LIQUID-GAS TRANSITION FOR HARD SPHERES WITH ATTRACTIVE YUKAWA TAIL INTERACTIONS

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We describe the liquid–gas transition in the hard sphere system with Yukawa tail interactions in the mean spherical approximation. The dependence of critical temperature and density on the range of the interaction is shown and the spinodal curve for a short-ranged potential and a long-ranged potential is presented. The compressibility, energy and virial pressures are presented for a long-ranged potential. Liquid phase pressures are calculated by integrating round the coexistence region, rather than through it.

1. Introduction

A great deal of work has been done recently [1–5] on the mean spherical approximation for a system of hard spheres with Yukawa tail interactions. The interparticle interaction is

\[ \phi(r) = \infty, \quad 0 < r < 1; \]
\[ = -A e^{-\xi(r^{-1})/r}, \quad r > 1. \]  

(1)

The model is solved by analysing the Ornstein–Zernike relation relating the total (h(r)) and direct (c(r)) correlation functions, the hard sphere exclusion constraint

\[ h(r) = -1, \quad 0 < r < 1, \]  

(2)

and the mean spherical approximation to the direct correlation function outside the hard core

\[ c(r) = K e^{-\xi(r^{-1})/r}, \quad r > 1, \]  

(3)

where \( K = A/kT \). The temperature enters into the calculation only via the parameter \( K \). The analysis was first carried out by Waisman [1] using the method introduced by Wertheim for simple hard spheres [6] and has also been carried out using Baxter’s Wiener–Hopf factorization technique [2, 3].

As Waisman pointed out in his original article, for positive \( K \) it is possible for the system to undergo a liquid–gas type phase transition. The critical point of this transition is naturally of classical type because of the use of the mean spherical approximation, eq. (3). The nature of the spinodal curve for this transition is of interest for a number of reasons. The first is that the model is a continuum system model which undergoes a liquid–gas type transition. The only other model potentials which give such a transition and which are amenable to even approximate analytic solution of the type described here are the adhesive sphere model introduced by Baxter [7] and solved in the Percus–Yevick approximation by him and the van der Waals limit model in which rigorous results may be obtained for the limit in which the interaction becomes infinitely long-ranged and weak [8]. Both these potentials are somewhat unphysical, corresponding to zero and infinite ranged attractive potentials respectively. In the model discussed in this paper, the range \( \xi^{-1} \) of the potential is an adjustable parameter. Another reason for interest in the spinodal region for the system is its use in theories of hard sphere system [9], in adsorption studies [10, 11] and in thermodynamic perturbation theories [12]. Uniform states inside the spinodal region have unphysical thermodynamic properties, so it is necessary to know where the spinodal region is before using the model in one of these applications. Otherwise unphysical behaviour may be built into the application at the beginning [11, 13].
We now present an outline of the salient parts of the solution. The Fourier transform of the standard Ornstein–Zernike equation may be written in the form

\[ [1 + e^{i\phi(k)}][1 - \rho e(k)] = 1. \] (4)

where \( \rho \) is the number density of particles in the system,

\[
\hat{h}(k) = 2\pi \int_{-\infty}^{\infty} e^{ikr} J(t) \, dt,
\]

\[
\hat{c}(k) = 4\pi \int_{0}^{\infty} e^{ikr} S(r) \, dr,
\]

\[
J(r) = \int_{r}^{\infty} \rho(t) \, dt
\]

and

\[
S(r) = \int_{r}^{\infty} \rho(t) \, dt.
\] (5)

The second factor on the lhs of eq. (4) may be factorized in the form

\[ 1 - \rho e(k) = \hat{Q}(k) \hat{Q}(-k), \] (6)

where \( \hat{Q}(k) \) is a function which is analytic in the upper half \( k \)-plane and free of zeros and poles there. It may be shown that \( \lim_{k \to \infty} \hat{Q}(k + ir) = 1 \) and \( \lim_{k \to -\infty} \hat{Q}(k) = 1 \). This means that \( \hat{Q}(k) \) must be positive on the positive imaginary axis, though a zero at \( k = 0 \) is permissible. The function \( 1 - \hat{Q}(k) \) has an inverse Fourier transform given by

\[
2\pi \rho q(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikr} [1 - \hat{Q}(k)] \, dk.
\] (7)

The function \( q(r) \) is given by [3]

\[
q(r) = 0, \quad r < 0,
\]

\[
= \frac{1}{2} (a(r^2 - 1) + b(r - 1)) + d[1 - e^{-2(r - 1)}] + \beta e^{-\xi r - 11}, \quad 0 < r < 1;
\]

\[
= \beta e^{-\xi r - 11}, \quad r > 1. \] (8)

In eq. (8), using \( \eta = \frac{1}{2}\pi \rho \),

\[
a = (1 - \eta)^{-2} \left\{ 1 + 2\eta + 12\eta \xi^{-1} \beta e^{\xi} [1 + 2\eta - 6\eta/\xi] \times (d - 1 - d e^{-\xi}(1 + \xi)) + 3\eta d \xi e^{-\xi} \right\} \]

\[
b = -(1 - \eta)^{-2} \left\{ \frac{3}{2} \eta + 12\eta \xi^{-1} \beta \left[ (3\eta + (1 - 4\eta)/\xi) \times (d - 1 - d e^{-\xi}(1 + \xi)) - \frac{1}{2}(1 - 4\eta) d \xi e^{-\xi} \right] \right\} \] (9a)

and

\[
d = 1 - 12\eta \xi^{-1} \hat{g}(\xi). \] (9c)

The value of \( \hat{g}(s) \), the Laplace transform of \( r[h(r) + 1] \) is given by [2, 3]

\[
\hat{g}(s) = [s^2 \xi^2 [a(s + 1) + bs] + \beta d \xi(\xi + s)] e^{-s} \times [1 - 12\eta \hat{q}(s)]^{-1}, \] (9d)

where \( \hat{q}(s) \), the Laplace transform of \( q(r) \) is given by

\[
\hat{q}(s) = \frac{s^3}{2\pi} \left\{ \xi^2 [a(s + 1) + bs] + \beta d \xi(\xi + s) \right\} e^{-s} \times [1 - 12\eta \hat{q}(s)]^{-1}.
\] (9e)

The parameter \( \beta \) is the solution of the quartic equation

\[
36\eta^2 \beta^4 - X \beta^3 + 12\eta K \beta^2 - KY \beta + K^2 = 0, \] (10)

where

\[
X = 6\eta \left\{ \xi e^{-\xi\beta} - \frac{6\eta}{\xi^2 (1 - \eta)} \left[ 2 - 2\xi - e^{-\xi (2 - \xi^2)} \right] - \frac{18\eta^2}{\xi^2 (1 - \eta)^2} \left[ 2 - \xi - e^{-\xi (2 + \xi)} \right] \right\}
\]

and

\[
Y = \xi - \frac{6\eta}{\xi^2 (1 - \eta)} \left[ 2 - \xi^2 - 2e^{-\xi (1 + \xi)} \right] - \frac{18\eta^2}{\xi^2 (1 - \eta)^2} \left[ 2 - \xi - e^{-\xi (2 + \xi)} \right]. \] (11b)

An alternative to eq. (9c) for the parameter is to consider the equation

\[
\beta \xi \hat{q}(i\xi) = K. \] (12)

This equation gives, using the Fourier transform

\[
\hat{Q}(k) = 1 - 2\pi \rho \int_{0}^{\infty} q(r) e^{ikr} \, dr \] (13)
and eq. (8) for \( q(r) \), a linear relation for \( d \). The relation may be solved to give the following rather messy relation for \( d \):

\[
d = \frac{\left(-K + \beta D\right)e^{-\xi} + E\beta^2}{F\beta^2},
\]

(14)

where

\[
D = \frac{(1 + 2\eta)}{(1 - \eta)^2}S + \frac{3\eta}{2(1 - \eta)^2}T,
\]

(15a)

\[
E = -6\eta + \frac{12\eta}{\zeta(1 - \eta)^2}\left(1 + 2\eta - 6\eta/\zeta\right)S
\]

\[-\frac{12\eta}{\zeta(1 - \eta)^2}\left[\frac{3\eta}{\zeta} + (1 - 4\eta)/\zeta\right]T,
\]

(15b)

\[
F = -6\eta(1 - e^{-\zeta})^2 + \frac{12\eta}{\zeta(1 - \eta)^2}\left(1 + 2\eta - 6\eta/\zeta\right)
\]

\[\times \left[1 - e^{-\zeta}(1 + \zeta) + 3\eta\zeta e^{-\zeta}\right]S
\]

\[-\frac{12\eta}{\zeta(1 - \eta)^2}\left[\frac{3\eta}{\zeta} + (1 - 4\eta)/\zeta\right]\left[1 - e^{-\zeta}(1 + \zeta)\right]
\]

\[-\frac{1}{2}(1 - 4\eta)\zeta e^{-\zeta}T,
\]

(15c)

\[
S = \frac{12\eta/\zeta^2}{[1 - \frac{1}{2}\zeta^2 - e^{-\zeta}(1 + \zeta)]}
\]

(15d)

and

\[
T = 12\eta(1 - \zeta - e^{-\zeta})/\zeta.
\]

(15e)

This particular form of the solution allows explicit construction of \( d \) and then \( a \) and \( b \) from the solution to the quartic equation (10).

Eq. (10) has four real or complex solutions, only one of which gives the known thermodynamic behaviour in the limit \( \rho \to 0 \) (ideal gas behaviour) or in the limit \( K \to 0 \) (hard sphere Percus–Yevick behaviour). From a graph of the roots of the equation it is thus possible to choose the correct root. We discuss this question of choice in the next section. Once the parameter \( \beta \) is known, the properties of the system may be calculated directly using results already reported in the literature [2, 3, 4].

The method used [2, 3] to obtain eq. (10), that of Baxter's Wiener–Hopf factorization of the Ornstein–Zernike equation, appears to be simpler than that used by Waisman. We suggest this because the method used gives the quartic equation (10) without too much difficulty. The method of Waisman gives a set of coupled non-linear equations which appear not to have been reduced to a single non-linear equation. Use of the coupled non-linear equations appears more difficult in practice than the use of eq. (10).

2. The phase transition

The solution for pure phases described in the introduction may break down in two ways. The first is that eq. (10) may fail to have any real solutions and the second is that the constraint \( \dot{Q}(0) > 0 \) may break down. In figs. 1 and 2 we plot graphs of the solutions to eq. (10) for \( \xi = 1.8 \) (fig. 1) and \( \xi = 7.5 \) (fig. 2) as a function of reduced density \( \eta \) for a range of values of \( K \) (that is, a range of temperatures). It is worthy of note that the quartic equation (10) has only two real solutions for \( K > 0 \). At small densities the asymptotic expansions of the four roots of the quartic are

\[
\beta_1 = (K/\zeta)[1 + \mathcal{O}(\eta)],
\]

\[
\beta_{2,3} = \pm(-K e^{\zeta}/6\eta)^{1/2}[1 + \mathcal{O}(\eta)]
\]

and

\[
\beta_4 = (\zeta e^{-\zeta}/6\eta)[1 + \mathcal{O}(\eta)],
\]

(16)

Fig. 1. Behaviour of the parameter \( \beta \) as a function of reduced density \( \eta \) for \( \xi = 1.8 \) along the isotherms \( K = 0.3 \) (---), \( K = 0.7 \) (---), \( K = 1.0 \) (---) and \( K = 1.5 \) (----). \( L_1 \) is the locus of points for which the discriminant of eq. (10) is zero; \( L_2 \) is the locus of points for which \( \dot{Q}(0) = 0 \).
Fig. 2. Behaviour of the parameter $\beta$ as a function of reduced density $\eta$ for $\zeta = 7.5$ along the isotherms $K = 2.0$ (---), $K = 5.0$ (---), $K = 7.0$ (---) and $K = 13.0$ (- - - -). $L_1$ and $L_2$ are defined as in fig. 1.

again showing only two real roots for $K > 0$. The root $\beta_1$ is the physical root, as can be seen from ideal gas thermodynamics.

In figs. 1 and 2 we also show the curves on which the roots of the quartic are equal ($L_1$) and on which $\tilde{Q}(0) = 0$ ($L_2$). At low temperatures, for a range of intermediate densities, the quartic has no solutions corresponding to physical states. On the high density side of this range the correlation functions are liquid-like while they are gas-like on the low density side if the smaller root $\beta$ is chosen [3]. Thus the unphysical region is identified as part of the coexistence region for a liquid–gas transition.

Series expansions in density for the compressibility have been published [4] and the root $\beta_1$ of eq. (16) gives the same behaviour to leading order in $\eta$. Since it is possible to get to any part of the $(\eta, T)$ plane from (0, T) in a continuous manner, it is clear that along each isotherm the root which lies below the curve $L_1$ is the correct one to choose. Thus the physical root of eq. (10) is always the smaller root for cases when $K > 0$.

The inverse compressibility is given by

$$\frac{1}{kT} \frac{\partial P}{\partial \rho} \bigg|_\tau = [\tilde{Q}(0)]^2,$$

so that the relation $\check{Q}(0) = 0$ defines a spinodal

region. In fig. 3, we plot the values of $K$, as a function of reduced density $\eta$ for which $\check{Q}(0) = 0$ for $\zeta = 1.8$ and 7.5 and also plot the values of $K$ for which the two real roots of the quartic are equal. Fig. 3 thus gives the spinodal region for $\zeta = 1.8$ and 7.5.

It is certainly striking to compare figs. 1 and 2 with the similar graphs obtained for solutions of a quadratic equation for a parameter which determines the properties of the adhesive sphere system in the Percus–Yevick approximation [7] and the plots found by Watts [14] in numerical studies of the Percus–Yevick equation for Lennard-Jones systems. The solutions in the cases considered in this paper look qualitatively very similar to those already encountered. One difference worth noting is that in the Yukawa tail system in the mean-spherical approximation, the curves $L_1$ and $L_2$ do not intersect, while they do intersect at the critical point in
or the criterion of equal roots of eq. (10) is used to identify the critical point. Because the values of \( \beta \) for which \( \hat{Q}(0) = 0 \) are always real, the Yukawa tail model may be used to describe metastable states on both sides of the coexistence region, right up to the spinodal limit.

The existence of a region of intermediate densities for which \( \beta \) is complex precludes use of the Maxwell construction to find the coexistence region. However, as we shall see in the next section, pressures (and also chemical potentials) at liquid densities and substantial temperatures may be found by using a path in the \( K - \eta \) plane which goes round the spinodal region.

3. The pressures

There are three commonly used routes to the pressure from approximate results on correlation functions, the compressibility, virial and energy pressures. The compressibility pressure may be found by integrating

\[
\frac{\partial p_T}{\partial P} = \left[ \hat{Q}(0) \right]_T^2 = a^2.
\]

The virial pressure is given analytically by \([3, 16]\)

\[
p^v/\rho kT = 1 + 4\eta(a + b + \beta d\xi)
+ 4\eta K e^{[\xi \hat{g}(\xi) - \hat{g}(\xi)]},
\]

while the energy pressure is given analytically by \([3]\)

\[
p^e/\rho kT = (p/\rho kT)_0 + 2\eta[(a + b + \beta d\xi)^2 - (a_0 + b_0)^2]
+ 4\eta K e^{[\xi \hat{g}(\xi) - \hat{g}(\xi)]},
\]

where \( a_0 \) and \( b_0 \) may be found from eqs. (9a) and (9b) by setting \( K = 0 \) (and so \( \beta = 0 \)) while the term \( (p/\rho kT)_0 \) refers to the pressure of a system of hard spheres. Choice of this reference pressure is fairly arbitrary: the Percus–Yevick compressibility or virial pressures may be used, for example. In this paper we used the values from the Carnahan–Starling equation of state for hard spheres \([15]\). We have been unable, thus far, to find an analytic expression for the integral of eq. (18). Numerical integration of eq. (18) readily gives the pressure at all densities for \( T \geq T_c \), but it is not immediately clear how to find \( p^v \) in the liquid phase for \( T < T_c \).
However, by integrating with respect to $\eta$ at $T = T_c$ and then with respect to $T$ at the liquid value of $\eta$ required, a pressure may be found by going around the spinodal region, rather than across it. That is, if $\eta_L(T)$ is the density on the liquid side of the spinodal curve at temperature $T$, then we may define a pressure for $\eta > \eta_L(T)$ and $T < T_c$ by the relation

$$
\rho'(\eta, T) = \int_0^{\eta_L(T)} \left( \frac{\partial \rho}{\partial \eta} \right)_{T=T_c} \, d\eta + \int_{T_c}^{T} \left( \frac{\partial \rho}{\partial T} \right)_{\eta} \, dT
$$

$$
- \int_0^{\eta_L(T)} \left( \frac{\partial \rho}{\partial \eta} \right)_{T=T_c} \, d\eta + \rho'(\eta, T) - \rho'(\eta, T_c).
$$

(21)

Use of eq. (20) for $\rho'$ makes evaluation of $\rho'$ via eq. (21) fairly simple. It should be noted that in eq. (21) the terms $(p/pkT)_o$ in $\rho'$ cancel one another. Thus the choice of hard sphere reference pressure in $\rho'$ is irrelevant to the definition of subcritical liquid phase compressibility pressures given in eq. (21). In eq. (21) we really replace the $(p/pkT)_o$ in eq. (20) by the compressibility pressure on the critical isotherm and then use the pressure-energy relation to go from the critical temperature to the desired subcritical temperature.

In fig. 6 we plot $p'\nu_0/kT$ for $\xi = 1.8$, where $\nu_0 = \pi/6$. Notice that the compressibility is infinite at higher densities than the spinodal density given by $Q(0) = 0$. This shift of the spinodal curve is due to the use of eq. (21). In the region where $Q(0) < 0$ but the roots of eq. (10) are still real, close to the critical point, it is interesting to note that the isotherms have a gradient $\approx 10^{-4}$. Another point to note is that the pressure on the spinodal curve on the gas side is higher than that on the liquid side, thus allowing the construction of a horizontal portion of the isotherm in the coexistence region. This may not occur automatically, as can be seen from the virial pressure isotherms for the adhesive sphere system in the Percus–Yevick approximation [14].

In fig. 7, we plot $p'/pkT$ and $p'/pkT$ for supercritical, critical and subcritical isotherms. Notice that $p'$ is consistently above $p''$, that the construction of horizontal parts of the isotherms in the coexistence region is possible in all cases, and that the compressibility is finite in all cases on the gas side of the spinodal region. The difference between $p'$ and $p''$ depends on temperature and thus is not simply an artifact of choosing the Carnahan–Starling equation of state for $(p/pkT)_o$. It should be noted that the energy pressures are much closer to the simulation results than the virial pressures. Further, comparison of the compressibility pressure along a supercritical isotherm ($K = 0.5$) with machine simulation values [5] indicates that the compressibility pressure is not as accurate as the energy pressure. In table 1 we give $p'/pkT$, $p'/pkT$, $p'/pkT$ and the Monte Carlo values for $p/pkT$ [5] for $\xi = 1.8$, $\rho = 0.4$, 0.6 and 0.8 for $K = 0.5$ and 0.667, which are supercritical temperatures and for $K = 1.0$, a subcritical temperature. As has been pointed out before [5], $p'$ gives better values than $p''$ or $p'''$. Table 1 also shows values of the Carnahan–Starling mixture $p^{CS} = \frac{1}{3}p' + \frac{2}{3}p''$, which is also not as good as $p'$.
A feature of the thermodynamic results derived in this paper is that they may be obtained by substitution of the value of the parameter $\beta$ into eqs (9a) and (9b) for the parameters $a$ and $b$, eq. (14) for the parameter $d$ and eqs. (9d) and (9c) for $\bar{g}(s)$ and $\bar{n}(s)$. This may be contrasted with the method used previously by Henderson et al. [5].

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References