

BRIEF REPORTS

Brief Reports are accounts of completed research which do not warrant regular articles or the priority handling given to Rapid Communications; however, the same standards of scientific quality apply. (Addenda are included in Brief Reports.) A Brief Report may be no longer than 3½ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Long-range attractions between solutes in near-critical fluids

Phil Attard,* C. P. Ursenbach, and G. N. Patey

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

(Received 14 October 1991)

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.

PACS number(s): 64.60.Fr, 68.35.Rh, 68.45.Gd, 82.70.Dd

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]

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

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

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

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 $\hat{h}_{11}(k) \rightarrow +\infty$, $k \rightarrow 0$. 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]

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

or, in Fourier space [7],

$$\hat{h}_{11}(k) \sim \frac{4\pi A_{11}}{k^2 + \xi^2}, \quad k \rightarrow 0. \quad (4)$$

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

$$\hat{c}_{11}(k) \sim \frac{4\pi A_{11}}{k^2 + \chi^2}, \quad k \rightarrow 0, \quad \chi^2 \equiv \xi^2 + 4\pi\rho_1 A_{11}. \quad (5)$$

Hence the direct correlation function is exponentially decaying near criticality, and $c_{11}(r)/h_{11}(r) \rightarrow 0$, $r \rightarrow \infty$, 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:

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

and for the solute-solute interaction:

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

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]

$$h_{01}(y) = c_{01}(y) + 2\pi\rho_1 \int_{-\infty}^{\infty} dz \int_0^{\infty} ds sh_{01}(z) \times c_{11}([(z-y)^2 + s^2]^{1/2}), \quad (8)$$

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]

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

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]

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

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

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

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]

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

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

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

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

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

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

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

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.

The financial support of the National Sciences and Engineering Research Council of Canada, and of the Network of Centres of Excellence Programme in association with the Natural Sciences and Engineering Research Council of Canada, is gratefully acknowledged. One of us (P.A.) thanks the Killam Foundation of the University of British Columbia for financial support.

*Present address: Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, Canberra, ACT 2601, Australia.

- [1] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1985)
- [2] L. S. Ornstein and F. Zernike, Proc. Akad. Sci. (Amsterdam) **17**, 793 (1914).
- [3] L. E. Reichl, *A Modern Course in Statistical Physics* (University of Texas Press, Austin, 1980).
- [4] G. Stell, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1976), Vol. 5(b), Chap. 3.
- [5] M. E. Fisher, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), Sec. III-8.
- [6] At least at the critical point one must expect nonclassical behavior, but the classical form is not a bad approximation for real fluids [M. E. Fisher and S. Fishman, Phys. Rev. Lett. **47**, 421 (1981)]. Also, here near criticality means close enough that the exponential behavior dominates the experimental measurement (i.e., the van der Waals algebraic tail beyond the exponential regime is immeasurably small) but not so close that the size of the container is no longer much greater than the correlation length (i.e., our results do not apply precisely at criticality).
- [7] The asymptotic behavior of a function in real space is determined by the singularity of its Fourier transform that lies closest to the origin. Here we take the region of interest to be determined by the pole at $k = i\xi$, which tends to the origin near criticality.
- [8] For the case of the product of two functions (a convolution in real space), Cauchy's residue theorem says that the transform of the more rapidly decaying function should simply be evaluated at the singularity of the other transform.
- [9] H. W. Diehl, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1986), Vol. 10, p. 76, and references therein.
- [10] M. Schick, in *Liquids at Interfaces*, Proceedings of Les Houches 1988 Session XLVIII, edited by J. Charvolin, J. F. Joanny, and J. L. Zinn-Justin (North-Holland, Amsterdam, 1990), p. 418, and references therein.
- [11] D. Henderson, F. F. Abraham, and J. A. Barker, Mol. Phys. **31**, 1291 (1976).
- [12] P. Attard, D. R. Bérard, C. P. Ursenbach, and G. N. Patey, Phys. Rev. A **44**, 8224 (1991).
- [13] J. W. Cahn, J. Chem. Phys. **66**, 1667 (1977).
- [14] M. P. Nightingale and J. O. Indekeu, Phys. Rev. B **32**, 3364 (1985).
- [15] C. Ebner and W. F. Saam, Phys. Rev. B **35**, 1822 (1987).
- [16] M. E. Fisher and P.-G. de Gennes, C. R. Acad. Sci. Ser. B **287**, 207 (1978).
- [17] J. L. Cardy, Phys. Rev. Lett. **65**, 1443 (1990).
- [18] M. Krech and S. Dietrich, Phys. Rev. Lett. **66**, 345 (1991).
- [19] T. W. Burkhardt and T. Xue, Phys. Rev. Lett. **66**, 895 (1991).
- [20] Recently, A. Jamnik, D. Bratko, and D. J. Henderson [J. Chem. Phys. **94**, 8210 (1991)] found numerically that the force between hard-sphere solutes vanished at the critical point of Baxter's sticky sphere fluid. This is possibly an artifact of either the unphysical sticky sphere model, or of its approximate solution, since it contradicts the present formal results, and also those of others [16, 17].