

Supplementary Material for The Young-Laplace equation for a solid-liquid interface

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I. EQUILIBRIUM BETWEEN A SOLID CLUSTER AND THE FLUID PHASE FOR HARD SPHERES

In NVT runs it is possible to have an equilibrium between a solid cluster and the fluid phase. This has been shown in previous work.[1] In Fig.1 an equilibrium configuration is shown for the system labeled as IV in Ref.[1]

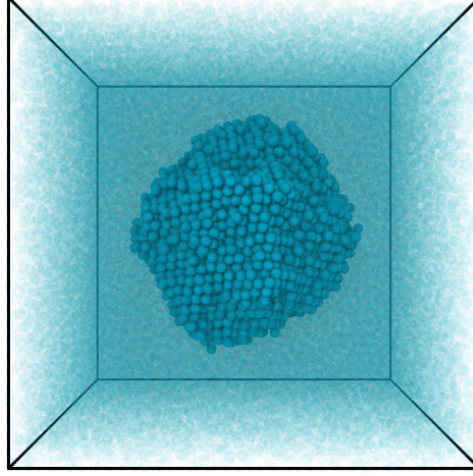


FIG. 1. Snapshot

In the Gibbsian formalism one assumes that the interface has zero volume, but it may contain molecules which are denoted as excess particles. For a system of N particles, the number of internal (N_{int}), external (N_{ext}), and excess molecules (N_{exc}) are defined from the relation:

$$N_{exc} = N - N_{int} - N_{ext} = N - 4/3\pi R^3 \rho_{int} - (V - 4/3\pi R^3)\rho_{ext} \quad (1)$$

Since the chemical potential μ is uniform in the system, it holds that

$$(N_{int} + N_{ext} + N_{exc})\mu = N\mu \quad (2)$$

and that explains the origin of the term $N\mu$ in the expression of F of the main text.

II. PRESSURE TENSOR PROFILE FOR SPHERICAL DROP OF LIQUID IN CONTACT WITH THE VAPOR IN THE LENNARD-JONES SYSTEM

The pressure tensor profile of a liquid-gas curved interface is different from that presented in the main text for a solid-liquid curved interface. Here we present a figure from Ref.[2] to illustrate this point. As can be seen the tangential component of the pressure is smaller than the normal one in the proximity of the interface. That explains why the pressure of the liquid is higher than that of the vapor for a liquid-gas interface. Notice also that for a gas-liquid curved interface (e.g. a bubble inside a liquid) the pressure of the internal phase is also higher than the external pressure.[3] Thus, for a fluid-fluid curved interface the pressure of the internal phase is always higher than that of the external phase.

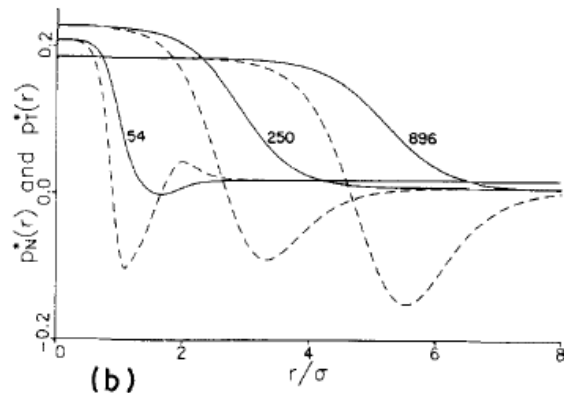


FIG. 2. Pressure tensor profile of a Lennard-Jones spherical droplet at $T^* = 0.71$ (i.e. fluid-vapor interface). Dashed lines stand for the tangential pressure. Solid lines: Normal pressure. Figure adapted from Ref.[2]

III. SPHERICAL PRESSURE TENSOR BY THE IRVING-KIRKWOOD DEFINITION

A. Derivation

The detailed derivation for the spherical pressure tensor has been discussed by Tjatjopoulos and Mann [4], but they only presented results for the normal pressure and one of the tangential components. Here we will present a full derivation for three diagonal elements in the spherical pressure tensor.

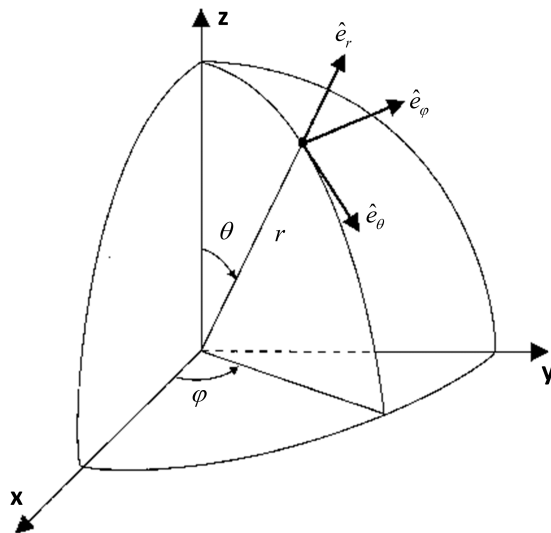


FIG. 3. Spherical coordinate system with corresponding unit vectors in each direction.

In spherical coordinates, (r, θ, φ) , due to the symmetry of the droplet, the local pressure tensor can be written as

$$\mathbf{p}(r) = p_N(r) \hat{e}_r \hat{e}_r + p_T(r) (\hat{e}_\theta \hat{e}_\theta + \hat{e}_\varphi \hat{e}_\varphi), \quad (3)$$

where $p_N = p_{rr}$ is the normal pressure in the radial direction; $p_T = p_{\theta\theta} = p_{\varphi\varphi}$ is the tangential pressure and the polar component, $p_{\theta\theta}$, is equivalent to the azimuthal component, $p_{\varphi\varphi}$. The orthogonal unit vectors are

$$\hat{e}_r = \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix} \quad \hat{e}_\theta = \begin{pmatrix} \cos \theta \cos \varphi \\ \cos \theta \sin \varphi \\ -\sin \theta \end{pmatrix} \quad \hat{e}_\varphi = \begin{pmatrix} -\sin \varphi \\ \cos \varphi \\ 0 \end{pmatrix}. \quad (4)$$

If a system is under the condition of hydrostatic equilibrium and there is no external field, we have $\nabla \cdot \mathbf{p} = 0$, i.e.,

$$p_T(r) = p_N(r) + \frac{r}{2} \frac{dp_N(r)}{dr}. \quad (5)$$

The total pressure tensor is composed of two parts: the kinetic part and the configurational part. The kinetic part is well defined and is given by $\mathbf{p}^K(r) = \rho(r) k_B T \mathbf{1}$, where $\rho(r)$ is the number density at a radial position r ; k_B is the Boltzmann constant, T is temperature and $\mathbf{1}$ is the second order unit tensor. For pairwise interactions, the configurational part is given by [5]

$$\mathbf{p}^C(\mathbf{r}) = \frac{1}{2} \left\langle \sum_{i \neq j} \mathbf{F}_{ij} \int_{C_{ij}} d\tilde{l} \delta(\mathbf{r} - \tilde{l}) \right\rangle, \quad (6)$$

where $\langle \dots \rangle$ is the ensemble average; \mathbf{F}_{ij} is the force vector between ij particle pair, and \tilde{l} is a path vector integrated over the contour C_{ij} ; prefactor 1/2 is to account for double counting of particles. This integral contour is not uniquely defined. Here we adopt the choice of Irving and Kirkwood [2, 6] which is a straight line connecting two interacting molecules. And such a path is given by

$$\tilde{l} = \mathbf{r}_i + \alpha \mathbf{r}_{ij}, \quad (7)$$

where position vector $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. Parameters α varies from 0 to 1. Differentiating the contour vector \tilde{l} gives,

$$d\tilde{l} = \mathbf{r}_{ij} d\alpha. \quad (8)$$

The delta function in Eq. 6 can be rewritten in spherical coordinates as

$$\delta(\mathbf{r} - \tilde{l}) = \frac{1}{r^2 \sin \theta} \delta(r - r_l) \delta(\theta - \theta_l) \delta(\varphi - \varphi_l). \quad (9)$$

Substituting Eq. 9 into Eq. 6 gives

$$\mathbf{p}^C(\mathbf{r}) = \frac{1}{2} \left\langle \sum_{i \neq j} \frac{\mathbf{r}_{ij}}{r_{ij}} f_{ij} \frac{1}{r^2 \sin \theta} \int_{C_{ij}} d\tilde{l} \delta(r - r_l) \delta(\theta - \theta_l) \delta(\varphi - \varphi_l) \right\rangle, \quad (10)$$

where r_{ij} is the scalar distance between ij -pair; f_{ij} is the ij -pair force for isotropic interactions.

1. Normal (Radial) Pressure p_N

The normal pressure is only a function of the radial distance r . We need to perform an average of the normal pressure over both polar and azimuthal angles so as to integrate out unnecessary variables (θ, φ) ,

$$p_N^C(r) = \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta [\hat{e}_r \cdot \mathbf{P}^C(\mathbf{r}) \cdot \hat{e}_r]. \quad (11)$$

The bracket double dot product term in Eq. 11 essentially takes the diagonal element p_{rr}^C out of the 2nd-order pressure tensor. Substituting Eq. 10 into Eq. 11 gives,

$$p_N^C(r) = \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \int_0^{2\pi} d\varphi \int_0^\pi d\theta \int_{C_{ij}} d\vec{l} \cdot \hat{e}_r \frac{\mathbf{r}_{ij} \cdot \hat{e}_r}{r_{ij}} f_{ij} \delta(r - r_l) \delta(\theta - \theta_l) \delta(\varphi - \varphi_l) \right\rangle. \quad (12)$$

Since

$$\int_{a-\varepsilon}^{a+\varepsilon} f(\alpha) \delta(\alpha - a) d\alpha = f(a), \varepsilon > 0, \quad (13)$$

we can perform the integration over polar and azimuthal angles and Eq. 12 becomes

$$p_N^C(r) = \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \int_{C_{ij}} d\vec{l} \cdot \hat{e}_{r,l} \frac{\mathbf{r}_{ij} \cdot \hat{e}_{r,l}}{r_{ij}} f_{ij} \delta(r - r_l) \right\rangle, \quad (14)$$

where $\hat{e}_{r,l}$ is the radial unit vector with $\theta = \theta_l$ and $\varphi = \varphi_l$. Using the differential in Eq. 8 and using the identity,

$$\int_c^d f(\alpha) d\alpha = \int_{-\infty}^{+\infty} f(\alpha) H(\alpha - c) H(d - \alpha) d\alpha. \quad (15)$$

Eq. 14 becomes

$$\begin{aligned} p_N^C(r) &= \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \int_0^1 d\alpha \frac{(\mathbf{r}_{ij} \cdot \hat{e}_{r,l})^2}{r_{ij}} f_{ij} \delta(r - r_l) \right\rangle \\ &= \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \int_{-\infty}^{+\infty} d\alpha \frac{(\mathbf{r}_{ij} \cdot \hat{e}_{r,l})^2}{r_{ij}} f_{ij} H(\alpha) H(1 - \alpha) \delta(r - r_l) \right\rangle, \end{aligned} \quad (16)$$

where $H(x)$ is the Heaviside step function ($x \geq 0$, $H(x) = 1$; $x < 0$, $H(x) = 0$). Applying Eq. 13 and the identity

$$\delta[f(\alpha)] = \sum_k \frac{1}{|f'(\alpha_k)|} \delta(\alpha - \alpha_k), \quad (17)$$

where $f'(\alpha) = df/d\alpha$ and α_k is a simple root of $f(\alpha_k) = 0$, to Eq. 16 yields

$$\begin{aligned} p_N^C(r) &= \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \int_{-\infty}^{+\infty} d\alpha \frac{(\mathbf{r}_{ij} \cdot \hat{e}_{r,l})^2}{r_{ij}} f_{ij} H(\alpha) H(1 - \alpha) \sum_k \frac{1}{|\mathbf{r}_{ij} \cdot \hat{e}_{r,l}|} \delta(\alpha - \alpha_k) \right\rangle \\ &= \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \sum_k \frac{|\mathbf{r}_{ij} \cdot \hat{e}_{r,\alpha_k}|}{r_{ij}} f_{ij} H(\alpha_k) H(1 - \alpha_k) \right\rangle, \end{aligned} \quad (18)$$

recalling $r_l(\alpha) = \sqrt{(x_i + \alpha x_{ij})^2 + (y_i + \alpha y_{ij})^2 + (z_i + \alpha z_{ij})^2}$ and α_k are the roots of a quadratic equation, $r = r_l$, i.e.,

$$(\mathbf{r}_{ij})^2 \alpha^2 + 2\alpha \mathbf{r}_i \cdot \mathbf{r}_{ij} + (\mathbf{r}_i)^2 - r^2 = 0. \quad (19)$$

If the discriminant of Eq. 19 is smaller than zero, there is no contribution to the surface r ; if the discriminant is equal to zero, contour \tilde{l} is tangent to the spherical surface of radius r , and $\mathbf{r}_{ij} \cdot \hat{e}_{r,\alpha_k} = 0$ thus there is no contribution to the surface r either. Only if the discriminant is larger than zero, the force between ij -pair then contributes to the local pressure. The radial unit vector \hat{e}_{r,α_k} at $\alpha = \alpha_k$ is given by

$$\hat{e}_{r,\alpha_k} = \begin{pmatrix} (x_i + \alpha_k x_{ij})/r \\ (y_i + \alpha_k y_{ij})/r \\ (z_i + \alpha_k z_{ij})/r \end{pmatrix}. \quad (20)$$

Because the contour from i to j and the contour from j to i are physically equivalent, we can further simplify Eq. 18 and do the summation over pairs ($i < j$),

$$p_N^C(r) = \frac{1}{4\pi r^2} \left\langle \sum_{i < j} \sum_{k=1}^2 \frac{|\mathbf{r}_{ij} \cdot \hat{e}_{r,\alpha_k}|}{r_{ij}} f_{ij} H(\alpha_k) H(1 - \alpha_k) \right\rangle. \quad (21)$$

Combining the kinetic and configurational contributions together, the total normal pressure is

$$p_N(r) = \rho(r) k_B T + \frac{1}{4\pi r^2} \left\langle \sum_{i < j} \sum_{k=1}^2 \frac{|\mathbf{r}_{ij} \cdot \hat{e}_{r,\alpha_k}|}{r_{ij}} f_{ij} H(\alpha_k) H(1 - \alpha_k) \right\rangle. \quad (22)$$

2. Polar Pressure $p_{\theta\theta}$

The local polar pressure only depends on the radial distance r , an integration over the polar and azimuthal angles must be carried out in a similar manner to Eq. 11. The polar pressure component is given by

$$p_{\theta\theta}^C(r) = \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta [\hat{e}_\theta \cdot \mathbf{p}^C(\mathbf{r}) \cdot \hat{e}_\theta]. \quad (23)$$

Applying Eq. 10 gives

$$p_{\theta\theta}^C(r) = \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \int_0^{2\pi} d\varphi \int_0^\pi d\theta \int_{C_{ij}} d\tilde{l} \cdot \hat{e}_\theta \frac{\mathbf{r}_{ij} \cdot \hat{e}_\theta}{r_{ij}} f_{ij} \delta(r - r_l) \delta(\theta - \theta_l) \delta(\varphi - \varphi_l) \right\rangle. \quad (24)$$

Integrating out variable θ and φ leads to

$$p_{\theta\theta}^C(r) = \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \int_{C_{ij}} d\tilde{l} \cdot \hat{e}_{\theta,l} \frac{\mathbf{r}_{ij} \cdot \hat{e}_{\theta,l}}{r_{ij}} f_{ij} \delta(r - r_l) \right\rangle, \quad (25)$$

where $\hat{e}_{\theta,l}$ is the polar unit vector with $\theta = \theta_l$ and $\varphi = \varphi_l$. Now, replacing the line element $d\tilde{l}$ in Eq. 25 with Eq. 8 results in

$$p_{\theta\theta}^C(r) = \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \int_0^1 d\alpha \frac{(\mathbf{r}_{ij} \cdot \hat{e}_{\theta,l})^2}{r_{ij}} f_{ij} \delta(r - r_l) \right\rangle. \quad (26)$$

Applying the identity (Eq. 17) to above Eq. 26 and carrying out the integration yields,

$$p_{\theta\theta}^C(r) = \frac{1}{8\pi r^2} \left\langle \sum_{i \neq j} \sum_{k=1}^2 \frac{(\mathbf{r}_{ij} \cdot \hat{e}_{\theta,\alpha_k})^2}{|\mathbf{r}_{ij} \cdot \hat{e}_{r,\alpha_k}| r_{ij}} f_{ij} H(\alpha_k) H(1 - \alpha_k) \right\rangle, \quad (27)$$

where

$$\hat{e}_{\theta, \alpha_k} = \begin{pmatrix} (x_i + \alpha_k x_{ij}) (z_i + \alpha_k z_{ij}) / (r d_{xy}) \\ (y_i + \alpha_k y_{ij}) (z_i + \alpha_k z_{ij}) / (r d_{xy}) \\ -d_{xy} / r \end{pmatrix}, \quad (28)$$

and $d_{xy} = \sqrt{(x_i + \alpha_k x_{ij})^2 + (y_i + \alpha_k y_{ij})^2}$; α_k are roots of Eq. 19. Thus, the local polar pressure is given by

$$p_{\theta\theta}(r) = \rho(r) k_B T + \frac{1}{4\pi r^2} \left\langle \sum_{i < j} \sum_{k=1}^2 \frac{(\mathbf{r}_{ij} \cdot \hat{e}_{\theta, \alpha_k})^2}{|\mathbf{r}_{ij} \cdot \hat{e}_{r, \alpha_k}|} \frac{f_{ij}}{r_{ij}} H(\alpha_k) H(1 - \alpha_k) \right\rangle. \quad (29)$$

3. Azimuthal Pressure $p_{\varphi\varphi}$

Following the similar derivation as shown above, we can obtain the local azimuthal pressure in a form of

$$p_{\varphi\varphi}(r) = \rho(r) k_B T + \frac{1}{4\pi r^2} \left\langle \sum_{i < j} \sum_{k=1}^2 \frac{(\mathbf{r}_{ij} \cdot \hat{e}_{\varphi, \alpha_k})^2}{|\mathbf{r}_{ij} \cdot \hat{e}_{r, \alpha_k}|} \frac{f_{ij}}{r_{ij}} H(\alpha_k) H(1 - \alpha_k) \right\rangle, \quad (30)$$

where

$$\hat{e}_{\varphi, \alpha_k} = \begin{pmatrix} -(y_i + \alpha_k y_{ij}) / d_{xy} \\ (x_i + \alpha_k x_{ij}) / d_{xy} \\ 0 \end{pmatrix}. \quad (31)$$

We note that the configurational part (second term on the right) in Eq. 30 is equivalent to Eq. (20) in Ref. [4] although they have different appearance. Unlike the method in Ref. [4] that takes an average over a number of φ -surface in computation, here we have already averaged over all possible φ analytically through integration. The final tangential pressure is calculated by $p_T(r) = [p_{\theta\theta}(r) + p_{\varphi\varphi}(r)]/2$.

B. Results and Discussions: Critical Nucleus in Liquids

In this section, we present the pressure profile for critical nucleus in liquids. The pseudo-hard sphere potential u_{PHS} is of Mie type (50-49) and is given by the expression[7]:

$$u_{PHS}(r) = \begin{cases} 50 \left(\frac{50}{49}\right)^{49} \epsilon \left[\left(\frac{\sigma}{r}\right)^{50} - \left(\frac{\sigma}{r}\right)^{49} \right] + \epsilon & r < \left(\frac{50}{49}\right) \sigma \\ 0 & r \geq \left(\frac{50}{49}\right) \sigma \end{cases} \quad (32)$$

where σ represents the hard sphere diameter and ϵ is the depth of the potential. It has been shown in previous work[7] that the properties of the PHS are quite close to that of the HS system when the reduced temperature $T^* = T/(\epsilon/k) = 1.5$. To simulate the PHS potential we shall use the parameters of the Lennard-Jones potential of Ar, namely $\sigma = 3.405 \text{ \AA}$, $\epsilon/k = 119.80667 \text{ K}$. Simulations were performed at $T = 179.71 \text{ K}$ ($T^* = 1.5$). Results, in reduced units of pressure (i.e in units of kT/σ^3) are shown in the main text. The discrete p_N data were fitted to a hyperbolic equation [2, 8]

$$p_N(r) = \frac{1}{2} (p_{sol} + p_{liq}) + \frac{p_{liq}}{2} \tanh \left[2(r - r_{liq}) / d_{liq} \right] - \frac{p_{sol}}{2} \tanh \left[2(r - r_{sol}) / d_{sol} \right], \quad (33)$$

where subscript sol denotes the solid, liq denotes the liquid; p_{sol} and p_{liq} are the normal pressure of the bulk solid and that of the bulk liquid, respectively; r_{sol} and r_{liq} are the radial positions of the inflection points on the normal pressure profile for the corresponding phase; d_{sol} and d_{liq} are the width of the interface for the corresponding phase. Fitting parameters are listed in Table I.

Label	p_{sol}	p_{liq}	r_{sol}	r_{liq}	d_{sol}	d_{liq}
IV	12.5996	12.7444	10.8752	10.8546	3.77093	3.78267
VII	12.3053	12.4039	15.5184	15.5037	3.83847	3.84728
VIII	12.2177	12.3005	17.6211	17.6094	4.01175	4.01468

TABLE I. Parameters of the fit to p_N . Pressure in reduced units (i.e in units of kT/σ^3). Distances in reduced units (i.e in units of σ).

The discrete data of p_T is not fitted. Instead, we estimate its functionality by applying the hyperbolic form of p_N along with the fit parameters to equation 5.

We show here the table from the main text on the values for pressure and density on the solid cluster and surrounding liquid. The values are obtained by linear regression only in the plateaus, hence, they slightly differ from the asymptotic values obtained from our previous fit.

Label	R_s	ρ_{sol}	ρ_{liq}	p_{sol}	p_{liq}	Δp
IV	10.791	1.0613	0.9619	12.6046	12.7437	-0.1391
VII	15.20	1.0548	0.9560	12.3053	12.4047	-0.0994
VIII	17.467	1.0529	0.9541	12.2199	12.3003	-0.0804

TABLE II. From the main text, densities and pressures (for the solid and fluid) as determined by the respectively plateaus in the density and pressure profiles. The difference in pressure is also given as $\Delta p = p_{sol} - p_{liq}$. The notation of IV, VII and VIII refers to the clusters labeled in this way in Ref.[1]. Results are given in reduced units.

IV. CLUSTER VII

In the main text, we show the profiles for clusters IV and VIII. Here we show cluster VII which is intermediate in size between the other two.

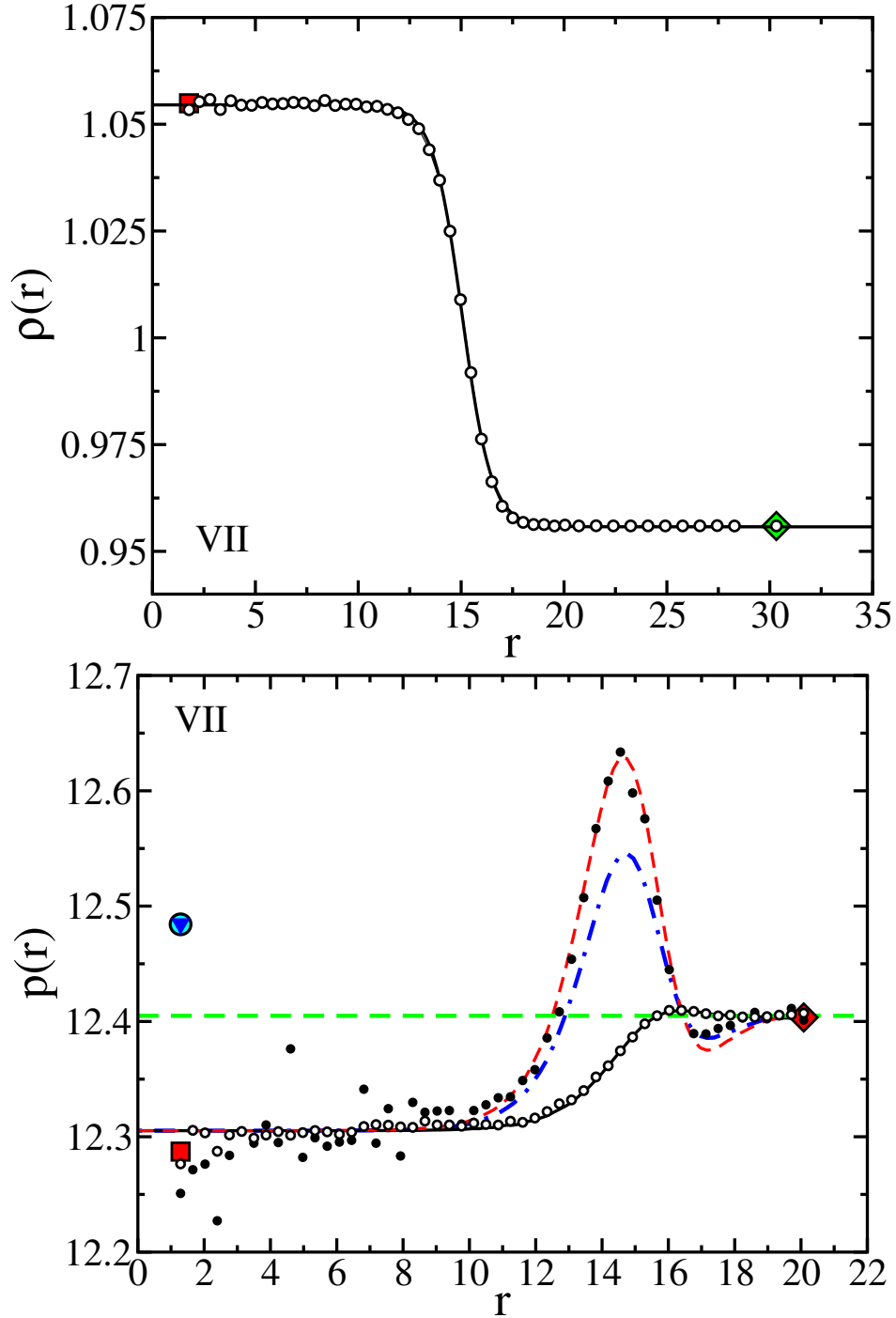


FIG. 4. Radial density (left) and pressure (right) profiles from the COM for cluster VII. See caption in Fig. 1 of main text for explanation.

V. THEOREM OF THE MEAN PRESSURE: $\langle p \rangle = p_{ext}$

It is simple to show that the average pressure obtained by applying the virial theorem to the entire inhomogeneous system (in the NVT ensemble) $\langle p \rangle$, or integrating the pressure tensor over the entire volume, is identical to the pressure of the external phase p_{ext} provided that both the normal and tangent components of the pressure tensor are identical at $L/2$ (half the value of the simulation box). We shall locate the center of mass of the solid cluster in the center of the simulation box. That it holds :

$$\langle p \rangle = p_{ext} \quad (34)$$

Let us prove this. Firstly one defines a local pressure as :

$$\bar{p}(r) = \frac{1}{3} [p_N(r) + 2p_T(r)] \quad (35)$$

We shall assume that beyond $L/2$ (in the corners of the simulation box) the normal and tangential components are equal and its value is p_{ext} . What is of interest is to determine the average pressure in the region between the center of mass of the solid cluster and $L/2$ and to show if this average is just p_{ext} . We shall now determine the average pressure by integration of the local net pressure over the spherical region with radius $L/2$:

$$\langle \bar{p} \rangle = \frac{24}{L^3} \int_0^{L/2} r^2 \bar{p}(r) dr \quad (36)$$

Substitution of equation 35 within equation 36 gives

$$\langle \bar{p} \rangle = \frac{8}{L^3} \left[\int_0^{L/2} r^2 (p_N(r) + 2 \cdot p_T(r)) dr \right] \quad (37)$$

Now, the mechanical equilibrium condition $\nabla \cdot \mathbf{p}$ implies

$$p_T(r) = p_N(r) + \frac{r}{2} \frac{dp_N}{dr} \quad (38)$$

Substitution in equation 37 gives

$$\langle \bar{p} \rangle = \frac{8}{L^3} \left[\int_0^{L/2} r^2 p_N(r) dr + 2 \int_0^{L/2} r^2 p_N(r) dr + \int_{p(0)}^{p(L/2)} r^3 dp_N \right] = \frac{8}{L^3} \left[3 \int_0^{L/2} r^2 p_N(r) dr + \int_{p(0)}^{p(L/2)} r^3 dp_N \right] \quad (39)$$

. By solving the second integral by parts, (i.e. $u = r^3$, $du = 3r^2 dr$; $dv = dp_N$; $v = p_N$), one finds

$$\langle \bar{p} \rangle = \frac{8}{L^3} \left[3 \int_0^{L/2} r^2 p_N(r) dr + r^3 p_N(r) \Big|_0^{L/2} - 3 \int_0^{L/2} r^2 p_N(r) dr \right] = \frac{8}{L^3} \left[\frac{L^3}{8} \cdot p_N(L/2) \right] \quad (40)$$

Thus,

$$\langle \bar{p} \rangle = p_N(L/2) = p_{ext} \quad (41)$$

In general at $L/2$ both the tangential and normal components are identical and they have already reached the value of the plateau of the pressure for the external phase and one may conclude that :

$$\langle \bar{p} \rangle = p_{ext} \quad (42)$$

The lower pressure of the normal component inside the cluster is exactly compensated by the higher pressure of the two tangential components. Thus the average pressure of the system (as given by the virial equation) will be identical to the pressure of the external phase. To derive this equation it was only needed to apply the equation of mechanical equilibrium and to assume that at $L/2$ the system has already reached the pressure of the external phase.

VI. CRYSTAL-LIQUID EQUATIONS OF STATE

The equations of state can be described by quadratic fits $p = \sum_{i=1}^n c_i \rho^i$. The corresponding parameters are presented below.

Phase	c_0	c_1	c_2
Crystal	132.175	-271.979	150.094
Liquid	97.6991	-235.516	153.029

TABLE III. Parameters of the fits to the equations of state of both solid and liquid.

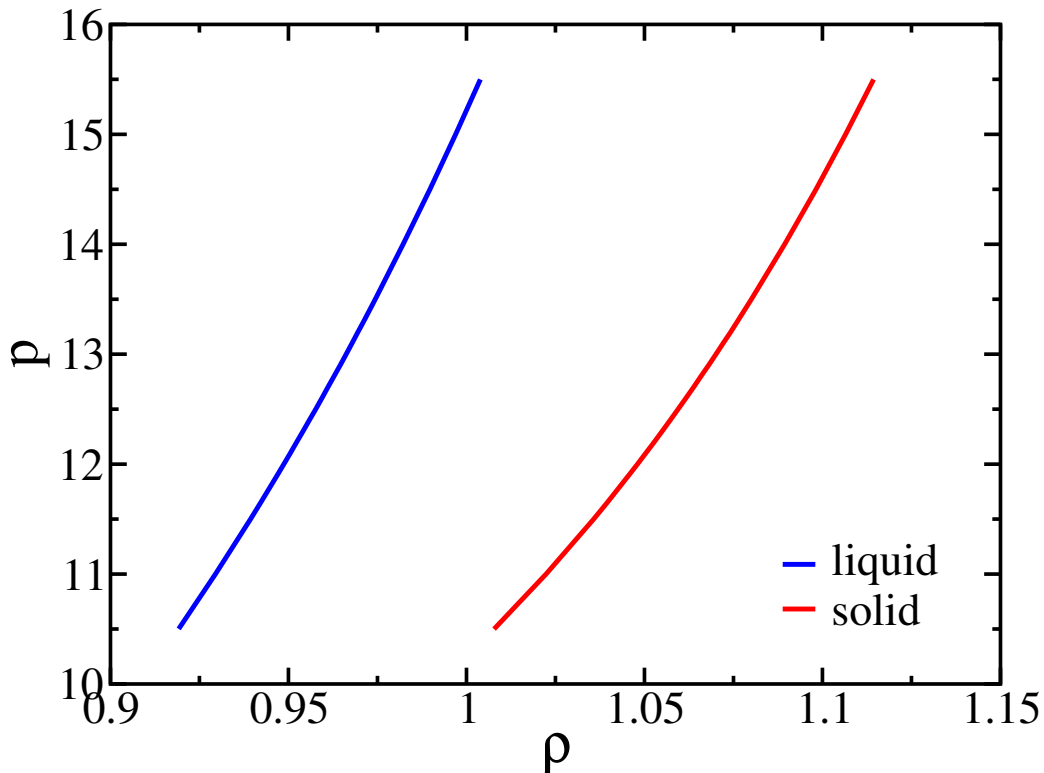


FIG. 5. Equations of state.

VII. ASSUMING THAT THE CHEMICAL POTENTIAL OF THE INHOMOGENEOUS SYSTEM μ IS CLOSE TO THE CHEMICAL POTENTIAL OF A BULK SOLID AT p_{sol} .

In the main text we assumed that the chemical potential μ (which strictly speaking must be determined in independent calculations) can be taken from that of a bulk fluid phase at p_{ext} . Here we shall analyze what would happen if the value of μ of the inhomogeneous system were closer to the properties of a bulk solid at p_{sol} . If this is the case then, it would be necessary to introduce p_{liq}^μ as the pressure of a bulk fluid with the same chemical potential as the bulk solid at p_{sol} . The Gibbrian formalism in this case would read:

$$F = N \mu - p_{sol} \frac{4}{3} \pi R^3 - p_{liq}^\mu (V - \frac{4}{3} \pi R^3) + 4\pi R^2 \gamma \quad (43)$$

Since F is invariant to arbitrary changes in R one then obtains (for the choice of R that leads to a minimum of γ):

$$p_{sol} - p_{liq}^\mu = \frac{2\gamma_s}{R_s} \quad (44)$$

Label	R_s	p_{sol}	p_{liq}^μ	$\Delta p^\mu = p_{sol} - p_{liq}^\mu$	$2\gamma_s/R_s$
IV	10.791	12.6046	12.523	0.0816	0.1164
VII	15.200	12.3053	12.250	0.0553	0.0793
VIII	17.467	12.2199	12.165	0.0549	0.0694

TABLE IV. Pressure of the solid and thermodynamic pressure of the fluid, obtained by assuming that the chemical potential of the inhomogeneous system μ can be estimated from that of a bulk solid at p_{sol} . By using the values of γ_s from nucleation studies we estimate the term $2\gamma_s/R_s$ and found to be in fair agreement with the difference in pressure obtained when using the thermodynamic pressure for the fluid. The notation of IV, VII, and VIII refers to the clusters labeled in this way in Ref.[1]. Results are given in reduced units.

In Table IV the value of p_{liq}^μ for the three systems considered in this work (IV, VII, VIII) is presented and also the difference in pressure $\Delta p^\mu = p_{sol} - p_{liq}^\mu$. The value of $2\gamma_s/R_s$ from nucleation studies is also shown. As can be seen, Δp^μ is in fair agreement with $2\gamma_s/R_s$. The agreement with the value $2\gamma_s/R_s$ from nucleation studies is somewhat worse than that presented in the main text, strongly suggesting that the chemical potential of the inhomogeneous system μ is probably closer to that of the bulk liquid external phase.

Probably if μ were calculated rigorously it would correspond to an intermediate case (neither that of the bulk fluid at p_{liq} nor that of the bulk solid at p_{sol} but at some intermediate value probably closer to the first one). In this case it would be necessary to introduce the thermodynamic pressures for both phases. However the expected value of Δp^μ would be intermediate between the value of the main paper and that presented in this Appendix and close to the value $2\gamma_s/R_s$ obtained from nucleation studies.

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