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Long-range attractions between solutes in near-critical fluids

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The Ornstein-Zernike equation is used to analyze adsorption at, and the forces between, solutes and walls in near-critical fluids. The density profile is shown to decay exponentially with the bulk correlation length. The forces between solutes and between walls are also exponentially long ranged with the bulk correlation length, and are always attractive for identical solutes.

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This paper is concerned with the forces between solutes in fluids near the critical point. We examine both spherical solutes and planar walls, and also consider solutes in binary mixtures near compositional instabilities. Our formal analysis is based upon the Ornstein-Zernike equation, and in particular the divergence of the compressibility at the critical point. We find certain universal behavior, namely, long-ranged attractions, independent of the specific solute-solvent interactions. Moreover, the range of the force is given by the correlation length of the bulk solvent. Therefore measurement of the forces between surfaces in near-critical fluids, with, for example, the apparatus of Israelachvili [1], would directly give the bulk correlation length.

Ornstein and Zernike, in their pioneering study of critical opalescence [2], postulated that the long-ranged total correlation function $h(r)$ was made up of chains of the shorter-ranged direct correlation function $c(r)$. Their exact equation forms the basis of the present work, and for a multicomponent atomic fluid it is [3]

$$h_{\alpha\beta}(r)=c_{\alpha\beta}(r)+\sum_{\gamma}\rho_\gamma\int h_{\alpha\gamma}(s)c_{\gamma\beta}(|\mathbf{r}-\mathbf{s}|)d\mathbf{s}\ , \qquad (1)$$

where ρ_γ is the number density of species γ. Taking the three-dimensional Fourier transform and using the convolution theorem, for a one-component fluid one has

$$\hat{h}_{11}(k)=\frac{\hat{c}_{11}(k)}{1-\rho_1\hat{c}_{11}(k)}\ . \qquad (2)$$

At the critical density, $\rho_1=\rho_c$, and temperature, $T=T_c$, the isothermal compressibility diverges due to the long-ranged character of the total correlation function, and hence $\hat{h}_{11}(k)\rightarrow+\infty$, $k\rightarrow0$. The direct correlation function remains short ranged, in the sense that its integral exists, and $\hat{c}_{11}(0)=\rho_c^{-1}$.

Experimentally one cannot access the critical point precisely, and we shall therefore be concerned with near criticality, $\rho_1\approx\rho_c$, $T\gtrsim T_c$. We assume the classical or Ornstein-Zernike form [3–6]

$$h_{11}(r)\sim A_{11}e^{-\xi r}/r,\quad r\rightarrow\infty\ , \qquad (3)$$

or, in Fourier space [7],

$$\hat{h}_{11}(k)\sim\frac{4\pi A_{11}}{k^2+\xi^2}\ ,\quad k\rightarrow0\ . \qquad (4)$$

Here $A_{11}>0$ because the compressibility of the fluid must be positive for it to be stable against density fluctuations. As one approaches criticality, the correlation length diverges with the universal critical exponent ν. Equations (2) and (4) imply that

$$\hat{c}_{11}(k)\sim\frac{4\pi A_{11}}{k^2+\chi^2}\ ,\quad k\rightarrow0\ ,\quad \chi^2\equiv\xi^2+4\pi\rho_1A_{11}\ . \qquad (5)$$

Hence the direct correlation function is exponentially decaying near criticality, and $c_{11}(r)/h_{11}(r)\rightarrow0$, $r\rightarrow\infty$, since $\chi>\xi$.

Now add to the near-critical bulk solvent spherical solutes at infinite dilution (i.e., $\rho_0=0$) and consider the Ornstein-Zernike equation for the solute-solvent interaction:

$$\begin{aligned}\hat{h}_{01}(k)-\hat{c}_{01}(k)&=\rho_1\hat{c}_{11}(k)\hat{h}_{01}(k)\\&=\rho_1\hat{h}_{11}(k)\hat{c}_{01}(k)\ ,\end{aligned} \qquad (6)$$

and for the solute-solute interaction:

$$\begin{aligned}\hat{h}_{00}(k)-\hat{c}_{00}(k)&=\rho_1\hat{h}_{01}(k)\hat{c}_{01}(k)\\&=\rho_1[1+\rho_1\hat{h}_{11}(k)]\hat{c}_{01}(k)^2\ .\end{aligned} \qquad (7)$$

One deduces from Eq. (6) that near bulk criticality the solute-solvent total correlation function becomes long ranged, and that the direct correlation function is shorter ranged [8]. The second conclusion follows from the first equality, because $\hat{c}_{11}(0)\rightarrow\rho_1^{-1}$, $\rho_1\rightarrow\rho_c$, $T\rightarrow T_c$. The pole in $\hat{h}_{11}(k)=i\xi$ determines the range of $h_{01}(r)$ to be the bulk correlation length ξ^{-1} consistent with earlier work [9,10]. [Note that there is no reason for $\hat{c}_{01}(0)$ to vanish near criticality.] The solute-solvent total correlation function represents the excess density profile about the solute. Whether there is a positive or a negative adsorption excess is given by the sign of $\hat{c}_{01}(i\xi)$, which is determined by the specific nature of the solute-solvent interactions.

Equation (7) implies that the solute-solute total correlation function becomes long ranged near criticality because of the pole at $k=i\xi$. [Note that the left side of Eq. (7) is, asymptotically, the negative of the excess potential of mean force, since the bridge function is as short ranged as is the direct correlation function.] Because the real number $\hat{c}_{01}(i\xi)$ occurs as a square, the sign of the potential of mean force is always negative. Thus there occur long-ranged attractions between solutes near bulk solvent criticality, irrespective of the particular solute-solvent interactions. Physically, one can rationalize this as an attempt by the solute to aggregate in whichever of the dilute or the dense phase it prefers.

We now consider the interaction between planar walls whose size is much larger than the correlation length of the bulk fluid. The wall-solvent Ornstein-Zernike equation is [11]

$$h_{01}(y)=c_{01}(y)+2\pi\rho_1\int_{-\infty}^{\infty}dz\int_{0}^{\infty}ds\, s h_{01}(z)\times c_{11}([(z-y)^2+s^2]^{1/2}) , \tag{8}$$

where the argument of the wall-solvent correlation function measures the distance from the wall $[h_{01}(z)=-1, z<0]$. The excess interaction free energy per unit area between walls in the hypernetted-chain approximation is [12]

$$w_{00}^{\text{ex}}(x)=-\rho_1 k_B T\int_{-\infty}^{\infty}h_{01}(z)c_{01}(x-z)dz , \tag{9}$$

where k_B is the Boltzmann constant. Equation (9) does not include any direct interaction between the walls nor the bridge function, which are short ranged and may be neglected at large separations. Hence Eq. (9) is exact asymptotically. The negative derivative of Eq. (9) with respect to separation, x, gives the net pressure between the walls [12].

The one-dimensional Fourier transform of Eq. (8) yields [12]

$$\tilde{h}_{01}(k)=\frac{\tilde{c}_{01}(k)}{1-\rho_1\hat{c}_{11}(k)} . \tag{10}$$

Near criticality of the bulk fluid, the denominator has a simple zero at $k=i\xi$, and one concludes that

$$h_{01}(z)\sim 2\pi\rho_1 A_{11}\tilde{c}_{01}(i\xi)e^{-\xi z}/\xi , \quad z\rightarrow\infty . \tag{11}$$

Hence near criticality the solvent profile decays exponentially off the wall at a rate given by the bulk correlation length [9,10]. Although $A_{11}>0$ [see Eq. (4)], the adsorption excess can be positive or negative (corresponding to wetting or drying) depending on the sign of $\tilde{c}_{01}(i\xi)$. Again we have assumed $c_{01}(z)/h_{01}(z)\rightarrow 0$, $z\rightarrow\infty$ [otherwise the asymptotic behavior of $h_{01}(z)$ would be determined by that singularity of $\tilde{c}_{01}(k)$ that lay closer to the origin than the pole in $\hat{h}_{11}(k)$ at $k=i\xi$].

The one-dimensional Fourier transform of the excess interaction free energy per unit area is [12]

$$\tilde{w}_{00}^{\text{ex}}(k)=-\rho_1 k_B T\tilde{h}_{01}(k)\tilde{c}_{01}(k)=\frac{-\rho_1 k_B T\tilde{c}_{01}(k)^2}{1-\rho_1\hat{c}_{11}(k)} , \tag{12}$$

which again has a simple pole at $k=i\xi$. Inverting this result one obtains

$$w_{00}^{\text{ex}}(x)\sim -2\pi\rho_1^2 k_B T A_{11}\tilde{c}_{01}(i\xi)^2 e^{-\xi x}/\xi , \quad x\rightarrow\infty , \tag{13}$$

which is negative, corresponding to an attractive force.

The above results were obtained for a pure bulk fluid, and depended upon the positive divergence of the compressibility near criticality. The generalization to a multicomponent bulk mixture is straightforward, and in this case the compositional instability is characterized by the zero of a determinant dependent upon the $\hat{c}_{\alpha\beta}(k)$. For example, for a binary mixture one has

$$\mathcal{D}_c=[1-\rho_1\hat{c}_{11}(k)][1-\rho_2\hat{c}_{22}(k)]-\rho_1\rho_2\hat{c}_{12}(k)^2 . \tag{14}$$

At the critical solution temperature, $\mathcal{D}_c\rightarrow 0+$, and again one concludes that the forces between identical solutes are long-ranged and attractive. Explicitly for walls, the excess interaction free energy per unit area as $x\rightarrow\infty$ is

$$\begin{aligned} w_{00}^{\text{ex}}(x)\sim -2\pi k_B T[& A_{11}\rho_1^2\tilde{c}_{01}(i\xi)^2 \\ & +2A_{12}\rho_1\rho_2\tilde{c}_{01}(i\xi)\tilde{c}_{02}(i\xi) \\ & +A_{22}\rho_2^2\tilde{c}_{02}(i\xi)^2]e^{-\xi x}/\xi , \end{aligned} \tag{15}$$

where the $A_{\alpha\beta}$ are as in Eq. (3). Stability conditions imply that $A_{11}A_{22}\geq A_{12}^2$, ensuring that the quantity in square brackets in Eq. (15) must be positive and hence the force must be attractive. In the context of force measurements, the consolute point of a binary mixture may be more accessible experimentally than is the critical point of a one-component fluid.

The critical point is the extremum of the spinodal curve delineating the absolute stability limit of the fluid. since the latter is defined by the divergence of the compressibility, one sees that the above results for near-critical fluids should also apply to metastable fluids near the absolute stability limit.

To summarize, we have used the Ornstein-Zernike equation to analyze the forces between solutes in near-critical fluids. We have treated both spherical solutes and planar walls, and also briefly discussed fluid mixtures and the spinodal line. We found that the density profile about a solute decayed exponentially with the bulk correlation length, which becomes increasingly long-ranged as criticality is approached [13–15]. Although the adsorption excess could be positive or negative, depending upon the specific solute-solvent interactions, we have shown that the force between identical solutes or walls is always attractive, and again exponentially decaying with the bulk correlation length. Earlier work by Fisher and de Gennes [16], Cardy [17], and others [9,18,19] was confined to the critical point itself, where the correlations decay algebraically rather than exponentially as in Eq. (3), and hence their results are not directly comparable to ours. Nevertheless, their small separation analysis (here we were concerned with large separation asymptotes, $x \gg \xi^{-1}$), indicated a certain universal behavior, to some extent independent of the boundary conditions at the walls [20].

Finally, we note that there exist various techniques for measuring the force acting between surfaces immersed in fluids, including one developed by Israelachvili [1]. Thus it should be possible to directly measure the forces described in the present analysis.

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