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Molecular simulation of nano-dispersed fluid phases

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HIGHLIGHTS

- Nanoscopic gas bubbles are investigated by molecular dynamics simulation.
- Corroborating previous work on droplets, two distinct size-dependent effects are found.
- Curvature induces a subsaturation of the system, leading to a smaller liquid density.
- For the gas in the centre of the bubble, the small diameter has an obverse effect.
- The excess equimolar radius is found to be positive, corresponding to a negative Tolman length.

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ABSTRACT

Fluid phase equilibria involving nano-dispersed phases, where at least one of the coexisting phases is confined to a small volume, are investigated by molecular dynamics simulation. Complementing previous studies on nanoscopic droplets, simulation volumes containing a nanoscopic gas bubble surrounded by a subsaturated liquid phase under tension, i.e. at negative pressure, are conducted in the canonical ensemble. The boundary conditions are chosen such that the phase equilibrium at the curved interface is thermodynamically stable. Two distinct size-dependent effects of opposite sign are found for the density of the gas in the centre of the bubble. The curvature dependence of the surface tension is considered, employing an approach based directly on the average radial density profiles.

1. Introduction

Dispersed phases are ubiquitous both in nature and technological applications. Their character poses a particular challenge to thermodynamic approaches which attempt to reduce the complexity of a system to a few macroscopic degrees of freedom. Even in the most bulk-like central region of a nanoscopic bubble or droplet, thermodynamic properties may deviate substantially from the bulk phase under corresponding conditions. Interfacial properties may dominate, and the heterogeneity of the dispersion further complicates its thermodynamic description.

Phenomenological thermodynamics was applied to fluid interfaces by Gibbs (1878), whose approach ultimately succeeded due to the rigour with which it unifies the macroscopic and microscopic points of view. In particular, it reduces the phase boundary, which is continuous on the molecular level, to a strictly two-dimensional dividing surface separating two bulk phases. The deviation between the actual system and the theoretical system, consisting of the two bulk phases only, serves as a definition of interfacial excess quantities to which phenomenological thermodynamic reasoning can be applied.

This reduction facilitates discussing and analysing systems which contain a nano-dispersed phase, but it does so at a prize. The task of representing physically complex behaviour is shifted to the interfacial excess quantities. Such quantities, and particularly the surface tension and the adsorption, have to account for all the aspects which distinguish, for instance, the bulk metal from a metal nanoparticle, or the bulk vapour from a gas bubble that contains a few molecules only. This explains why such fundamental and apparently simple issues such as the dependence of the surface tension of small gas bubbles and liquid droplets on their radius are still not fully settled, despite having been on the agenda of scientific discussions for decades.

Furthermore, for the development of molecular equations of state (Chapman et al., 1990; Müller et al., 1996; Gross and Sadowski, 2001), which mostly aim at describing the bulk phases, it is important to

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understand how precisely the intermolecular interactions affect the association of molecules to small nanoclusters, since the underlying thermodynamic perturbation theory (Zwanzig, 1954; Wertheim, 1984) is based on a statistical-mechanical cluster expansion (Mayer, 1937). In addition, a reliable description of natural phenomena such as atmospheric nucleation, as well as engineering problems such as nucleate pool boiling, spray cooling, or nucleation in expanding gases as it is ubiquitous in turbines, can only be obtained on the basis of quantitatively accurate models for the thermodynamic properties of the respective dispersed fluid phases, i.e. nanoscopic gas bubbles and liquid droplets. For such studies, both static and dynamic properties have to be captured, concerning physical objects which can fluctuate significantly in their size and shape or even disappear in the blink of an eye.

It is therefore attractive to apply molecular simulation to study these problems, supplementing experimental results where they are available, and replacing them where suitable experiments have not yet been devised. Molecular dynamics (MD) simulation is capable of elucidating the properties of nano-dispersed phases in equilibrium (Rusanov and Brodskaya, 1977; Vrabec et al., 2006; Napari et al., 2009) as well as dynamic phenomena including nucleation (Napari et al., 2009; Horsch and Vrabec, 2009), aggregation (Lümmen and Kvamme, 2008), coalescence (Gan and Carey, 2010), growth (Napari et al., 2004), and dynamic wetting (Nakamura et al., 2013), among many others (Hafskjold and Ikeshoji, 1996; Guevara Carrión et al., 2012), at molecular resolution. Even complex scenarios, such as gold clusters with an organic protection layer, are well accessible to MD simulation (Schapotschnikow et al., 2007). In a simulation, boundary conditions can be imposed which would be hard or impossible to guarantee in an experimental setting. For instance, transport processes can be sampled in a well-defined steady state by non-equilibrium MD simulation, including the coupled heat and mass transfer occurring at interfaces (Hafskjold and Ikeshoji, 1996) and during nucleation in a supersaturated vapour (Horsch and Vrabec, 2009). The critical nucleus of a nucleation process, which corresponds to a free energy maximum and is therefore thermodynamically unstable, can be investigated in detail by equilibrium simulation of a small system in the canonical ensemble (Napari et al., 2009).

As a massively parallel high performance computing application, MD simulation scales well both in theory and in practice. Up to trillions of interaction sites can be simulated (Eckhardt et al., 2013), so that a single modelling approach can be employed from the nanometre up to the micrometre length scale. As such, molecular simulation is a useful tool for investigating the size dependence of interfacial effects. MD simulations of the surface tension of curved vapour–liquid interfaces, comparing it with that of the planar phase boundary, were already conducted in the 1970s (Rusanov and Brodskaya, 1977). Many of the subsequent contributions to this problem, in particular more recently, have been guided by the analysis of molecular simulation results (Vrabec et al., 2006, 2009; Napari et al., 2009; Schrader et al., 2009; Block et al., 2010; Sampayo Hernández et al., 2010; Das and Binder, 2011; Tröster and Binder, 2011; Horsch et al., 2012a; Malijevský and Jackson, 2012).

The present work illustrates the contribution that molecular modelling and simulation can make to the discussion of nano-dispersed phases, with a focus on MD simulation of a gas bubble in equilibrium with a liquid at negative pressure. This case is both of fundamental scientific interest and technically important, e.g. for cavitation. In Section 2, a brief survey is given on the relevant aspects of the theory of vapour–liquid interfaces, including the dependence of the surface tension on curvature and its relation to the excess equimolar radius; for an introduction to dispersed phase thermodynamics from a more general point of view, the interested reader is referred to the books by Hill (1964), Kashchiev (2000), Rowlinson and Widom (1982), as well as Vehkamäki (2006). Section 3 introduces the employed molecular simulation methods. Simulation results, consistently finding the excess equimolar radius to be positive, are presented in Section 4. A possible interpretation of the present results is suggested in Section 5, relating it to previous work and leading to the conclusion which is given in Section 6.

2. Thermodynamics of dispersed phases

2.1. Vapour–liquid surface tension

The tension of a planar fluid interface can be defined in different ways, following a thermodynamic or a mechanical approach. Thermodynamically, the surface tension γ can be expressed by the partial derivative of the free energy A over the surface area F at constant number of molecules $\mathbf{N}$ (of all components), volume V, and temperature T:

$$\gamma = \left(\frac{\partial A}{\partial F}\right)_{\mathbf{N},V,T}. \tag{1}$$

The surface free energy can then be obtained by integration

$$A_F = \int_0^F \gamma \, dF, \tag{2}$$

over a process during which the interface is created.

By molecular simulation, the thermodynamic surface tension can be computed from the test area method (de Miguel, 2008), while grand canonical Monte Carlo simulation can be employed to obtain A_F from the excess Landau free energy corresponding to the respective density (Binder, 1982; Schrader et al., 2009).

Neglecting size effects on γ, the surface free energy can be approximated by $A_F \approx \gamma F$. While such a simplification is justified for macroscopic systems, it may violate the thermodynamics of small systems (Hill, 1964), where, in general, significant finite size effects can be present even for planar phase boundaries (Gelfand and Fisher, 1990; Werth et al., 2013).

For a mechanical definition, the surface tension is treated as causing a force f_τ acting in the tangential direction (with respect to the interface), i.e. a tendency of the interface to contract. The mechanical surface tension

$$\gamma = \frac{f_\tau}{l} \tag{3}$$

relates the magnitude of this force to the length of the contact line l between the interface and the surface of another mechanical object, e.g. a confining wall, on which the force f_τ acts.

In a cuboid box with the extension $V = l_x \times l_y \times l_z$, which contains a planar interface normal to the z-axis, the interface and the two faces of the box which are normal to the x-axis have contact lines with an elongation of l_y, cf. Fig. 1. Each of these faces (normal to x) has an area of $F_{yz} = l_y \times l_z$. The tangential force $f_\tau = f_x = \gamma l_y$ thus constitutes a negative (contracting) contribution

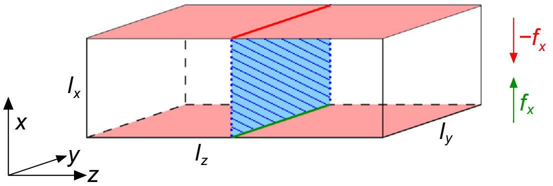

Fig. 1. Diagram illustrating the mechanical definition of the surface tension. The two faces of the box with an orientation perpendicular to the x-axis experience forces in opposite directions, expressing the tendency of an interface situated in the centre of the box to contract. The magnitude of the force f_x is proportional to the surface tension γ and the length of the contact line l_y.