interfacial tensions) for a model system and, when possible, their evolution with the temperature. We finally compared the prediction of the GT equation, using these estimated properties, to the melting temperature obtained by HPT-GCMC of the confined system, as a function of the pore size.

While the chosen model system turned out not to be ideal for this study, we found that the order of magnitude of the GT predictions is consistent with the simulations down to very narrow pores (a few molecular diameters) but is not quantitative even for the larger pores considered (\(\approx 20\) molecular diameters). Importantly, though unsurprisingly, the GT equation fails to capture the transition to a different regime for small pores, dominated by disjoining pressure effects, i.e., the mutual influence of the two interfaces. Beyond the study of the GT equation, the present work highlights some difficulties related to the sampling of crystallization under confinement. Evaluating the relevant quantities separately and using the GT equation may provide an interesting alternative route to predict the behavior in large pores from molecular simulations, without resorting to computationally intensive techniques to determine the melting temperature for each confining length.

The accuracy of the approximations leading to the GT equation depends, of course, on the nature of the fluid and of its...
interactions with the walls. However, the present approach to test them can be applied not only for model fluids such as the one considered here but also for more complex ones such as water or ionic liquids, provided that the relevant solid phases are known. When several solid phases need to be considered, the “confined Clapeyron” approach may not be efficient to explore the full phase diagram of the confined system. The GT equation, in fact, also implicitly assumes that a single phase transition is relevant in the range of considered thermodynamic conditions.

One could further use molecular simulations to go beyond some of the assumptions leading to the standard GT equation. For example, the temperature dependence of the density, melting entropy, and difference in surface tensions could be explicitly included in the integral along the thermodynamic path connecting the bulk and confined systems. The evolution of ∆T with temperature remains, however, computationally more demanding than that of the bulk properties reported here. Another direction for future work is to investigate other thermodynamic conditions in the reservoir. The case considered here corresponds to recent experiments on the capillary freezing of ionic liquids between the tip of an AFM and a substrate in mind, but the extension to other conditions or ensemble is straightforward. For this particular system, we will also need to consider more realistic models of the liquid and of the substrate, including the effect of its metallicity. Of particular interest in this context is also the fact that the crystallization of confined fluids may also depends on the presence of an electric field. Finally, the coupling between phase transitions under confinement and mechanical properties could similarly be investigated by combining continuum thermodynamics with molecular simulations to compute the relevant quantities.

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APPENDIX A: CALCULATION OF dμ/dT FOR AN EXTERNAL LIQUID-GAS EQUILIBRIUM

In order to express the temperature dependence of the chemical potential, dμ/dT, imposed by the liquid–gas coexistence in the bulk reservoir, we study the corresponding bulk system in the μVT ensemble and consider the liquid–gas transition (the gas phase will be noted with the subscript G). The thermodynamic potential is the grand potential Ω = U − TS − μN = −PV. Along the coexistence line, the grand potential is equal in the two phases, i.e., ΩG = ΩL, and so are the associated variations, i.e., dΩG = dΩL. From the expression of the grand potential, the former equality immediately leads to

\[ P_G = P_L, \]

while the latter results in

\[ -S_G dT - P_G dV - N_G dμ = -S_L dT - P_L dV - N_L dμ. \]

Using the equality of pressures, this yields

\[ \frac{dμ}{dT} = -\frac{p_L S_L - p_G S_G}{p_L - p_G}. \]  \hspace{1cm} (A1)

Equation (A1) relates the variations in the chemical potential μ to the variations in temperature T at the liquid–gas coexistence.

In general, one can expect the density of the liquid to be larger than that of the gas (ρL ≫ ρG) and the entropy per particle to be larger for the gas compared to the liquid (S_G ≫ S_L). In order to make further progress, we consider the well-known van der Waals fluid, which is a good approximation to both the gas and the liquid phases, and use its equation of state, which amounts to a modified ideal gas law including an excluded volume b and an attractive term a. A review of the ideal gas and van der Waals fluid properties is given in Ref. 66 and gives the entropy per particle of the van der Waals fluid as

\[ s = \frac{1}{k_B} \left( \frac{1}{\rho b^3} + \frac{5}{2} \right). \]  \hspace{1cm} (A2)

where \( \rho \) is the density and \( \lambda^3 \) is the quantum volume with \( \lambda \) being the De Broglie wavelength. We introduce \( e_p = \rho_G/\rho_L \ll 1 \) and estimate the ratio \( \rho_G S_G / \rho_L S_L \) over \( \rho_G S_G / \rho_L S_L \) as

\[ \frac{\rho_G S_G}{\rho_L S_L} = \frac{e_p [\ln(1 - b \rho_G) - \ln(p_G \lambda^3) + 5/2] - e_p \ln e_p}{\ln(1 - b \rho_L) - \ln(p_L \lambda^3) + 5/2}. \]  \hspace{1cm} (A3)

In the limit where \( e_p \to 0 \) and \( b \rho_G \to 0 \) while \( \rho_L \) is large but fixed, we have \( \rho_G S_G / \rho_L S_L \ll 1 \) so that Eq. (A1) can be reasonably approximated as

\[ \frac{dμ}{dT} \approx -S_L. \]  \hspace{1cm} (A4)

A numerical test of this approximation is shown in Fig. 7 for a van der Waals fluid, using the coexistence properties given in Ref. 66.

**FIG. 7.** Evolution of dμ/dT as a function of temperature in reduced units for a van der Waals fluid (μred = μ/μVT, and Tred = T/TTc, where the c subscript refers to the critical point). Values of dμ/dT computed by Eq. (A1) (open black circles) are compared to −S_L using Eq. (A2) (open blue squares). The green solid line is the relative error corresponding to approximating the former by the latter [Eq. (B)], with values indicated on the right y-axis.
for \( b = \sqrt{2}a^3 \) and \( a/b = 5\pi/e/9 \). The results are expressed in reduced units with respect to the critical temperature \( T_c = 8a/(27b^2) \), pressure \( p_c = a/(27b^2) \), and volume \( v_c = 3b \). Reduced quantities are given in Fig. 7 along with the relative error made using the approximation in Eq. (A4). The values show an excellent agreement for temperatures small with respect to \( T_c \) and a relative error smaller than 10% on the relevant temperature range.

**APPENDIX B: BULK SIMULATION DETAILS**

The Gibbs–Duhem Integration method (GDI) method was implemented using the Python interface to LAMMPS, which allowed running two instances in parallel and coupling them during the run. The integration of the Clausius–Clapeyron equation [Eq. (17)] was done using the predictor–corrector procedure as described by Kofke et al. in Ref. 38 using steps in reciprocal temperature \( dB = 0.01 \) for the liquid–vapor curve and steps in pressure of \( d\ln P = 0.4 \) for the vertical part of the solid–liquid one to minimize integration errors. Each iteration of the predictor–corrector procedure was 20 ps long (with a timestep of 2 fs), and after convergence, equilibrated data for \( \Delta H \) and \( \Delta V \) were collected for 200 ps. Gibbs ensemble Monte Carlo simulations and Widom insertion method were also run using an in-house code based on the Python interface to LAMMPS to compute the interactions.

**APPENDIX C: COLLECTIVE VARIABLE \( Q_6 \)**

The collective variable considered in this work is based on the sixth order Steinhardt parameters, which allow to measure the degree of order in the first coordination shell of a given atom. We use a continuous version of the Steinhardt parameter, which is the degree of order in the first coordination shell of a given atom.

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In the main text, we use the average and half difference for our final estimate of $\Delta T^*$; the average position of the walls is indicated by vertical dotted lines.

cured by simulated annealing, i.e., heating the system at $T^* = 0.751$ for 100 ps and cooling it back to $T_{II}$.

3. Surface excess

The separation between volume and surface contributions to the Gibbs free energy $\Delta G^{II}$ in Eq. (20) requires the computation of the surface excess $\Gamma$ at each interface (or equivalently the number $N_{wall}$ of "bulk" atoms per unit surface of the system). This can be achieved from the density profiles $\rho(z)$ across the pore, shown for the liquid and solid phases in Fig. 8.

The thermodynamic definition of the surface excess is based on the position of the Gibbs dividing surface (GDS), $z_{GDS}$, which corresponds to an equivalent sharp interface between two homogeneous regions with densities $\rho_{wall} = 0$ (in the wall) and $\rho_{bulk} = \rho_1$ or $\rho_2$ in the bulk region of the pore (averaged over a lattice spacing in the case of the solid phase),

$$\int_{z_{wall}}^{z_{bulk}} (\rho(z) - \rho_{wall})dz = \int_{z_{GDS}}^{z_{bulk}} (\rho(z) - \rho_{bulk})dz, \tag{D10}$$

with $z_{wall}$ and $z_{bulk}$ being two positions in the wall and the bulk regions, respectively (we take $z_{wall} = 0$ in the center of the pore). The bulk densities of the solid and liquid phases are $\rho_s = 0.936$ and $\rho_l = 0.826$. In practice, we find that the GDS is approximately located near the center of the first density peak, as expected. The surface excess can then be computed as $\Gamma = \int_{z_{GDS}}^{z_{bulk}} (\rho(z) - \rho_{bulk})dz$, from which we obtain $\Gamma_{bulk} = N/AW - 2\Gamma$. Slightly different values of $\rho_{bulk}$ are obtained from the density profiles for the liquid and the solid phases. In the main text, we use the average and half difference for our final estimate of $\Gamma_{bulk} = 17.0 \pm 0.2$ and its uncertainty. Equation (20) then leads straightforwardly to the difference $\Delta y = \gamma_{LW} - \gamma_{SW}$ from $\Delta G^{II}$ and $\Gamma_{bulk}$.

APPENDIX E: HYPER-PARALLEL TEMPERING GRAND CANONICAL MONTE CARLO SIMULATIONS (HPT-GCMC)

The hyper-parallel tempering technique\textsuperscript{1} is an extended version of the parallel tempering method in which replicas of the system exist at different thermodynamic conditions (e.g., temperature, pressure, and chemical potential) are considered in parallel. This method can be extended to the grand canonical ensemble (constant volume, temperature, and chemical potential) to determine the freezing and melting of a nanoconfined fluid in equilibrium with a bulk reservoir of the same fluid.\textsuperscript{2,7} Each of the $M$ replicas consists of the Lennard-Jones fluid at a given set of temperature/chemical potentials $[T, \mu]$ with $\mu(T)$ chosen to correspond to its value at the bulk liquid–gas phase coexistence (in practice, $M = 16$ was chosen in the present work). For each replica, conventional Monte Carlo moves in the grand canonical ensemble are carried out (particle translation, deletion, and insertion). In addition, swap moves between configuration 1 (energy $U_1$, $N_1$ particles) in replica A and configuration 2 (energy $U_2$, $N_2$ particles) in replica B are attempted. Swapping is accepted or rejected according to the following Metropolis probability:

$$P_{acc}(A_1, B_2 \rightarrow A_2, B_1) = \min \left\{ 1, \frac{\rho_A(U_2, N_2)\rho_B(U_1, N_1)}{\rho_A(U_1, N_1)\rho_B(U_2, N_2)} \right\}, \tag{E1}$$

where $\rho_A(U, N) \sim N^2/\Lambda_A^{2N} \times \exp[-\beta_A(U - \mu_A N)]$ and $\rho_B(U, N) \sim N^2/\Lambda_B^{2N} \times \exp[-\beta_B(U - \mu_B N)]$ are the density of states in the grand canonical ensemble for a system having a constant volume taken at $[T_A, \mu_A]$ and $[T_B, \mu_B]$, respectively. In these expressions, $\beta = 1/k_B T$ is the reciprocal thermal energy, while $\Lambda_A$ and $\Lambda_B$ are De Broglie thermal wavelengths at temperatures $T_A$ and $T_B$, respectively. Equation (E1) then leads to

$$P_{acc}(A_1, B_2 \rightarrow A_2, B_1) = \min \left\{ 1, \left[ \frac{\Lambda_A}{\Lambda_B} \right]^{(N_1 - N_2)} \exp((\beta_B - \beta_A)(U_2 - U_1) + (\beta_B \mu_B - \beta_A \mu_A)(N_1 - N_2)) \right\}. \tag{E2}$$

In this work, the temperature of the different replicas were chosen to correspond to a constant step in the reciprocal temperature $\beta$ between two successive replicas (roughly corresponding to a temperature step $\Delta T = 1$–3 K). As shown in Ref. 74, HPT provides an accurate estimate of melting/freezing if both liquid and crystal configurations are considered in the initial replicas. In order to quantify the hysteresis between melting and freezing for each pore size, we performed two sets of simulations starting from either only crystal configurations or only liquid configurations. The convergence is monitored by following the number of atoms. Swapping between the crystal and liquid at different temperatures/chemical potentials improves the sampling of phase space, although it remains limited once the replicas have diverged in terms of number of particles and energy.

A confidence interval for the melting temperature $T_m$ can be obtained by identifying the transition region between solid (at low $T$) and liquid (at high $T$) phases. To that end, we analyze the average number of atoms per replica for each pore size, as illustrated in Fig. 9 for $H^* = 11.6$. The approximately linear evolution of the number $N$ with temperature in the low and high temperature regions corresponds to the thermal expansion of the solid and liquid phases (also illustrated by typical snapshots in Fig. 9), respectively. Even though these two regimes are identical in the two sets of simulations starting from only crystal or only liquid configurations, we observe a hysteresis in the transition region. The corresponding range of temperatures is used as our confidence interval for $T_m$, reported for all pore sizes in Fig. 6.
FIG. 9. Average number of atoms N in each HPT-GCMC replica as a function of the replica’s temperature $T^*$ for a pore size $H^* = 11.6$. The two sets of data are obtained starting either from crystal (black circles) or liquid (red triangles) configurations in all replicas. Black dashed lines are linear fits to the low and high temperature regions, which are used to locate the melting temperature $T_m$ (blue shaded area indicating the confidence interval). The snapshots illustrate typical crystal (top right) and liquid (bottom) configurations.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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