Analytical solution of the mean-spherical approximation for a system of hard spheres with a surface adhesion

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(Received 16 August 1988)

The solution of a model for adhesive hard spheres is obtained within the mean-spherical approximation. The adhesive part of the potential is modeled as the limit of a Yukawa tail when both the amplitude and the inverse range tend to infinity. Use is then made of the analytical solution of the Ornstein-Zernike equation with a Yukawa closure, developed by Waisman, Hoye, Stell, and Blum. The system presents a liquid-gas phase transition, and the critical exponents γ and δ are those of the spherical model.

The study of systems that present phase transitions is one of the most fascinating fields of statistical physics. A great deal of analytic results has been obtained involving properties of phase transitions in lattice magnetic systems and in lattice gases. For continuum systems, there is not such a large number of analytic results. The enormous majority of the existent results for these systems has been gained by using considerable amounts of computing time.

One continuum model, on which there are analytic results, is the adhesive hard-sphere fluid (AHSF) proposed by Baxter.[1] He considered a system of particles with an interaction given by

$$\beta u(r)=\begin{cases}\infty, & r<\sigma\\ \ln[12\tau(R-\sigma)/R], & \sigma<r<R\\ 0, & R<r\end{cases} \tag{1}$$

in the limit when $\sigma \to R$. In Eq. (1), $\beta=1/k_B T$, where k_B is Boltmann's constant and T is the absolute temperature. The dependence upon temperature on the right-hand side (rhs) of Eq. (1) comes from the parameter τ. Baxter[1] was able to solve the Percus-Yevick approximation for this system. He found a critical point (η_c,τ_c) and for $\tau<\tau_c$ a liquid-gas phase transition. Baxter found $\tau_c=(2-\sqrt{2})/6$ and a critical density given by $\eta_c=(3\sqrt{2}-4)/2$, where $\eta=(\pi/6)\rho R^3$ and ρ is the number of spheres per unit volume. The critical exponents coincided with the classical ones.

Perram and Smith[2] extended the analysis of Baxter to an m-component mixture, and later on, Cummings *et al.*[3] considered in detail the correlation functions for the Baxter model.

Adhesive hard-sphere models are interesting in their own right, because they are among the few models that can by analytically solved, therefore giving more insight into the different critical behavior obtained from the Ornstein-Zernike equation, where different closures are used. Their importance also rests on the applicability that can be made to model real systems. For example, it is well known[4] that spherical colloidal particles have a van der Waals (or dispersion) force of attraction that, at very short distances, closely resembles that of adhesive spheres.

In this article we wish to consider another model for adhesive spheres that can be solved analytically within the mean-spherical approximation[5] (MSA). We use the analytic solution of the Ornstein-Zernike equation in this approximation for a system of hard spheres interacting with a potential of a Yukawa form, developed subsequently by Waisman, Hoye, Stell, and Blum in several articles.[6–10]

The system of particles we want to consider, interacts through the following pair potential function:

$$u(r)=\begin{cases}\infty, & r<1\\ -Je^{-z(r-1)}/r, & r>1\end{cases} \tag{2}$$

in the limit $J\to+\infty$, $z\to+\infty$, such that $J/z=\kappa=$const. In the MSA we therefore have a Yukawa closure. This is

$$\begin{aligned} h(r)&=-1, \quad r<1\\ c(r)&=\beta J e^{-z(r-1)}/r, \quad r>1\end{aligned} \tag{3}$$

where $h(r)$ and $c(r)$ are the total and direct correlation functions, respectively.

The limit now becomes $\beta J\to\infty$, $z\to\infty$, such that $\beta\kappa=\theta$ is constant. Observe that in (2) and (3) we have already renormalized the distances by the hard-sphere diameter.

We can now use the results given in Refs. 6–10. For our purposes, it will be easier to use the equations of Hoye and Blum,[10] developed originally for an arbitrary number of Yukawas, but specialized here to a single Yukawa. We rewrite their four equations [Eqs. (20a–20c) and Eq. (28) of Ref. 10] defining the unknowns a, b, c

and d, in the following fashion:[11]

$$\frac{a}{8}+\left[\frac{1}{12\eta}+\frac{1}{6}\right]b-\frac{c+d}{z^2}+\frac{z^2+2z+2}{2z^2}\frac{c}{e^z}=0\ , \tag{4}$$

$$\left[\frac{1}{3}-\frac{1}{12\eta}\right]a+\frac{b}{2}-\frac{c+d}{z}+\frac{z+1}{z}\frac{c}{e^z}+\frac{1}{12\eta}=0\ , \tag{5}$$

$$\left[\frac{z^2-2}{2z^3}(c+d)+\frac{z+1}{z^3}\frac{c}{e^z}\right]a+\left[\frac{z-1}{z^2}(c+d)+\frac{c}{z^2e^z}\right]b$$
$$-\frac{(c+d)^2}{2z}+\frac{c+d}{z}\frac{c}{e^z}+\frac{c+d}{12\eta}-\frac{1}{2z}\left[\frac{c}{e^z}\right]^2=0\ , \tag{6}$$

$$\left[\frac{z^2-2}{2z^3}+\frac{(z+1)e^{-z}}{z^3}\right]a+\left[\frac{z-1}{z^2}+\frac{e^{-z}}{z^2}\right]b-\frac{c+d}{2z}$$
$$+\left[\frac{1}{z}-\frac{e^{-z}}{2z}\right]\frac{c}{e^z}-\frac{\beta J}{12z\eta}\frac{e^z}{d}+\frac{1}{12\eta}=0\ . \tag{7}$$

Assuming that a and b remain finite, one can see that in the above-mentioned limit d grows as θe^z and $c+d$ vanishes as $6\eta\theta^2/z$. Hence, in the limit, we obtain the following set of equations for a and b:

$$\frac{a}{4}+\frac{1}{3}\left[1+\frac{1}{2\eta}\right]b=\theta\ , \tag{8}$$

$$\frac{1}{3}\left[1-\frac{1}{4\eta}\right]a+\frac{b}{2}=\theta-\frac{1}{12\eta}\ . \tag{9}$$

This system has the solution

$$a=\frac{2\eta+1}{(1-\eta)^2}-\frac{12\theta\eta}{1-\eta}\ , \tag{10}$$

$$b=\frac{12\eta}{1+2\eta}\left[\frac{\theta}{2}+\frac{3\theta\eta}{2(1-\eta)}-\frac{2\eta+1}{8(1-\eta)^2}\right]\ . \tag{11}$$

Using the last two equations and Eqs. (24), (25), (33), and (36) of Ref. 10, we can write the direct correlation function of a AHSF in the MSA as

$$-rc(r)=a_0r+b_0r^2+(\eta/2)a_0r^4+12\eta\theta^2,\quad r<1 \tag{12}$$

where

$$a_0=a^2\ , \tag{13a}$$

$$b_0=-12\eta[\tfrac{1}{2}(a+b)^2-a\theta]\ . \tag{13b}$$

We now identify[10] a_0 with the inverse compressibility, which is everywhere finite except at the critical point and spinodal curve of a phase transition, where it becomes infinite. The spinodal line is therefore defined by the condition $a_0=0$. A plot of Eq. (10) as a function of η is shown in Fig. 1. From Eqs. (10) and (13a), this curve is given by

$$12\theta\eta^2+2(1-6\theta)\eta+1=0\ . \tag{14}$$

This equation has two real solutions for $T<T_c$ and two complex solutions for $T>T_c$, where $T_c=\kappa/k_B\theta_c$, and $\theta_c=(2+\sqrt{3})/6=0.6220$. The corresponding critical density is $\eta_c=(\sqrt{3}-1)/2=0.3660$.

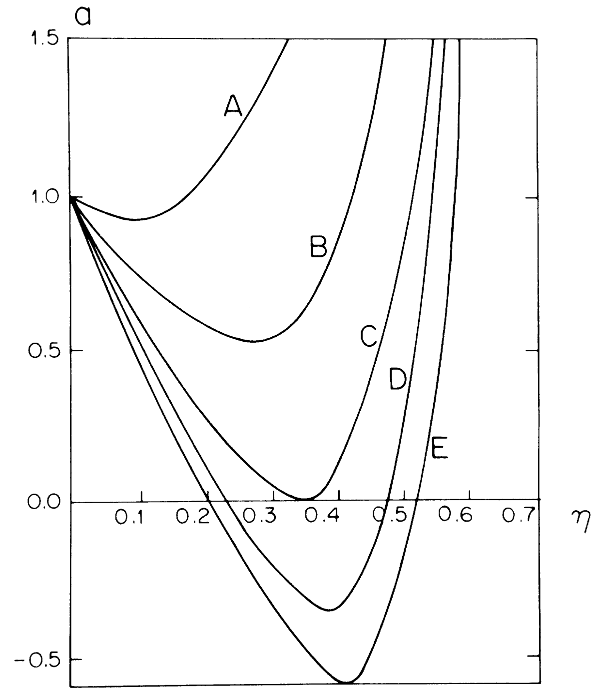

FIG. 1. A plot of a, Eq. (10), as a function of η for different values of the temperature. The isotherms displayed are curve A, $T=1.6T_c$; curve B, $T=1.20T_c$; curve C, $T=T_c$; curve D, $T=0.95T_c$; and curve E, $T=0.91T_c$.

An analysis of the critical neighborhood reveals that the isothermal compressibility diverges, along the critical isochore $\eta=\eta_c$ from $T>T_c$, as

$$\chi_T\equiv\left[\frac{\partial\rho}{\partial\beta p}\right]_T=\frac{1}{a_0}\simeq\frac{3(7-4\sqrt{3})}{4}\left[\frac{T-T_c}{T_c}\right]^{-\gamma}\ , \tag{15}$$

where $\gamma=2$. The compressibility pressure can be obtained by integrating the inverse compressibility with respect to η:

$$\frac{\pi}{6}\beta p=(12\theta)^2(\eta-1)-84\theta+4(36\theta^2+30\theta+1)/(1-\eta)$$
$$-6(6\theta+1)/(1-\eta)^2+3/(1-\eta)^3$$
$$+24\theta(6\theta+1)\ln(1-\eta)^2-1\ . \tag{16}$$

The last formula allows us to determine the shape of the equation of state along the critical isotherm, $\theta=\theta_c$. The result is

$$\frac{\pi}{6\kappa}(p-p_c)\simeq2^5(\tfrac{26}{15}+\sqrt{3})(\eta-\eta)^\delta\ , \tag{17}$$

with $\delta=5$.

Additionally, with the use of Eq. (14) we can determine the critical exponent $\beta_{\rm sp}$ associated with the shape of the spinodal line in the vicinity of the critical point. We obtain

$$\left|\frac{\eta_{l,g}-\eta_c}{\eta_c}\right|\simeq3^{1/4}\left[\frac{T_c-T}{T_c}\right]^{\beta_{\rm sp}},\quad T<T_c\ , \tag{18}$$

with $\beta_{sp}=\frac{1}{2}$. In Eq. (18) $\eta_{l,g}$ represents the liquid and gas spinodal densities. This equation shows symmetrical asymptotic behavior of the top of the spinodal curve. If we assume, as usually happens, that the exponent β of the coexistence curve, obtained from the compressibility equation equation of state, coincides with β_{sp}, the exponents obtained thus far agree with those of the spherical model,[12] as it should happen for a short-ranged potential in the MSA.[13-16]

The analytic solution for the AHSF in the MSA can be extended straight to the case in which a sum of Yukawa tails is added to the adhesive hard-sphere potential. This extended solution and a comparison between the Percus-Yevick[1] and MSA solutions for the AHSF will be presented in a forthcoming longer publication.

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[11]In this respect one should note a misprint in the definition of $\sigma(s)$ [Eq. (24) of Ref. 10]. The exponential should read e^{-z_i} instead of e^{z_i}.

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