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Evaluating the Laplace pressure of water nanodroplets from simulations

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Abstract

We calculate the components of the microscopic pressure tensor as a function of radial distance r from the centre of a spherical water droplet, modelled using the TIP4P/2005 potential. To do so, we modify a coarse-graining method for calculating the microscopic pressure (Ikeshoji *et al* 2003 *Mol. Simul.* **29** 101) in order to apply it to a rigid molecular model of water. As test cases, we study nanodroplets ranging in size from 776 to 2880 molecules at 220 K. Beneath a surface region comprising approximately two molecular layers, the pressure tensor becomes approximately isotropic and constant with r . We find that the dependence of the pressure on droplet radius is that expected from the Young–Laplace equation, despite the small size of the droplets.

Keywords: water, nanodroplets, Laplace pressure, microscopic pressure, TIP4P/2005, molecular dynamics simulations

(Some figures may appear in colour only in the online journal)

1. Introduction

Small droplets of liquid water are important to atmospheric science and technological applications, and understanding the properties and role of the surface is increasingly important as droplets become nanoscopic. Surface effects can profoundly influence the mechanism and rate of crystallization in general. In water, the role of surface freezing is still unresolved [1].

Significant to much of the discussion is the Laplace pressure, the pressure difference between the interior and exterior of a droplet of radius R arising from the liquid–vapour surface tension γ , as quantified by the Young–Laplace equation for droplets,

$$\Delta P = \frac{2\gamma}{R}. \quad (1)$$

Galli and coworkers modelled the effect within nanodroplets of the Laplace pressure on nucleation rates [2]. They argued

that since the interior of the nanodroplet is at a higher pressure, the liquid there is less supercooled on account of the decreasing melting temperature of ice Ih with increasing pressure. Hence nucleation rates should be greatly diminished in the interior. Espinosa *et al* [3] went on to show that the liquid-Ih surface tension also increases with increasing pressure, further suppressing nucleation. By contrast, the nanodroplet surface, though prone to disorder, experiences a negative pressure, and should thus be more supercooled and therefore enhance nucleation rates. The simulations of [2] showed that nucleation rates for mW [4] water nanodroplets are progressively and greatly suppressed as nanodroplet size decreases, and that the rates are the same within error for $R \geq 3.1$ nm when compared to the bulk at the same density. For smaller nanodroplets, the difference in rates between droplets and bulk at the same density is significant. The authors argue, however, that for real water, for which the density difference between liquid and crystal at melting is larger than in mW water, surface nucleation should be favoured in microdroplets. We note that while the authors estimated the Laplace pressure through

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equation (1) and provided a check of the equation by determining the pressure of the bulk at the same density as inside the nanodroplets, they did not explicitly calculate the pressure inside the droplets. Nor is it clear to what extent equation (1) should hold for more realistic models of water, such as the TIP4P model [5] and related potentials [6].

The insights of [2] have been enriched by the work of Haji-Akbari and Debenedetti [7] on water nanofilms. They found that nucleation rates obtained using the TIP4P/ice [8] model of water are enhanced by a factor of 10^7 within the nanofilm in comparison to the bulk. The enhancement stems not from the interface, where crystal-like ordering is reduced, but rather from a relative abundance of ‘double-diamond cages’ over hexagonal cages in the interior of the film compared to bulk. The latter cage type is less favourable for nucleation. Their work therefore indicates the importance of subtle changes in structure arising from the finite extent of the system, and diminishes the importance of the negative pressure near the interface. However, this study was conducted on films, where the internal pressure is no different from the ambient, and therefore did not address the role of the Laplace pressure on the interior.

Recent experiments on microdroplets, for which the Laplace pressure is likely negligible, have pushed the limits of observing liquid water below the bulk homogeneous nucleation limit of 235 K by determining nucleation rates down to 227 K [9]. Nucleation rates at significantly lower temperatures have been measured for nanodroplets with radii of just a few nanometers [10, 11], for which the Laplace pressure is likely significant. An experimental study of water clusters in the range of 100–1000 molecules showed that crystallization may be entirely suppressed below roughly 275 molecules [12], at which point surface effects may dominate and the Laplace pressure would be quite high. Given that experiments probe ever smaller systems, it is crucial to develop a better understanding of the basic physical properties of nanodroplets, including the pressure.

The theoretical and experimental developments described above all point to the need for a detailed analysis of the microscopic pressure tensor within water nanodroplets and its connection to the Laplace pressure. This is the subject of this paper. The work on ST2 water clusters of Brodskaya *et al* [13, 14] found significantly elevated pressures within nanodroplet interiors. Thompson *et al* [15] provided a detailed description of the methodology for calculating the pressure tensor in droplets in the context of Lennard-Jones particles. We base our calculations on the work by Ikeshoji *et al* [16], who developed a coarse-grained scheme for calculating the molecular-scale pressure for simple particles interacting with radial potentials. The advantages of their method include improved statistics over non-coarse-grained methods (e.g. [15]), as well as the ability to directly calculate both the normal and transverse components of the pressure tensor. The method was applied to a molecular model of water, SPC/E [17], in a study of methane hydrate droplets embedded in ice [18], but no details on how the method was modified for molecules were given. The method of [16] was later generalized to molecules in a way that considered multibody intramolecular interactions, and applied to non-rigid chain-like organic molecules interacting with a coarse grained-model for water [19]. However, for

rigid multi-site water models such as TIP4P/2005, it is more straightforward to modify [16] in a way that does not require the consideration of intramolecular interactions, i.e. forces of constraint. It is this latter approach that we present here. That is, we adapt the method of [16] to TIP4P/2005 water nanodroplets, and give details of the calculation.

This paper is organized as follows. Section 2 describes our molecular dynamic simulations of TIP4P/2005 water nanodroplets. In section 3 we show in detail how we adapt and apply the method introduced in [16] to water, comment on the utility of the method in terms of independently calculating the normal and transverse components of the local pressure tensor, and introduce an energy-based approximate method of calculating the local isotropic pressure and use it as a check of our results. We present the pressure components as functions of radial distance from the centre of mass of a nanodroplet and validate the form of equation (1) in section 4, before concluding in section 5.

2. Simulations

We simulate nanodroplets of $N = 776, 1100, 1440$ and 2880 water molecules interacting through the TIP4P/2005 water model [20]. All simulations are done at temperature $T = 220$ K, where the vapour pressure is negligible. For $N = 1440$ and 2880 , we initially prepare a droplet system of a given size by placing N water molecules randomly in a rather large cubic simulation box and simulating at constant volume. The molecules naturally condense into a droplet surrounded by a very low density vapour. The equilibrated configuration is then run for many relaxation times to get equilibrium properties of the droplets. We produce two spherical droplets of size $N = 776$ and 1100 by removing molecules beyond an appropriate radial distance from the centre of an equilibrated $N = 1440$ droplet. For the $N = 776$ system, the simulation box length $L = 15$ nm. For the larger droplets $L = 20$ nm. We use a potential cutoff of $L/2$, and employ periodic boundary conditions to ensure that vapour molecules can return to the droplet in order to avoid eventual evaporation. The box is large enough to avoid any direct interaction between the water droplet and its periodic images. With this setup, molecules within the droplet interact through the full, untruncated potential, including electrostatic interactions. We use Gromacs v4.6.1 [21] to carry out the molecular dynamics simulations. We hold T constant with the Nosé-Hoover thermostat. The equations of motion are integrated with the leap-frog algorithm with a time step of 2 fs. The total simulation times for the four droplet sizes, in order of increasing N , are 862, 633, 593 and 182 ns.

To determine equilibration and relaxation times, we monitor the decay of the bond autocorrelation function $\phi(t)$, which gives the probability that a bond present at time $t = 0$ remains unbroken until time t [22]. Two molecules i and j are considered bonded if the distance between their O atoms is less than 0.32 nm, the location of the first minimum in the oxygen–oxygen radial distribution function of bulk water at ambient conditions. The calculation of $\phi(t)$ is sensitive to the sampling interval, which in our case falls between 0.2 and 0.8 ns. We

cannot discriminate between persistent and reformed bonds on times shorter than our sampling time, and so our $\phi(t)$ provides an upper bound on the true value.

Error bars for various quantities are calculated by taking the standard deviation in a quantity over all sampled equilibrium configurations, and dividing by $\sqrt{n_{\text{ind}}}$, where $n_{\text{ind}} = t_{\text{eq}}/\tau_\phi$ is the estimated number of independent configurations sampled, t_{eq} is the duration of the equilibrated time series used for averaging, and τ_ϕ is the time at which $\phi(t) \leq e^{-1} \approx 0.368$. For example, for the $N = 1100$ droplet, the simulation is carried out for a total of 633 ns, the first 129 ns of which are discarded, leaving $t_{\text{eq}} = 504$ ns. Our determination of $\phi(t)$ is not very well resolved in time, but we determine that $\phi(0.8 \text{ ns}) = 0.08$ and so we set $\tau_\phi = 0.8$ ns and hence $n_{\text{ind}} \approx 500/0.8 = 625$. Our estimates for the number of independent configurations sampled in equilibrium for the other sizes are 1917 ($N = 776$), 1588 ($N = 1440$) and 48 ($N = 2880$).

3. Microscopic pressure

3.1. Pressure profiles

To calculate the normal $P_N(r)$ and tangential $P_T(r)$ components of the pressure tensor as a function of radial distance r from the centre of mass of the water nanodroplet, we follow the prescription of Ikeshoji *et al* [16] for a spherical geometry. Below we reproduce their approach, which uses a coarse graining wherein the pressure components at r are calculated as averages over a thin spherical shell of finite thickness in order to improve statistics and to avoid divergences in $P_T(r)$.

Their method was presented for particles interacting through central forces. We introduce adaptations required since the pair force between water molecules is not central (although the site-site interactions are). The generalization is straightforward since only the intermolecular forces need to be considered and they need not be central [13, 14, 23]. In order to present the reader with a self-contained explanation of the method, we have reproduced relevant portions of [16] here. To be more explicit, equations (2)–(14) and their development are adapted from [16], albeit with slightly different notation, while equations (15)–(24) have been modified because of the non-central force between molecules. Figure 1 is adapted from [16] to explicitly include all types of molecular pair contributions. We introduce table 1 to provide mathematical details that complement figure 1.

Schofield and Henderson [24] showed that the pressure tensor at a point \mathbf{R} in space is given by [15, 24],

$$P'_{\alpha\beta}(\mathbf{R}) = \langle P'_{c,\alpha\beta}(\mathbf{R}) \rangle + \langle P'_{k,\alpha\beta}(\mathbf{R}) \rangle, \quad (2)$$

where

$$\langle P'_{k,\alpha\beta}(\mathbf{R}) \rangle = k_B T \rho(\mathbf{R}) \delta_{\alpha\beta}, \quad (3)$$

is the kinetic part, and follows directly from the local equilibrium density $\rho(\mathbf{R})$. The brackets $\langle \dots \rangle$ indicate an ensemble average, i.e. an average over a set of equilibrated configurations, and $\delta_{\alpha\beta}$ is the Kronecker delta. Pressures annotated with a prime indicate that the pressure is calculated at a single

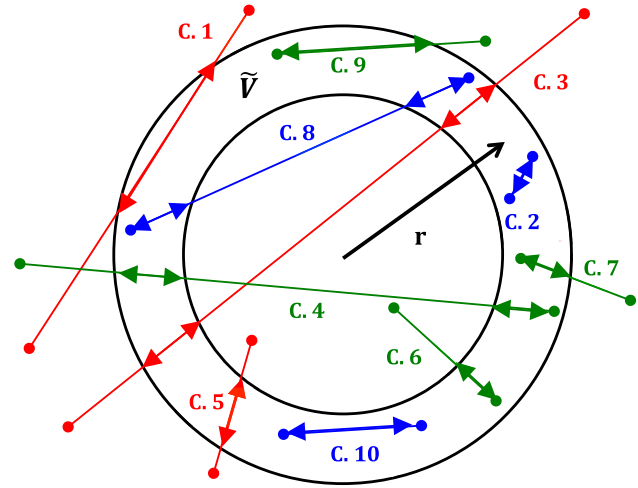


Figure 1. A sketch of all possible contributions to P in \tilde{V} from the coarse-graining method of Ikeshoji *et al* [16]. See table 1 for details. The contours C_{ij} are line segments between molecules i and j (filled circles). The portions of C_{ij} between arrows contribute to the pressure. \tilde{V} is a spherical shell of inner radius $R_{\text{in}} = r - \Delta R/2$ and outer radius $R_{\text{out}} = r + \Delta R/2$.

point in space. Pressures without primes refer to quantities that are coarse-grained (averaged) over a small volume.

The configurational contribution is obtained from intermolecular pair forces, and is given by,

$$P'_{c,\alpha\beta}(\mathbf{R}) = \frac{1}{2} \sum_i \sum_{j \neq i} P'_{ij,\alpha\beta}(\mathbf{R}), \quad (4)$$

where the molecular pair-wise contribution to the pressure is given by,

$$P'_{ij,\alpha\beta}(\mathbf{R}) = \int_{C_{ij}} f_{ij,\alpha} \delta(\mathbf{R} - \mathbf{l}) dl_\beta, \quad (5)$$

where $f_{ij,\alpha}$ is the α component of the force on molecule j due to molecule i , \mathbf{f}_{ij} , $\delta(\mathbf{R} - \mathbf{l})$ is the Dirac delta function, C_{ij} is a contour from i to j , \mathbf{l} is a vector indicating a point on C_{ij} , and dl_β is the β component of an infinitesimal portion of the path along C_{ij} . We stress that \mathbf{f}_{ij} is the force between two molecules, i.e. the quantity that is responsible for the acceleration of the centres of mass of the molecules. We consider neither torques nor forces between atoms on the same molecule nor forces of constraint [23]. For TIP4P/2005, \mathbf{f}_{ij} is obtained by summing over all of the interactions between charge and Lennard-Jones sites on molecule i and those on molecule j . The freedom in choosing C_{ij} renders the definition of the microscopic pressure non-unique. Ikeshoji *et al* [16] follows the convention of defining C_{ij} to be a straight line segment connecting the centres of mass of molecules i and j , consistent with the Irving-Kirkwood definition of the pressure tensor [25]. As we comment below, this simple and intuitive choice of C_{ij} leads to divergences in $P_T(r)$ that coarse-graining eliminates.

The coarse-graining procedure amounts to carrying out an integration of equation (2) over \mathbf{R} within a spherical shell of radius r , thickness Δr and volume $\tilde{V} = 4\pi[R_{\text{out}}^3 - R_{\text{in}}^3]/3$, with $R_{\text{out}} = r + \Delta r/2$ and $R_{\text{in}} = r - \Delta r/2$. We set $\Delta r = 0.05$ nm. The coarse-grained pressure $P_{\alpha\beta}(r)$ is given by,

Table 1. List of all 16 solution sets of equation (11) that contribute to equation (13) and the resulting limits of integration. In all cases $D_{\text{out}} > 0$. Entries in the rightmost column refer to curve labels in figure 1.

D_{in}	λ_{-}^{in}	λ_{+}^{in}	λ_{-}^{out}	λ_{+}^{out}	λ_a	λ_b	λ'_a	λ'_b	Case
<0			[0, 1]	[0, 1]	λ_{-}^{out}	λ_{+}^{out}			C.1
>0	<0	<0	<0	>1	0	1			C.2
>0	>1	>1	<0	>1	0	1			C.2
>0	[0, 1]	[0, 1]	[0, 1]	[0, 1]	λ_{-}^{out}	λ_{-}^{in}	λ_{+}^{in}	λ_{+}^{out}	C.3
>0	[0, 1]	[0, 1]	<0	[0, 1]	0	λ_{-}^{in}	λ_{+}^{in}	λ_{+}^{out}	C.4
>0	[0, 1]	[0, 1]	[0, 1]	>1	λ_{-}^{out}	λ_{-}^{in}	λ_{+}^{in}	1	C.4
>0	<0	[0, 1]	<0	[0, 1]	λ_{+}^{in}	λ_{+}^{out}			C.5
>0	[0, 1]	>1	[0, 1]	>1	λ_{-}^{out}	λ_{-}^{in}			C.5
>0	<0	[0, 1]	<0	>1	λ_{+}^{in}	1			C.6
>0	[0, 1]	>1	<0	>1	0	λ_{-}^{in}			C.6
>0	<0	<0	<0	[0, 1]	0	λ_{+}^{out}			C.7
>0	>1	>1	[0, 1]	>1	λ_{-}^{out}	1			C.7
>0	[0, 1]	[0, 1]	<0	>1	0	λ_{-}^{in}	λ_{+}^{in}	1	C.8
<0			<0	[0, 1]	0	λ_{+}^{out}			C.9
<0			[0, 1]	>1	λ_{-}^{out}	1			C.9
<0			<0	>1	0	1			C.10

$$P_{\alpha\beta}(r) = \frac{1}{\tilde{V}} \int_{\tilde{V}} P'_{\alpha\beta}(\mathbf{R}) d\mathbf{R} = \langle P_{c,\alpha\beta} \rangle + \langle P_{k,\alpha\beta} \rangle. \quad (6)$$

The kinetic part is still calculated from the density, but now averaged over \tilde{V} . The configurational part maintains the same form as before,

$$P_{c,\alpha\beta} = \frac{1}{2} \sum_i \sum_{j \neq i} P_{ij,\alpha\beta}, \quad (7)$$

but now the coarse-grained contribution to the pressure from an interaction between a pair of molecules is given by,

$$\begin{aligned} P_{ij,\alpha\beta} &= \frac{1}{\tilde{V}} \int_{\tilde{V}} \int_{C_{ij}} f_{ij,\alpha} \delta(\mathbf{R} - \mathbf{l}) dl_{\beta} d\mathbf{R}, \\ &= \frac{1}{\tilde{V}} \int_{C_{ij}} f_{ij,\alpha} \left[\int_{\tilde{V}} \delta(\mathbf{R} - \mathbf{l}) d\mathbf{R} \right] dl_{\beta}, \\ &= \frac{1}{\tilde{V}} \int_{C_{ij} \in \tilde{V}} f_{ij,\alpha} dl_{\beta}, \end{aligned} \quad (8)$$

where the force between molecules i and j contributes to the pressure in \tilde{V} only along the parts of C_{ij} that are in \tilde{V} . Regardless of the location of i and j , i.e. whether they are in \tilde{V} or not, as long as the line between them passes through \tilde{V} , their interaction contributes to the pressure.

To determine the part of C_{ij} that contributes to the pressure in \tilde{V} , one first uses a parametric expression for $\mathbf{l}(\lambda)$ that defines points located on C_{ij} ,

$$\mathbf{l}(\lambda) = \mathbf{r}_i + \lambda \mathbf{r}_{ij}, \quad (9)$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, i.e. the vector pointing from i to j . (For repulsion, \mathbf{f}_{ij} points approximately along \mathbf{r}_{ij} .) Points on C_{ij} correspond to $\lambda \in [0, 1]$.

Figure 1 shows a sketch of all possible contributions from molecular pair interactions to \tilde{V} in the coarse-grained method.

The contributions from C_{ij} that contribute to the pressure in \tilde{V} are portions of lines between arrows, while the line between small filled circles is the line segment connecting particles i and j . For a given line, the portion between arrows corresponds to $\lambda_a \leq \lambda \leq \lambda_b$, with a and b labelling entry and exit points. If the line intersects \tilde{V} over two segments (yielding two contributions to the pressure), there is a second set of entry and exit points that define the segment $\lambda'_a \leq \lambda \leq \lambda'_b$. If $\mathbf{r}_i \in \tilde{V}$ then $\lambda_a = 0$, while if $\mathbf{r}_j \in \tilde{V}$ then λ_b (or λ'_b if it exists) = 1.

A precise determination of relevant intersections between the line $\mathbf{l}(\lambda)$ and the spheres bounding \tilde{V} requires solving the equation,

$$\mathbf{l}(\lambda) \cdot \mathbf{l}(\lambda) = r_i^2 + \lambda 2\mathbf{r}_i \cdot \mathbf{r}_{ij} + \lambda^2 r_{ij}^2 = R_{\text{out}}^2, \quad (10)$$

and a similar one for R_{in} . The magnitudes of \mathbf{r}_i and \mathbf{r}_{ij} are r_i and r_{ij} , respectively. The solutions to these quadratic equations are,

$$\lambda_{\pm}^{\text{in/out}} = -\frac{\mathbf{r}_i \cdot \mathbf{r}_{ij}}{r_{ij}^2} \pm \frac{1}{r_{ij}^2} \sqrt{D_{\text{in/out}}}, \quad (11)$$

where the discriminants are given by,

$$D_{\text{in/out}} = (\mathbf{r}_i \cdot \mathbf{r}_{ij})^2 - r_{ij}^2 (r_i^2 - R_{\text{in/out}}^2). \quad (12)$$

If $D_{\text{out}} < 0$, there are no intersections and the pair interaction gives no contribution to the pressure in \tilde{V} . All of the possible cases for solution sets yielding pressure contributions and the resulting limits of integration are given in table 1.

Having determined all intersections and limits on our integration variable λ , equation (8) becomes,

$$P_{ij,\alpha\beta} = \frac{1}{\tilde{V}} \left[\int_{\lambda_a}^{\lambda_b} (\mathbf{f}_{ij} \cdot \mathbf{e}_{\alpha})(\mathbf{r}_{ij} \cdot \mathbf{e}_{\beta}) d\lambda + \int_{\lambda'_a}^{\lambda'_b} (\mathbf{f}_{ij} \cdot \mathbf{e}_{\alpha})(\mathbf{r}_{ij} \cdot \mathbf{e}_{\beta}) d\lambda \right], \quad (13)$$

where the integrand is expressed in terms of the unit vectors \mathbf{e}_r , \mathbf{e}_θ , and \mathbf{e}_ϕ . Note that if there is only one portion of C_{ij} intersecting \tilde{V} , then the second integral in equation (13) (with limits λ'_a and λ'_b) is absent. These unit vectors are not constant as $\mathbf{l}(\lambda)$ moves along C_{ij} , and the unit vectors in Cartesian coordinates are,

$$\begin{aligned} \mathbf{e}_r &= \left\{ \frac{l_x}{l}, \frac{l_y}{l}, \frac{l_z}{l} \right\}, \\ \mathbf{e}_\theta &= \left\{ \frac{l_x l_z}{l(l_x^2 + l_y^2)^{1/2}}, \frac{l_y l_z}{l(l_x^2 + l_y^2)^{1/2}}, \frac{-(l_x^2 + l_y^2)^{1/2}}{l} \right\}, \\ \mathbf{e}_\phi &= \left\{ \frac{-l_y}{(l_x^2 + l_y^2)^{1/2}}, \frac{l_x}{(l_x^2 + l_y^2)^{1/2}}, 0 \right\}, \end{aligned} \quad (14)$$

where ϕ is the azimuth angle in the xy -plane, θ is the angle between \mathbf{l} and the z -axis, $l = |\mathbf{l}|$, and l_α is the α component of \mathbf{l} .

The P_{ij} tensor can be written in terms of two components, normal and tangential. These components are obtained from equation (13) using equations (9) and (14). The contribution from the interaction between molecules i and j to the normal component is given by

$$P_{ij,N} \equiv P_{ij,rr} = \frac{1}{\tilde{V}} \int_{\lambda_a}^{\lambda_b} (\mathbf{f}_{ij} \cdot \mathbf{e}_r)(\mathbf{r}_{ij} \cdot \mathbf{e}_r) d\lambda \quad (15)$$

$$= \frac{1}{\tilde{V}} \int_{\lambda_a}^{\lambda_b} \frac{a_n + b_n \lambda + c_n \lambda^2}{d_n + e_n \lambda + f_n \lambda^2} d\lambda \quad (16)$$

$$= \frac{1}{\tilde{V}} \left\{ \Sigma_N(\lambda) \Big|_{\lambda_a}^{\lambda_b} - \Sigma_N(\lambda) \Big|_{\lambda'_a}^{\lambda'_b} \right\}, \quad (17)$$

where we omit in equations (15) and (16) the second integral simply for brevity, and,

$$\begin{aligned} a_n &= (\mathbf{r}_i \cdot \mathbf{f}_{ij})(\mathbf{r}_i \cdot \mathbf{r}_{ij}) \\ b_n &= (\mathbf{r}_{ij} \cdot \mathbf{f}_{ij})(\mathbf{r}_i \cdot \mathbf{r}_{ij}) + (\mathbf{r}_i \cdot \mathbf{f}_{ij})(\mathbf{r}_{ij} \cdot \mathbf{r}_{ij}) \\ c_n &= (\mathbf{r}_{ij} \cdot \mathbf{f}_{ij})(\mathbf{r}_{ij} \cdot \mathbf{r}_{ij}) \\ d_n &= \mathbf{r}_i \cdot \mathbf{r}_i \\ e_n &= 2 \mathbf{r}_i \cdot \mathbf{r}_{ij} \\ f_n &= \mathbf{r}_{ij} \cdot \mathbf{r}_{ij} \end{aligned} \quad (18)$$

$$\begin{aligned} \Sigma_N(\lambda) &= \frac{1}{2f_n^2} \{ 2c_n f_n \lambda + (b_n f_n - c_n e_n) \\ &\quad \times \ln [d_n + e_n \lambda + f_n \lambda^2] \\ &\quad + \frac{2}{\sqrt{4d_n f_n - e_n^2}} \arctan \left[\frac{e_n + 2f_n \lambda}{\sqrt{4d_n f_n - e_n^2}} \right] \\ &\quad \times (f_n(2a_n f_n - b_n e_n) + c_n(e_n^2 - 2d_n f_n)) \}, \end{aligned} \quad (19)$$

while the tangential component is given by,

$$P_{ij,T} \equiv P_{ij,\phi\phi} = \frac{1}{\tilde{V}} \int_{\lambda_a}^{\lambda_b} (\mathbf{f}_{ij} \cdot \mathbf{e}_\phi)(\mathbf{r}_{ij} \cdot \mathbf{e}_\phi) d\lambda \quad (20)$$

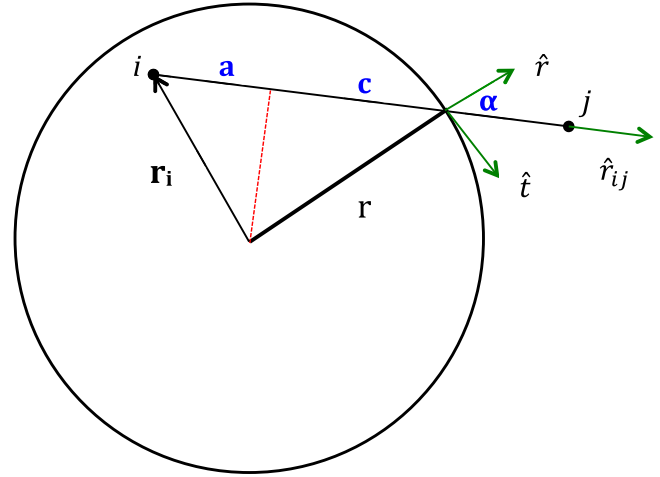


Figure 2. A sketch of the geometry for a sample calculation of the transverse pressure component at a radius r . The straight line contour intersects the sphere when $\lambda = \lambda_0$ (see equation (9)), at which point $a + c = \lambda_0 r_{ij}$. Here, the force between i and j is taken to be radial, and forms an angle α with \hat{r} , with $\cos \alpha = c/r$ and $a = -\mathbf{r}_i \cdot \hat{r}_{ij}$.

$$= \frac{c_t}{\tilde{V}} \int_{\lambda_a}^{\lambda_b} \frac{a_t + b_t \lambda}{d_t + e_t \lambda + f_t \lambda^2} d\lambda \quad (21)$$

$$= \frac{c_t}{\tilde{V}} \left\{ \Sigma_T(\lambda) \Big|_{\lambda_a}^{\lambda_b} - \Sigma_T(\lambda) \Big|_{\lambda'_a}^{\lambda'_b} \right\}, \quad (22)$$

where we omit in equations (20) and (21) the second integral for brevity, and,

$$\begin{aligned} a_t &= r_{i,x} f_{ij,y} - r_{i,y} f_{ij,x} \\ b_t &= r_{ij,x} f_{ij,y} - r_{ij,y} f_{ij,x} \\ c_t &= r_{i,x} r_{ij,y} - r_{i,y} r_{ij,x} \\ d_t &= r_{i,x}^2 + r_{i,y}^2 \\ e_t &= 2(r_{i,x} r_{ij,x} + r_{i,y} r_{ij,y}) \\ f_t &= r_{ij,x}^2 + r_{ij,y}^2 \end{aligned} \quad (23)$$

$$\begin{aligned} \Sigma_T(\lambda) &= \frac{b_t \ln [d_t + e_t \lambda + f_t \lambda^2]}{2f_t} \\ &\quad + \arctan \left[\frac{e_t + 2f_t \lambda}{\sqrt{4d_t f_t - e_t^2}} \right] \frac{(2a_t f_t - b_t e_t)}{f_t \sqrt{4d_t f_t - e_t^2}}. \end{aligned} \quad (24)$$

Having assembled all the pieces required to calculate the coarse-grained pressure tensor components, we now report on the following radial quantities related to the pressure (see equation (6)).

$$P_N(r) = \langle P_{c,rr} \rangle + k_B T \rho(r) \quad (25)$$

$$\bar{P}_{c,N}(r) = \langle P_{c,rr} \rangle \quad (26)$$

$$P_T(r) = \langle P_{c,\phi\phi} \rangle + k_B T \rho(r) \quad (27)$$

$$\bar{P}_{c,T}(r) = \langle P_{c,\phi\phi} \rangle \quad (28)$$

$$P(r) \equiv \frac{1}{3}P_N(r) + \frac{2}{3}P_T(r) \quad (29)$$

where $\rho(r)$ is the average number density of molecules in \tilde{V} as determined from molecular centres of mass and $P(r)$, the mean (or isotropic) pressure, is one third the trace of the pressure tensor. As noted in [16], the tangential component may be calculated from $P_{ij,\theta\theta}$. However, the analytic expression for the resulting antiderivative is very cumbersome.

3.2. Comment on calculating $P_T(r)$

Without coarse-graining, the transverse component of the pressure tensor is calculated from the first of two equivalent equations relating pressure components derived from the condition of mechanical stability [15, 16],

$$P_T(r) = P_N(r) + \frac{r}{2} \frac{dP_N(r)}{dr} \quad (30)$$

$$P_N(r) = \frac{2}{r^2} \int_0^r P_T(r') r' dr', \quad (31)$$

rather than directly from configurations on account of divergences occurring in equation (5). (We note that equations (30) and (31) are valid regardless of whether the quantities are coarse-grained or not.) To illustrate this, let us use equation (5) in the context of calculating the transverse pressure component over a sphere (not a spherical shell) of radius r and assume for simplicity, for the purposes of this illustration only, that $\mathbf{f}_{ij} = f_{ij}\hat{r}_{ij}$, with f_{ij} a scalar and the unit vector is the one derived from \mathbf{r}_{ij} , i.e. that the force is central—acting along the line joining the particles. Our setup for this illustration is shown in figure 2, where we take the transverse direction to be in the plane of \mathbf{r}_{ij} and \hat{r} , the radial unit vector at the point of intersection of C_{ij} with the sphere, at which point $\lambda = \lambda_0$. As we are now considering the contribution to the pressure over the spherical surface, equation (5) becomes,

$$P'_{ij,T}(r) = \frac{1}{2} \frac{1}{4\pi r^2} \int_{C_{ij}} (\mathbf{f}_{ij} \cdot \hat{t}) (\mathbf{dl} \cdot \hat{t}) \delta(r-l) \quad (32)$$

$$= \frac{1}{8\pi r^2} f_{ij} r_{ij} \sin^2 \alpha \int_0^1 d\lambda \delta(r-l(\lambda)) \quad (33)$$

$$= \frac{1}{8\pi r^2} f_{ij} r_{ij} \sin^2 \alpha \int_0^1 d\lambda \frac{\delta(\lambda - \lambda_0)}{|l'(\lambda_0)|} \quad (34)$$

$$= \frac{1}{8\pi r^2} f_{ij} \frac{\sin^2 \alpha}{\cos \alpha}, \quad (35)$$

where the extra factor of $\frac{1}{2}$ comes from \hat{t} having both θ and ϕ components and, with the help of equation (10) and the geometrical arrangement shown in figure 2, it can be shown that $l'(\lambda_0) = r_{ij} \cos \alpha$. Equation (35) appears in [16] as equation (12), which is itself referenced from [26]. The cosine in the denominator causes a divergence when $\cos \alpha = 0$, i.e. when the C_{ij} becomes tangent to the sphere. Attempts to use

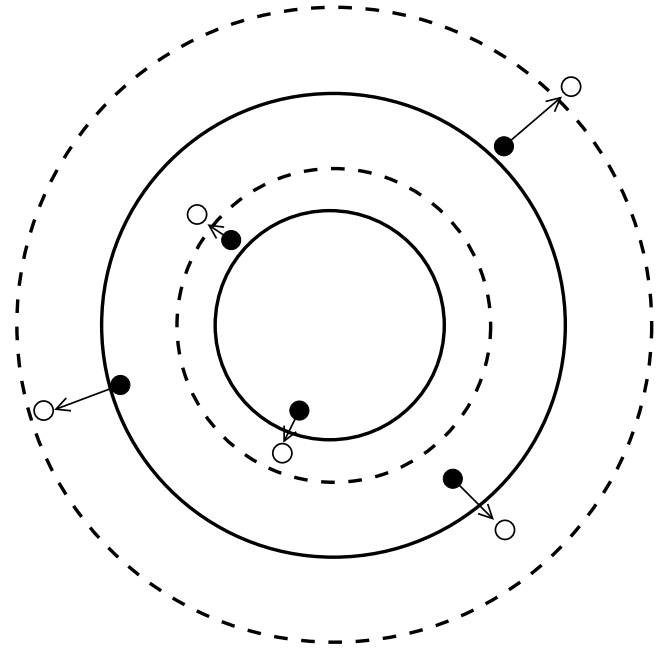


Figure 3. A sketch for the calculation of the derivative of the local potential energy $U(r)$ with respect to volume. All particles coordinates are rescaled isotropically according to $\mathbf{r} \rightarrow (1 + \alpha)\mathbf{r}$ (filled to open circles), resulting in a commensurate change in spherical shell volume \tilde{V} (solid lines) to $(1 + \alpha)^3\tilde{V}$ (dashed lines).

equation (35) to calculate the transverse pressure illustrate the problem, which is formally absent in the coarse-graining method because of the order in which the integration is carried out in obtaining equation (8).

3.3. Obtaining the local pressure from the potential energy

Ikeshoji *et al* [16] also discusses the method of determining the pressure tensor in \tilde{V} by using the virial expression for the bulk pressure, but only considering particle interactions for which at least one of the particles is in \tilde{V} . While this intuitive approach is only a low-order approximation [27], the authors demonstrate for a planar geometry that it fails to respect mechanical equilibrium (equations (30) and (31)) only at the interface.

In the same spirit, we define an expression inspired by the thermodynamic meaning of pressure in the bulk,

$$P_U(r) \equiv \rho(r)k_B T - \left\langle \frac{dU(r)}{d\tilde{V}} \right\rangle_{T,N}, \quad (36)$$

where the derivative is calculated in the following way (see figure 3). For a given nanodroplet configuration, all molecular centres of mass are isotropically expanded according to $\mathbf{r}_{CM,i}^+ \rightarrow (1 + \alpha_+)\mathbf{r}_{CM,i}$, and in this rescaled system we calculate the binding energy $u_i^+ = \sum_{j \neq i} u_{ij}$ for each molecule i originally in \tilde{V} , where u_{ij} is the interaction energy between molecules i and j . The rescaled shell volume is $\tilde{V}_+ = (1 + \alpha_+)^3\tilde{V}$, and the potential energy associated with the rescaled shell is $U_+ = \frac{1}{2} \sum_{i \in \tilde{V}_+} u_i^+$. To use the centred difference scheme to approximate the derivative,

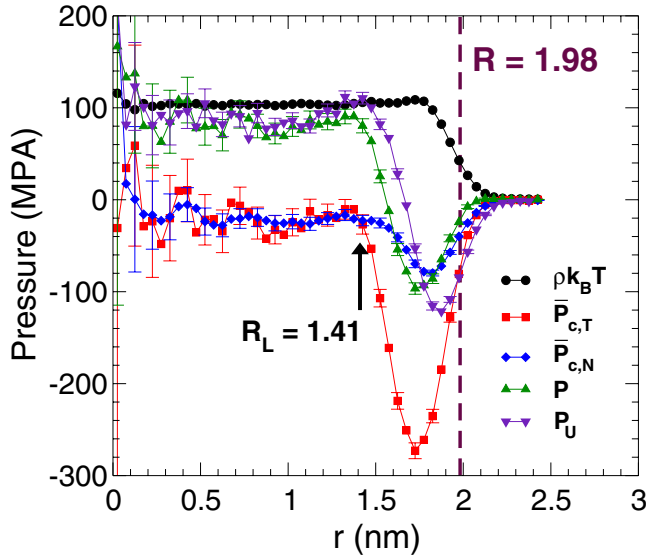


Figure 4. Pressure as a function of radial distance from the centre of a nanodroplet of size $N = 1100$ at $T = 220$ K. The radial extent of the droplet is estimated by $R = \sqrt{5/3}R_g = 1.98$ nm, while the configurational contributions to the tangential and radial pressures are approximately equal below the point of crossing at $R_L = 1.41$ nm.

$$\frac{dU(r)}{d\tilde{V}} \approx \frac{U_+ - U_-}{\tilde{V}_+ - \tilde{V}_-}, \quad (37)$$

we similarly rescale the molecular centres of mass according to $\mathbf{r}_{CM,i}^- \rightarrow (1 + \alpha_-)\mathbf{r}_{CM,i}$ to obtain U_- and \tilde{V}_- . We use $\alpha_+ = 10^{-4}$, and then to ensure that $\tilde{V}_+ - \tilde{V} = \tilde{V} - \tilde{V}_-$, we use $\alpha_- = [2 - (1 + \alpha_+)^3]^{1/3} - 1$ (approximately equal to $-\alpha_+$). Note that the same particles are in \tilde{V} , \tilde{V}_+ and \tilde{V}_- and that the same molecular pairs are used to calculate U_+ and U_- . This derivative is then averaged over nanodroplet configurations.

4. Results

4.1. Radial pressure profiles

In figure 4 we plot various pressure contributions for a nanodroplet of size $N = 1100$. The radial density is proportional to the ideal gas term (black circles), which for this state point accounts for most of the roughly 100 MPa of pressure in the interior of the nanodroplet. There is a small maximum in the density at or near the surface (at $r \approx 1.75$ nm), where the configurational contributions to the normal [$\bar{P}_{c,N}(r)$ —blue diamonds] and tangential [$\bar{P}_{c,T}(r)$ —red squares] components of the pressure are maximally negative. Despite the large negative values near the surface, $\bar{P}_{c,N}(r)$ and $\bar{P}_{c,T}(r)$ become indistinguishable from each other within the precision of our simulations below $R_L \approx 1.41$ nm, indicating that the pressure tensor is isotropic within this radius.

We note that an accurate determination of the centre of mass of the cluster is vital for determining all the radial quantities. It is thus important to exclude gas-like molecules when calculating the centre of mass. When calculating the pressure

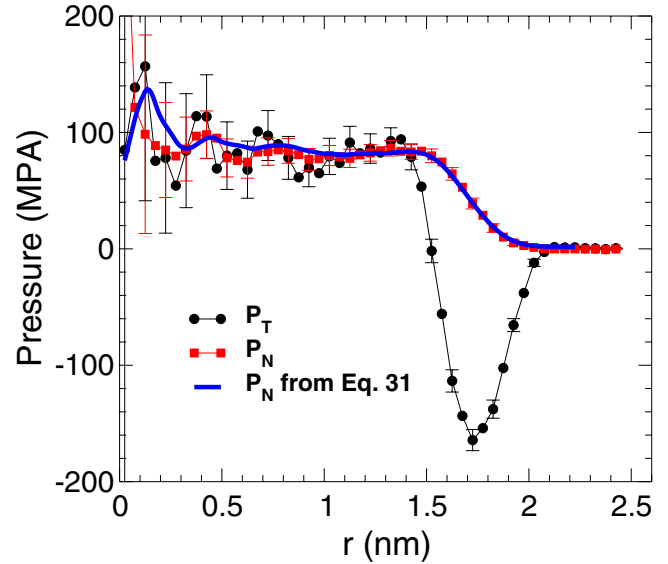


Figure 5. Consistency check on the calculation of $P_N(r)$ and $P_T(r)$ for $N = 1100$ and $T = 220$ K.

all particles in the system are used. However, the vapour pressure at $T = 220$ K is nearly zero. For example, a search of the $N = 1100$ configurations sampled, using the definition that a gas-like molecule has two or fewer neighbours within $r_n = 0.63$ nm, found no such molecules. A cluster search employing the definition that two molecules within $r_n = 0.35$ belong to the same cluster yields the same result [28].

Notwithstanding the progressively larger error bars as $r \rightarrow 0$, there appear to be oscillations within both $\bar{P}_{c,N}(r)$ and $\bar{P}_{c,T}(r)$ that may correlate with small oscillations in $\rho(r)$. However, given the precision of our calculations, we can do no better than to assume that $\bar{P}_{c,N}(r)$ and $\bar{P}_{c,T}(r)$ are both equal to the same constant below R_L .

As a consistency check on our results, we verify that our calculated pressure components satisfy mechanical equilibrium by using equation (31) to recover $P_N(r)$ from $P_T(r)$. We use equation (31) instead of equation (30) since numerical integration reduces noise. In figure 5 we plot both $P_N(r)$ calculated directly from the droplets and as calculated from equation (31). We see that the two curves are the same within error, even though equation (31) yields a curve with less pronounced oscillatory behaviour. A global estimate of the numerical integration error can be taken to be the difference between equation (31) and $P_N(r)$ where the latter decays to zero.

$P_U(r)$ for the same state point is shown in figure 4, where it agrees, to within error, with $P(r)$ in the interior of the droplet where the pressure is constant with r . At the interface, there is a significant difference, in which $P_U(r)$ exaggerates the extremal values of $P(r)$, and shows a positive pressure peak near the surface. Despite this exaggeration near the surface, $P_U(r)$ shows none of the apparent oscillations seen in $P(r)$.

As this method only relies on the potential energy, it is comparatively a rather straightforward calculation, and so may be of use when interactions are complex and precise determination of the properties near the interface is not required. Furthermore, that the two methods agree within the interior provides a useful check on the results for $P(r)$.

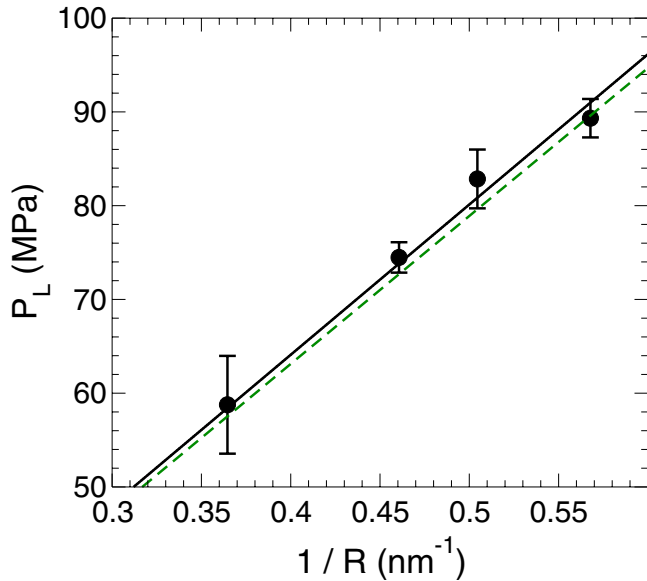


Figure 6. Test of the Laplace pressure relation. Plotted is the average isotropic pressure from the interior of nanodroplets as a function of $1/R$, where $R = \sqrt{5/3}R_g$. Solid line is the result of a one-parameter least-squares fit, $P_L = 2(80.1)/R$. The dashed line uses an estimate of $\gamma = 78.9 \text{ mN m}^{-1}$ for a planar interface at 220 K [29].

4.2. Laplace pressure relation

To test equation (1), and noting that the vapour pressure is so small compared to the interior pressure of the nanodroplets, we simply define P_L to be the average of $P(r)$ from $r_{\min} = 0.025$ (our first data point) to R_L , the radial distance to which the pressure tensor is isotropic, i.e. below which point $P_T(r)$ and $P_N(r)$ are indistinguishable:

$$P_L \equiv \frac{3}{4\pi(R_L^3 - r_{\min}^3)} \int_{r_{\min}}^{R_L} 4\pi r^2 P(r) dr. \quad (38)$$

Operationally, we take R_L to be the first crossing of $P_{c,T}(r)$ and $P_{c,N}(r)$ as r decreases below the location of the minimum in $P_{c,T}(r)$. As a measure of the radius of the droplet, treating the nanodroplets as spheres of uniform density, we choose $R = \sqrt{5/3}R_g$, where R_g is the radius of gyration.

In figure 6 we plot P_L as a function of $1/R$. We fit the data to $2\gamma_{\text{fit}}/R$ and find $\gamma_{\text{fit}} = 80.1$. This estimate of γ agrees well with the value $\gamma = 78.9 \text{ mN m}^{-1}$ obtained using equation (6) in [29]; the dashed line in figure 6 shows $2\gamma/R$ using this value of γ .

5. Discussion and conclusions

Calculating the local pressure is a non-trivial task and requires good averaging because of significant statistical fluctuations, particularly at small radial distances. We note the discrepancy between our results and the early work on ST2 water clusters of Brodskaya *et al* [13, 14]. They reported a significant drop in the pressure, even to significantly negative values, towards the centre of the droplet. While the droplet sizes they investigated were smaller and at higher T , we speculate that this unexpected result may have arisen from an imprecise determination of

the centre of mass or even from sample bias since these early simulations had much shorter run times. A given configuration may have an extremely large (positive or negative) value of $P(r \rightarrow 0)$, depending on whether there is a high or low density fluctuation at the centre, which can be considerable given the small number of particles there. As a general remark, statistics for larger r are not only better because of the greater volume over which the average is determined, but because mobility is likely greater the closer a layer is to the surface. However, in the present study we have not excluded the possibility that for smaller droplets, such as those studied in [13, 14], there exists an effect that reduces the pressure at the centre.

It is important to directly calculate the pressure instead of relying only on the local density and the known bulk equation of state, even when done as elegantly as in a recent test of the Young–Laplace equation for the SPC/E model by pressuring water through a nanopore [30]. We already see a dense region near the surface of the nanodroplet, where the pressure is negative. Clearly, the water in this layer does not follow the bulk equation of state. Further, subtle finite size effects on structure, as noted already in regard to nucleation [7], may affect local pressure more than local density. Thus, water in sufficiently small nanodroplets may not follow the bulk equation of state.

Whether or not droplet interiors represent bulk water also depends on how deeply surface effects propagate inside. At $T = 220 \text{ K}$, we see, coming in from large r , that the density rises from zero to a local maximum (where $P(r)$ is most negative) in about 0.3 nm (see black curve with circles in figure 4). Another 0.4 nm further inside and $P_N(r)$ and $P_T(r)$ become indistinguishable within uncertainty. This non-bulk-like region is 0.7 nm thick and encompasses approximately two molecular layers. This estimate of the size of non-bulk-like region is somewhat smaller than pointed out in [7], for which there is also observed a local maximum in the stress before quickly tending to a constant at smaller r . However, in our case the interior is at a high pressure and the definition of the local stress used in [7] differs from that of the pressure. We note that $P_U(r)$ also produces a peak near R_L , and would thus also produce a larger estimate of the extent of the non-bulk-like region. This should not be an issue if one is in search of a conservative estimate of what is perhaps bulk-like.

Equation (1) formally models a droplet with a sharp interface at $R = R_s$, at the so-called surface of tension, that separates interior and exterior fluids with isotropic and homogeneous pressures, and ΔP refers to the difference between these fluid pressures. For our droplets, the pressure tensor components become equal and constant with r near the centre (and hence bulk-like), and so we identify ΔP with P_L obtained from the pressure tensor. In using equation (1) we approximate R_s with $\sqrt{5/3}R_g$. In a more systematic study aiming to quantify the curvature corrections to γ (through the Tolman length δ), the choice of dividing surface should be carefully considered. Nonetheless, our use of $R = \sqrt{5/3}R_g$ yields a γ remarkably consistent with the expected planar value. This may indicate that curvature corrections to γ , and hence δ itself, are small. Calculations for both Lennard-Jones [31] and TIP4P/2005 [32] yield small negative values of δ ,

around -0.1σ and -0.05 nm respectively, with the magnitude of δ decreasing with decreasing T for TIP4P/2005 [33]. For a future study of smaller droplets, for which curvature effects may become more apparent, the pressure calculation presented here provides the means of directly determining δ from simulation data, as has been done for Lennard-Jones droplets [34]. In addition, density functional theory suggests that δ becomes positive for very small droplets, as implied by a decreasing γ with R_s [35], and hence in the present study we may be in a droplet size regime where $\delta \approx 0$.

While working with forces between molecules and their centres of mass is more convenient compared to treating molecules as collections of atoms held rigidly by forces of constraint, there is another important advantage of our approach. As recently pointed out by Sega *et al* [36], when constraints are used and the kinetic energy tensor is calculated from atomic velocities, the kinetic energy tensor may become anisotropic at a liquid–vapour interface. Failure to consider these anisotropies may, for example, lead to underestimates of γ by approximately 15% for a planar interface. It is thus insufficient, when working with constraints, to only calculate the configuration contribution to the virial and assume an isotropic ideal gas contribution. Velocities are thus required for the pressure calculation. In contrast, we work with the velocities of the molecular centres of mass and intermolecular forces, thus avoiding these difficulties [23]. The molecular approach works essentially because the calculation of pressure stems from the calculation of the force, i.e. the rate of change of the linear momentum with time [24]. The validity of the molecular approach used here, where we assume an isotropic ideal gas contribution, is confirmed in figure 5, where $P_N(r)$ and $P_T(r)$ are shown to be consistent with mechanical stability. If our ideal gas contribution were incorrect, mechanical stability would appear to be violated. Regardless of the concerns raised by Sega *et al* [36], our estimates for P_L are made solely based on the behaviour of the pressure tensor in the interior of the droplets. As a result, anisotropy arising in the region of the surface does not affect our results for P_L .

In summary, we have provided a detailed description of the calculation of the microscopic pressure for spherical droplets of molecular liquids, and checked the results by introducing an approximate energy-based method of calculating the microscopic isotropic pressure. Our calculation paves the way for a detailed analysis of effects of the local pressure on nucleation, and for direct checks on whether the bulk equation of state remains valid in nanodroplet interiors. For the size range studied, and at fairly deeply supercooled T , we find that γ determined from a flat interface predicts the pressure in the interior of the nanodroplet quite well, despite significant surface features in the radial dependence of the pressure.

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