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Fluid mixtures at curved walls

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Abstract

We study the curvature dependence of thermodynamical quantities such as the surface tension γ and the excess adsorptions Γ_i of fluid mixtures in contact with curved walls. If mixtures with short-ranged interaction at state points away from any phase separation are considered, all intrinsic length scales remain small, and we can generalize to mixtures recent findings for the one-component fluid. In addition, we relate the excess surface grand potential to B_2 , the effective second virial coefficient between big particles of a mixture after integrating out the degrees of freedom of the smaller components.

1. Introduction

Close to a wall, a fluid develops in general an inhomogeneous structure which gives rise to surface thermodynamic quantities like γ , the interfacial wall–fluid tension, or Γ , the excess (over the bulk) amount of fluid adsorbed at the wall. If the wall is curved, Ω , the grand potential of the system, as well as surface thermodynamic quantities, depends on the shape S of the wall in a potentially complicated way, which makes a direct calculation of these quantities in complex geometries practically impossible. However, in recent studies of the connection between the shape of the wall and thermodynamic quantities [1] and structure [2] of a pure fluid away from the critical point and in absence of wetting or drying phenomena, it was shown that the curvature can enter thermodynamic quantities in a simple and elegant way. For state points of the fluid for which all intrinsic length scales, like the correlation length ξ , remain small, we can follow [1] in its application of Hardwiger’s theorem [3–5] and extend these considerations to the case of fluid mixtures.

In addition, we relate Ω^{surf} the surface grand potential of a fluid mixture in contact with one big particle to the effective second virial coefficient B_2 between big particles in a sea of small ones, after the degrees of freedom of the small particles are integrated out. This virial coefficient corresponds to an average over the two-body term of the effective Hamiltonian [6].

To illustrate this relation, we consider the special case of hard-sphere mixtures and calculate a closed expression for B_2 within an approximate thermodynamic approach [7].

2. Theory

We consider a ν -component fluid mixture in the grand ensemble close to a curved wall. All fluid–fluid and wall–fluid interactions are assumed to be short-ranged (finite-ranged, exponentially or faster decaying). If all intrinsic length scales remain small we can argue, following [1], that it is reasonable to assume that the functional $\Omega[S]$, the grand potential of a fluid mixture adsorbed on a curved wall, satisfies (at least to a very good approximation) the following three conditions. (i) Motion invariance: the functional remains unchanged under all rotations and translations g : $\Omega[gS] = \Omega[S]$. (ii) Continuity: for a series S_n approximating the shape of the wall S , the functional $\Omega[S_n] \rightarrow \Omega[S]$ for $n \rightarrow \infty$ if S_n approaches S in the same limit. (iii) Additivity: the functional of the union of two domains S_i , $i = 1, 2$, is given by $\Omega[S_1 \cup S_2] = \Omega[S_1] + \Omega[S_2] - \Omega[S_1 \cap S_2]$. According to Hardwiger's theorem [3–5], all functionals $\Omega[S]$ that satisfy conditions (i)–(iii) can be written in the form

$$\Omega[S] = -pV[S] + \sigma A[S] + \kappa C[S] + \bar{\kappa} X[S], \quad (1)$$

where the accessible volume $V[S] = \int_S dV$, the surface area $A[S] = \int_{\partial S} dA$, the integrated mean curvature $C[S] = \int_{\partial S} H dA/(4\pi)$ and the integrated Gaussian curvature or Euler characteristic $X[S] = \int_{\partial S} K dA/(4\pi)$ are the only morphometric measures required to describe the geometrical shape of the wall. We have used that at any point \mathbf{r} on the surface ∂S of the wall there are two principal radii of curvature $R_1(\mathbf{r})$ and $R_2(\mathbf{r})$ from which the local mean curvature $H(\mathbf{r}) = (1/R_1(\mathbf{r}) + 1/R_2(\mathbf{r}))/2$ and the local Gaussian curvature $K(\mathbf{r}) = 1/(R_1(\mathbf{r})R_2(\mathbf{r}))$ follow. The corresponding thermodynamic coefficients in equation (1) are the pressure p , the surface tension at a *planar* wall σ , and two bending rigidities of the fluid mixtures κ and $\bar{\kappa}$. Thus equation (1) separates completely the thermodynamic properties of the mixture, that depend on the state point of the fluid and the wall–particle interactions, from the shape of the wall. As a consequence, it is possible to determine the coefficients σ , κ and $\bar{\kappa}$ in *simple* geometries with high symmetry, like spherical and cylindrical walls.

It is important to appreciate the importance of the choice of a dividing interface when calculating surface thermodynamic quantities. The total grand potential Ω of the mixture is, of course, uniquely defined; however, when split into volume, surface and curvature terms, the particular choice of the dividing surface is reflected in the magnitude and possibly in the sign of the thermodynamic coefficients. Once the location of the dividing interface is fixed, *all* morphometric measures V , A , C and X must be calculated consistently using this definition, and the thermodynamic coefficients σ , κ and $\bar{\kappa}$ correspond to this definition.

From the morphometric form of the grand potential, equation (1), it follows immediately that surface thermodynamic quantities also possess a morphometric form. For example the interfacial tension γ of the fluid mixture in contact with a curved wall has, beside the planar wall term σ , only *two* curvature terms [1] and can be written as

$$\gamma \equiv \frac{1}{A} \Omega^{\text{surf}} = \sigma + \kappa \bar{H} + \bar{\kappa} \bar{K} \quad (2)$$

where we have used that $\Omega^{\text{surf}} \equiv \Omega + pV$ and $\bar{H} = C/A$ and $\bar{K} = X/A$. This is an important result and clearly requires numerical tests. The interfacial tension at a spherical wall should display a quadratic dependence on the curvature $1/R_c$, where R_c is the radius of curvature, while that at a cylindrical wall should depend only linearly on the curvature. Since the number

of parameters is too large and in fact infinite, it is impossible to verify this result systematically. We have performed density functional theory (DFT) calculation calculations [8–10] for binary hard-sphere mixtures with radii R_b and R_s and various values of the size ratio $q = R_s/R_b$ at curved spherical and cylindrical walls with different radii of curvatures. We always found full agreement between our DFT results and the morphometric form of γ , equation (2).

From the interfacial tension γ , equation (2), it is straightforward to calculate the excess adsorption of species i with the help of the Gibbs adsorption theorem:

$$\Gamma_i \equiv \frac{1}{A} \int_V d^3r (\rho_i(\mathbf{r}) - \rho_i) = - \sum_j \left(\frac{\partial \mu_i}{\partial \rho_j} \right)^{-1} \frac{\partial \gamma}{\partial \rho_j} = \Gamma_i^\sigma + \Gamma_i^\kappa \bar{H} + \Gamma_i^{\bar{\kappa}} \bar{K}, \quad (3)$$

where ρ_i are the bulk densities at given chemical potentials $\{\mu_i\}$. For hard walls the sum over the integrated (over the surface) contact densities ρ_i^c becomes a thermodynamic quantity through the wall theorem [1]:

$$\frac{1}{A} \sum_i \rho_i^c = \beta p + 2\beta\sigma \bar{H} + \kappa \bar{K}, \quad (4)$$

where $\beta = 1/k_B T$.

2.1. Effective second virial coefficient

In the case of a size asymmetric mixture, it can be useful to integrate out the degrees of freedom of the smaller particles and describe the remaining degrees of freedom of the big ones, denoted in the following by b , within an effective Hamiltonian [6]. The big particles then interact via an effective potential, which can be calculated in various ways, e.g. by fixing a single big particle, calculating the density distribution of the smaller particles s around it and finally inserting a second big particle into the inhomogeneous sea of small ones [11]. The approach we describe here is valid for general shapes and multi-component mixtures of small ones; however, in order to keep the notation simple, we specialize here to the case of mixtures of *hard* spheres. The resulting depletion potential $W(r)$, which in our case has spherical symmetry, is connected to the density profile $\rho_b(r)$ of big spheres around the fixed big sphere by [11]

$$\lim_{\rho_b \rightarrow 0} \frac{\rho_b(r)}{\rho_b} = \exp(-\beta W(r)). \quad (5)$$

While $W(r)$ is a microscopic quantity, the effective second virial coefficient B_2 between big spheres, which results from the bare and the effective interactions, is a thermodynamic quantity and can be calculated from the surface grand potential Ω^{surf} . From equation (5) and the Gibbs–Duhem relation $\partial p / \partial \mu_b = \rho_b$ at fixed T and V , we obtain

$$\lim_{\rho_b \rightarrow 0} \frac{1}{\rho_b} \frac{\partial \Omega^{\text{surf}}}{\partial \mu_b} = \lim_{\rho_b \rightarrow 0} \int_V d^3r \left(1 - \frac{\rho_b(r)}{\rho_b} \right) = c + 4\pi \int_{2R_b}^{\infty} dr r^2 (1 - e^{-\beta W(r)}), \quad (6)$$

where c is a constant depending on the choice of the dividing interface. Here we fix the dividing interface to be the surface of the big sphere and obtain $c = R_b^3 28\pi/3$. Equation (6) can be rewritten easily to express B_2 , the effective second virial coefficient:

$$B_2 = B_2^{\text{HS}} + 2\pi \int_{2R_b}^{\infty} dr r^2 (1 - e^{-\beta W(r)}) = \lim_{\rho_b \rightarrow 0} \frac{1}{2\rho_b} \frac{\partial \Omega^{\text{surf}}}{\partial \mu_b} + \frac{2\pi}{3} R_b^3, \quad (7)$$

where $B_2^{\text{HS}} = R_b^3 16\pi/3$ is the hard-sphere second virial coefficient. Equation (7) is an exact relation. Note that the constant on the rhs of equation (7) is $B_2^{\text{HS}} - c/2$ and depends on the definition of the dividing interface.

3. Application within a bulk approach

We consider a mixture of hard spheres in the bulk. The reduced excess free-energy density of this mixture corresponding to the approximate MCSL equation of state [12] is given by [8, 9]

$$\beta\Phi = -n_0 \log(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{n_2^3 (n_3 + (1 - n_3)^2 \log(1 - n_3))}{36\pi (1 - n_3)^2 n_3^2} \quad (8)$$

where Φ is a function of the weighted densities n_α , $\alpha = 0, \dots, 3$, which for a homogeneous bulk mixture reduce to $n_0 = \sum_i \rho_i$, $n_1 = \sum_i \rho_i R_i$, $n_2 = \sum_i \rho_i 4\pi R_i^2$ and $n_3 = \sum_i \rho_i 4\pi R_i^3/3$, and the sum runs over all ν components of the mixture. Following the bulk approach for a pure hard-sphere fluid [7], we start with a bulk mixture, for which we know the grand potential to be $-pV_{\text{tot}}$, and insert a single big sphere with radius R_b . From the change in grand potential of the system we can identify closed approximate expressions for σ the surface tension and κ and $\bar{\kappa}$, the bending rigidities [7]:

$$\sigma = \frac{\partial\Phi}{\partial n_2}, \quad \kappa = \frac{\partial\Phi}{\partial n_1}, \quad \bar{\kappa} = \frac{\partial\Phi}{\partial n_0}. \quad (9)$$

From this we can obtain an approximate expression for the interfacial tension of a hard-sphere mixture at a curved hard wall. We have verified with a density functional theory calculation [8–10] for binary hard-sphere mixtures at spherical and cylindrical walls that γ obtained by inputting the approximate bulk expressions for σ , κ and $\bar{\kappa}$ from equation (9) into (2) gives a reasonable account for the interfacial tension of binary hard-sphere mixtures if the size ratio $q = R_s/R_b$ remains sufficiently large. We assume that similar agreement can also be found for multi-component mixtures as long as the total packing fraction and size ratios remain moderate.

3.1. B_2 in hard-sphere mixtures

The approximate bulk expressions for σ , κ and $\bar{\kappa}$ can be employed to evaluate the second virial coefficient in a binary mixture of spheres in the dilute limit of big spheres using equation (7). It is possible to obtain a closed expression for B_2/B_2^{HS} ; however, it is quite lengthy and we shall discuss here only the limiting behaviour $\rho_s \rightarrow 0$ and compare the approximate form with numerical results.

In the limit of $\rho_s \rightarrow 0$, the depletion potential $W(r)$ entering equation (7) reduces to the well-known Asakura–Oosawa–Vrij expression [13–15]. In the same limit the exponential function in equation (7) can be linearized and the low-density behaviour of the second virial coefficient is given to be

$$\lim_{\rho_s \rightarrow 0} B_2/B_2^{\text{HS}} = 1 + \eta_s c^{\text{AO}} + \mathcal{O}(\eta_s^2), \quad (10)$$

where $\eta_s = 4\pi R_s^3/3 \rho_s$ with the *exact* first order in η_s contribution

$$c^{\text{AO}} = -\frac{1}{8} \{12 + q [15 + q (6 + q)]\} < 0, \quad (11)$$

which is exactly recovered by the approximate expression for B_2 based on equation (9). For sufficiently small values of ρ_s , the effective second virial coefficient in a mixture of hard spheres decreases linearly.

In figure 1 we show the effective second virial coefficient B_2/B_2^{HS} as a function of η_s for various values of the size ratio $q = R_s/R_b$. For small values of η_s , we find B_2 to decrease linearly, as predicted by equation (10). Although not visible on the scale of figure 1, we find, in agreement with equation (11), that the slope of B_2/B_2^{HS} for small values of η_s is larger for more symmetric mixtures and smaller for asymmetric ones. For $q = 1/3$ we

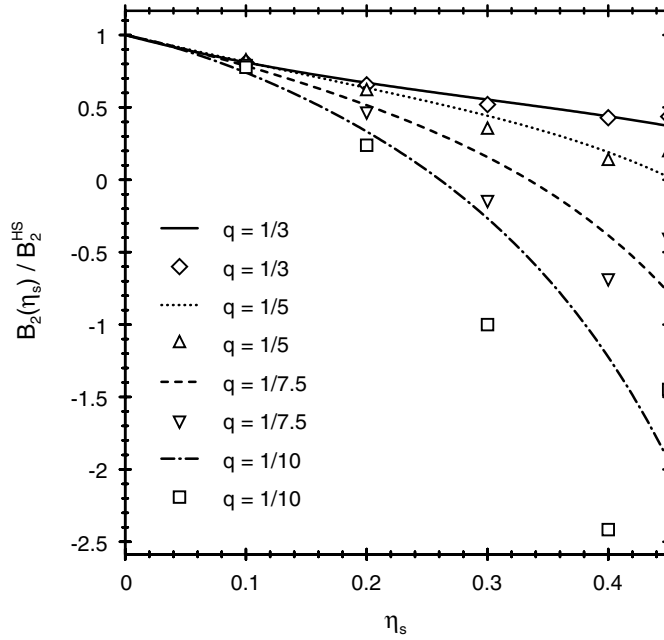


Figure 1. The effective second virial coefficient B_2/B_2^{HS} in a binary hard-sphere mixture as a function of $\eta_s = 4\pi R_s^3/3\rho_s$ for various values of the size ratio $q = R_s/R_b$. The lines denote results obtained from the closed approximate expression within the bulk approach. The symbols are calculated from depletion potentials using density functional theory.

find very good agreement between the approximate form of B_2/B_2^{HS} (full line) and values of the second virial coefficient calculated from the depletion potential (circles) [11, 16] for all values of η_s in the fluid regime. B_2/B_2^{HS} remains always positive, indicating the overall weak effect of the depletion potential for $q = 1/3$. As the mixture becomes more asymmetric, the depletion potential becomes more attractive close to contact and develops more structure at larger distances [11]. Therefore the second virial coefficient can become negative for sufficiently high values of η_s . In contrast to the behaviour of B_2/B_2^{HS} based on the numerical depletion potential (symbols), which displays a minimum around $\eta_s \approx 0.4$ [16] for all values of q , the bulk approximation predicts a monotonic decay (lines). Given the simplicity of the bulk approximation, the magnitude of the second virial coefficient is predicted surprisingly well.

4. Conclusion

We have studied fluid mixtures at curved walls. Following the morphometric approach [1] for pure fluids, we assume that the geometry of the curved wall and the thermodynamical properties of the fluid mixture separate into morphometric measures V , A , C and X , and corresponding thermodynamical coefficients p , σ , κ and $\bar{\kappa}$. As a consequence, thermodynamic quantities like the interfacial tension γ or the excess adsorptions Γ_i , $i = 1 \dots, v$, have a very simple curvature dependence. We have verified this within density functional theory for binary hard-sphere mixtures (not shown here).

We have shown that the effective second virial coefficient can be calculated from the surface grand potential Ω^{surf} . This relation can be employed within a bulk approximation to systematically study the behaviour of B_2 and the corresponding depletion potential for multi-component mixtures.

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