Percus–Yevick theory of correlation functions and nucleation effects in the sticky hard-sphere model

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We use the Percus–Yevick approximation to study indirect correlation functions in the sticky hard-sphere model introduced by Baxter. The model has a critical point below which there is a liquid gas transition. We illustrate the changes in the structure of the correlation function as the density increases on the critical isotherm and on supercritical and subcritical isotherms. We also examine the local effects on this structure of introducing a large isolated sticky particle. For the gas part of the subcritical isotherm, such a particle can act as a condensation nucleus. We examine the dependence of the structure changes on the radius of the large particle.

1. INTRODUCTION

A great deal of work has been done on the properties of correlation functions in lattice models of magnetic systems and in lattice gases [1–6]. The general features of the correlation functions at critical points and on either side of a phase transition are known fairly well for many lattice systems. For simple lattice models (especially two-dimensional ones), much of the fine detail is also understood [7, 8]. Further, the effects of impurities in lattice systems have been studied fairly extensively [9, 10]. Most of these studies have been carried out on the Ising model, where the available exact results have greatly facilitated progress. However, for continuum systems, there is not such a large body of results, and very few exact ones. The results are almost all numerical, and have been gained by using prodigious amounts of computer time. The effect of impurities on the equilibrium classical statistical mechanical description of liquid and gas properties has not, to our knowledge, been studied very extensively.

One continuum model, on which there has been a certain amount of analytic progress, is the penetrable sphere model of Widom and Rowlinson [11]. This is the only continuum model with short-range forces for which it is possible to prove that a phase transition occurs [12]. The Percus–Yevick equations for this system have been solved by Ahn and Lebowitz [13]. They find, as would be expected, a classical critical point for the system in the P–Y approximation. Guerrero et al. [14] studied the molecular field, Percus–Yevick and hypernetted chain approximations for the penetrable sphere system. They find that the mean field and P–Y equations give a classical critical point. For the HNC
approximation they computed the first eleven virial coefficients of the pressure and compressibility equations of state. These coefficients were formed into Padé approximants, and the critical exponent $\gamma$ [which describes the divergence of the critical compressibility] evaluated. In three dimensions this exponent did not appear to have its classical value of 1.

In this paper we study another continuum model. The model was first proposed by Baxter [15] and has several virtues. There is unfortunately no rigorous proof of the existence of a phase transition, but within the context of the Percus–Yevick approximation, the model has a liquid–gas transition, the direct correlation function may be calculated analytically and the indirect correlation function may be computed easily. Since we use the Percus–Yevick approximation, we expect a classical critical point, and hence expect no real insight into the exact critical properties of the system. We do, however, analyse the classical critical point in some detail, since there are very few such calculations for continuum systems, even for classical critical points.

However, at ordinary liquid and gas densities (i.e. not close to the critical point) the Percus–Yevick approximation gives the correlation functions fairly accurately, if the bulk of the interparticle potential is repulsive. Thus, for our system we are able to understand how the microscopic structure of the system changes as the system undergoes a gas–liquid condensation away from the critical point. Further (and perhaps most interestingly) we are able to study the modification of the microscopic structure caused by an impurity, and thus examine the way an impurity may nucleate the condensation of the metastable gas.

The model is Baxter’s ‘sticky sphere’ model. We first consider a system of particles with an interaction given by

$$
\phi(r)/kT = \begin{cases} 
+\infty & r < \sigma \\
-\log \left[R/12\tau(R-\sigma)\right] & \sigma < r < R \\
0 & r > R.
\end{cases}
$$

(1.1)

We then consider this system in the limit $\sigma \to R$, when the Boltzmann factor $\exp \left[-\phi(r)/kT\right]$ develops a delta function at $r = R$. This means that the probability of finding a particle touching any given particle is finite. We may rewrite the definition of $\phi(r)$ in the limit $\sigma \to R$ in the form

$$
\exp \left(-\phi(r)/kT\right) = \begin{cases} 
\frac{R}{12\tau} \delta(r-R) & r \leq R \\
1 & r > R.
\end{cases}
$$

(1.2)

A problem arises with the use of a definition like (1.2): how can temperature be given a sensible meaning? The temperature dependence must come through the parameter $\tau$. If we wish to use this system to model a system with a potential $\phi_S(r)$, then we make the second virial coefficient for the potential $\phi_S(r)$ match that for the potential in (1.2). That is, the dependence of $\tau$ upon temperature is given by

$$
\frac{R^3}{12\tau} = \frac{R^3}{3} + \int_0^\infty r^2 \left[\exp \left(-\phi_S(r)/kT\right) - 1\right] \, dr.
$$

(1.3)
For the rest of this paper we attempt to anchor our discussion in reality by choosing for \( \phi_S \) the square-well hard-sphere potential
\[
\phi_S(r) = \begin{cases} 
+\infty & 0 < r < R \\
-\epsilon & R < r < 2R \\
0 & r > 2R 
\end{cases}
\] (1.4)
so that
\[
\tau = \frac{1}{\beta} \left( \exp\left( \frac{\epsilon}{kT} \right) - 1 \right)^{-1}.
\] (1.5)

Note that as \( T \to \infty \), \( \tau \sim (k/28\epsilon)T \) and as \( T \to 0 \), \( \tau \sim \frac{1}{2\beta} \exp\left( -\epsilon/kT \right) \) so that as \( T \) goes from 0 to \( +\infty \), so does \( \tau \).

Baxter [15] has solved the Percus–Yevick approximation for this system. He found a critical point and for \( \tau < \tau_c \) there is a liquid–gas phase transition. He calculated both the virial pressure and the compressibility pressure, but the virial pressure gave an unphysical structure to the phase transition. Thus, in this work, we consider only the compressibility pressure. Baxter found that \( \tau_c = (2 - \sqrt{2})/6 \) which gives, from (1.5) for \( \epsilon/k = 100 \) K, \( T_c \sim 320.77 \) K, \( \epsilon/kT_c \sim 0.312 \).

For particles of diameter \( R \), the critical density \( \rho_c \) is given by
\[
(\pi/6)\rho_c R^3 = (3\sqrt{2} - 4)/2 \approx 0.12132 \text{ or } \rho_c \approx 0.2371/R^3.
\]

Perram and Smith [16] have extended the analysis of Baxter to an \( m \)-component mixture of particles with the \( \alpha-\beta \) interaction being given by
\[
\exp\left( -\phi_{\alpha\beta}(r)/kT \right) = \begin{cases} 
\frac{R_{\alpha\beta}}{12\tau_{\alpha\beta}} \delta(r - R_{\alpha\beta}) & 0 < r < R_{\alpha\beta} \\
1 & r > R_{\alpha\beta}.
\end{cases}
\] (1.6)

The parameters \( \tau_{\alpha\beta} \) are again chosen by identification of second virial coefficients. To study the effects of an impurity (and especially to study nucleation effects) we consider a two-component mixture. Component 2 is the original sticky sphere gas, present with density \( \rho_2 \). Component 1 is a gas of hard spheres of radius \( R_1 \) (to which the 2-species may stick) which is present with density \( \rho_1 \). If we let \( \rho_1 \to 0 \), then when we study \( h_{12}(r) \), the indirect correlation function between 1- and 2-species, we are looking at the density variation in the 2-species about an isolated 1-species particle—i.e. at the distortion of the microscopic 2-species structure by an isolated nucleus. We again model square-well potentials:

\[
\phi_{S, 2\delta}(r) = \begin{cases} 
+\infty & 0 < r < R \\
-\epsilon_{22} & R < r < 2R \\
0 & 2R < r,
\end{cases}
\] (1.7)

\[
\phi_{S, 2\alpha}(r) = \begin{cases} 
+\infty & 0 < r < \frac{1}{2}(R + R_1) \\
-\epsilon_{12} & \frac{1}{2}(R + R_1) < r < \frac{1}{2}(3R + R_1) \\
0 & \frac{1}{2}(3R + R_1) < r,
\end{cases}
\] (1.8)

\[
\phi_{S, 1\delta}(r) = \begin{cases} 
+\infty & 0 < r < R_1 \\
0 & R_1 < r.
\end{cases}
\] (1.9)
This choice of potentials then gives
\[ \tau_{22} = \frac{1}{\epsilon_{22}} [\exp (\epsilon_{22}/kT) - 1]^{-1}, \quad (1.10 \, a) \]
\[ \tau_{12} = \left\{ 4 \left[ \frac{(R_1 + 3R_2)^3}{R_1 + R_2} \right] - 1 \right\} \left\{ \exp (\epsilon_{12}/kT) - 1 \right\}^{-1}. \quad (1.10 \, b) \]

Physically we expect \( R_1, \epsilon_{22} \) and \( \epsilon_{12} \) to be fixed and so \( \tau_{12} \) and \( \tau_{22} \) are not independent quantities. For the rest of this paper we consider \( \tau_{22} \) and \( \tau_{12} \) as given by equations (1.10 a, b), and consider distances to be measured in units of \( R \), so that \( R = 1 \cdot 0 \).

In the next three sections we outline the exact solution of the P–Y approximation for a sticky m-component mixture and develop the equations for the indirect correlation functions for the two-component mixture discussed above in the limit \( \rho_1 \to 0 \). We then go on to examine the microscopic structure of the sticky fluid and the distortion of this structure caused by the presence of an impurity.

2. ANALYTIC SOLUTION FOR MODEL

We consider an m-component mixture of species 1, . . . , \( \alpha \), . . . , m, the \( \alpha \)th species having density \( \rho_\alpha \) and diameter \( R_\alpha \). The Ornstein–Zernike relation may be written
\[ h_{\alpha \beta}(|r|) = c_{\alpha \beta}(|r|) + \sum_\gamma \rho_\gamma \int d^3s c_{\gamma \gamma}(|s|) h_{\gamma \beta}(|r - s|). \quad (2.1) \]

In the Percus–Yevick approximation, we supplement the Ornstein–Zernike relation with the equation
\[ c_{\alpha \beta}(r) = \left\{ 1 - \exp \left[ \frac{\phi_{\alpha \beta}(r)/kT}{s} \right] \right\} h_{\gamma \beta}(r) + 1. \quad (2.2) \]

This has the result that
\[ c_{\alpha \beta}(r) = 0 \quad \text{for} \quad r > R_{\alpha \beta} \equiv \frac{1}{4}(R_\alpha + R_\beta) \quad (2.3) \]
and thus we may use the formalism of Baxter [17] to solve the Ornstein–Zernike relation.

This formalism requires that we introduce the functions \( q_{\alpha \beta}(r) \) with the properties
\[ q_{\alpha \beta}(r) = 0 \quad \text{for} \quad r < S_{\alpha \beta} \equiv \frac{1}{4}(R_\alpha - R_\beta) \quad \text{or} \quad r > R_{\alpha \beta}. \quad (2.4) \]
The functions \( \mathcal{Q}_{\alpha \beta}(k) \) defined by
\[ \mathcal{Q}_{\alpha \beta}(k) = \delta_{\alpha \beta} - 2\pi(\rho_\alpha \rho_\beta)^{1/2} \int_{S_{\alpha \beta}}^{R_{\alpha \beta}} q_{\alpha \beta}(r) \exp (ikr) \, dr \quad (2.5) \]
may be determined in terms of the correlation functions by the relations
\[ \delta_{\alpha \beta} - 2\pi(\rho_\alpha \rho_\beta)^{1/2}\hat{c}_{\alpha \beta}(k) = \sum_\gamma \mathcal{Q}_{\alpha \gamma}(k)\hat{c}_{\gamma \beta}(k) \quad (2.6 \, a) \]
and
\[ \sum_\gamma \mathcal{Q}_{\alpha \gamma}(k)\left[ \delta_{\gamma \beta} + 2\pi(\rho_\gamma \rho_\beta)^{1/2}\hat{c}_{\gamma \beta}(k) \right] = (\hat{Q}(k))^{-1}_{\alpha \beta}. \quad (2.6 \, b) \]
The functions $\ell_{\alpha\beta}$ and $h_{\alpha\beta}$ are given by

\begin{equation}
\ell_{\alpha\beta}(k) = \frac{2}{k} \int_{0}^{\infty} dr \sin kr \ell_{\alpha\beta}(r) \tag{2.7a}
\end{equation}

and

\begin{equation}
h_{\alpha\beta}(k) = \frac{2}{k} \int_{0}^{\infty} dr \sin kr h_{\alpha\beta}(r). \tag{2.7b}
\end{equation}

Fourier inversion of (2.6a) and (2.6b) yields the equations [17]: for $r > S_{\alpha\beta}$ :

\begin{equation}
r h_{\alpha\beta}(r) = -q_{\alpha\beta}(r) + 2\pi \sum_{\gamma} \rho_{\gamma} \int_{S_{\alpha\gamma}}^{R_{\alpha\gamma}} dt \int g_{\gamma\gamma}(t)(r-t)q_{\gamma\beta}(r-t) \tag{2.8a}
\end{equation}

and for $S_{\alpha\beta} < r < R_{\alpha\beta}$ :

\begin{equation}
r \ell_{\alpha\beta}(r) = -q_{\alpha\beta}(r) + 2\pi \sum_{\gamma} \rho_{\gamma} \int_{S_{\alpha\gamma}}^{R_{\alpha\gamma}} dt \int g_{\gamma\gamma}(t)q_{\gamma\beta}(r+t), \tag{2.8b}
\end{equation}

the range of integrations in equation (2.8b) being $S_{\alpha\gamma} < t < \min [R_{\gamma\gamma}, R_{\gamma\beta} - r]$.

For the potentials given by (1.6), the virial expansions of the indirect correlation functions $h_{\alpha\beta}(r)$ have delta functions at $r = R_{\alpha\beta}$. Thus on $0 < r < R_{\alpha\beta}$, we may write $h_{\alpha\beta}(r)$ in the form

\begin{equation}
h_{\alpha\beta}(r) = -1 + \frac{\lambda_{\alpha\beta}R_{\alpha\beta}}{12} \delta(r-R_{\alpha\beta}), \tag{2.9}
\end{equation}

where the numbers $\lambda_{\alpha\beta}$ are to be determined later. If we insert (2.9) into (2.8a) for $S_{\alpha\beta} < r < R_{\alpha\beta}$, we see that $q_{\alpha\beta}(r)$ is linear in $r$ on $S_{\alpha\beta} < r < R_{\alpha\beta}$. We now solve for the coefficients in $q_{\alpha\beta}(r)$, and find, on $S_{\alpha\beta} < r < R_{\alpha\beta}$,

\begin{equation}
q_{\alpha\beta}(r) = \frac{1}{2}a_{\alpha}(r^2 - R_{\alpha\beta}^2) + b_{\alpha}(r - R_{\alpha\beta}) + \frac{\lambda_{\alpha\beta}R_{\alpha\beta}^2}{12} \tag{2.10}
\end{equation}

with

\begin{align*}
a_{\alpha} &= (1 - \xi_{\alpha} + 3R_{\alpha}\xi_{\alpha})(1 - \xi_{\alpha})^2 - X_{\alpha}/(1 - \xi_{\alpha}), \\
b_{\alpha} &= -3R_{\alpha}^2\xi_{\alpha}/2(1 - \xi_{\alpha})^2 + R_{\alpha}X_{\alpha}/2(1 - \xi_{\alpha})
\end{align*}

and

\begin{align*}
\xi_{\alpha} &= \frac{\pi}{6} \sum_{\gamma} \rho_{\gamma}R_{\gamma}^{-1}, \\
X_{\alpha} &= \frac{\pi}{6} \sum_{\gamma} \rho_{\gamma}\lambda_{\alpha\gamma}R_{\alpha\gamma}^{-2}R_{\gamma}^{-1}.
\end{align*}

Perram and Smith [16] show that the numbers $\lambda_{\alpha\beta}$ are the solutions of the equations

\begin{equation}
\lambda_{\alpha\beta}^2 = a_{\alpha} + b_{\alpha}/R_{\alpha\beta} + \frac{\pi}{6} \sum_{\gamma} \rho_{\gamma} \frac{\lambda_{\alpha\gamma}R_{\alpha\beta}^{-2}}{R_{\gamma\beta}} q_{\alpha\gamma}(S_{\alpha\gamma}). \tag{2.11}
\end{equation}

A little care (see Baxter [15] for the one-component case) must be exercised in choosing the correct solutions of (2.11).

We have now 'solved' the Percus–Yevick approximation for a mixture of sticky spheres. To apply the solution to our problem we consider a two-component mixture and take the limit $\rho_1 \to 0$. The equation for $\lambda_{22}$ becomes

\begin{equation}
\eta \frac{\lambda_{22}^2}{12} - \left( \frac{\eta}{1 - \eta} + \tau \right) \lambda_{22} + \frac{1 + \eta/2}{(1 - \eta)^2} = 0, \tag{2.12}
\end{equation}

where $\eta = \rho_2/(\rho_1 + \rho_2)$.
with \( \eta = (\pi/6)\rho \sigma^3 R^2 \), and we take the smaller of the two solutions \([15]\). The equation for \( \lambda_{12} \) becomes

\[
\lambda_{12} = \left[ \frac{\eta R_{12}}{2 R_2(1 - \eta)} - \frac{\eta R_{12} \lambda_{22}}{12 R_2} \right]^{-1} \left[ \frac{1}{1 - \eta} + \frac{3\eta R_1}{2 R_{12}(1 - \eta)^2} - \frac{R_1 \eta \lambda_{22}}{2 R_{12}(1 - \eta)} \right]. \tag{2.13}
\]

The functions \( g_{\alpha \beta}(r) \) which are of interest are given by (2.10) with

\[
a_2 = \frac{1 + 2\eta - \mu}{(1 - \eta)^2}, \quad b_2 = R_2 \left( -3\eta + \mu \right) / (1 - \eta)^2 \tag{2.14}
\]
and

\[
a_1 = \frac{1 + \eta \left( \frac{3R_1}{R_2} - 1 \right) - \nu \left( \frac{R_{12}}{R_2} \right)^2}{(1 - \eta)^2}, \quad b_1 = \frac{-3R_1 \eta + \nu \left( \frac{R_{12}}{R_2} \right)^2}{2(1 - \eta)}, \tag{2.15}
\]

where \( \mu = \eta(1 - \eta)\lambda_{22} \) and \( \nu = \eta(1 - \eta)\lambda_{12} \).

Baxter has shown \([15]\) that the bulk system of pure species 2 has compressibility pressure

\[
P(\eta, \tau_{22}) = \frac{1 + \eta + \eta^2 - \mu(1 + \eta/2) + \mu^2/36\eta}{(1 - \eta)^2} \tag{2.16}
\]
and gives isotherms which resemble those for a real system. In figure 1 we show compressibility pressure isotherms for a sticky sphere system with the potential (1.6) with \( \tau_{22} \) given by (1.10 a) with \( \epsilon_{22}/k = 100 \) K (i.e. 0.312\( T_C \)).

Figure 1. Graph of compressibility equation of state and limits of metastability. For \( \tau = 0.105, T/T_C = 1.064 \) for \( \tau = 0.0976, T = T_C = 329.77 \) K and for \( \tau = 0.092, T/T_C = 0.950 \).
Equation (2.12) fails to have real solutions for
\[ \eta_G(\tau_{z2}) = \frac{1 - 2\tau_{z2}(1 - \tau_{z2}) - \sqrt{(2\tau_{z2}^2 - 4\tau_{z2}/3 + 1/9)}}{2(\tau_{z2}^2 - 2\tau_{z2} + 5/6)} < \eta < \frac{1 - 2\tau_{z2}(1 - \tau_{z2}) + \sqrt{(2\tau_{z2}^2 - 4\tau_{z2}/3 + 1/9)}}{2(\tau_{z2}^2 - 2\tau_{z2} + 5/6)} \equiv \eta_L'(\tau_{z2}) \] (2.17)

and \( P(\eta_G(\tau_{z2}), \tau_{z2}) \) represents the gas side of the spinodal curve. The Fourier inversion of the right-hand side of (2.6 b) requires that the right-hand side exists for \( \text{im}(k) > 0 \), that is, that \( \det[Q(k)] \neq 0 \) for \( \text{im}(k) > 0 \). For
\[ \lambda'(\tau_{z2}) < \lambda(\tau_{z2}) = \left(\frac{2}{\tau_{z2} - 2\tau_{z2} + 5/6} \right) \] (2.18)

there is a pure imaginary value of \( k \) in the upper half \( k \)-plane for which \( \det[Q(k)] = 0 \). Thus the liquid side of the spinodal curve is given by \( P(\eta_L(\tau_{z2}), \tau_{z2}) \). These spinodal curves are also illustrated in figure 1. Another difficulty arises when the denominator in \( \lambda(\tau_{z2}) \) (cf. equation (2.13)) is zero. In this case the limit \( \rho_1 \to 0 \) is not uniform. When this happens, \( \det[Q(k)] \) may be zero in the upper half \( k \)-plane and the behaviour of \( h_{12}(r) \) becomes unphysical. We discuss this point further in § 4.

For the one component gas, equation (2.8 a) may be differentiated three times to yield a third-order differential difference equation for \( f(r) = r h_{z2}(r) \).

The equation is
\[ f''(r) + 2\eta \rho_2 q_{z2}(0) f'(r) - 2\eta \rho_2 q_{z2}'(0) f(r) + 2\eta \rho_2 q_{z2}''(0) f(r) = \frac{\lambda_{z2}}{R_2} q''(r - R_2) + 2\eta \frac{\lambda_{z2}}{R_2} f''(r - R_2) - 2\eta \rho_2 q_{z2}'(R_2) f'(r - R_2) + 2\eta \rho_2 q_{z2}''(R_2) f(r - R_2). \] (2.19)

The auxiliary equation of the homogeneous equation has three solutions \( \xi_1, \xi_2, \xi_3 \), one of which is almost always real and negative for physically accessible \( \eta \) and \( \tau_{z2} \), thus apparently giving exponentially decaying correlation functions. The exception is when \( q_{z2}'(0) = 0 \) (and thus \( Q_{z2}(0) = 0 \), i.e. at the critical point and along the liquid side of the spinodal curve) when one of the solutions to the auxiliary equation is zero, thus leading to \( 1/r \) type decay of the correlation function \( h_{z2}(r) \). For \( \eta_L'(\tau_{z2}) < \eta < \eta_L(\tau_{z2}) \), this root is positive and thus gives real but exponentially increasing functions \( h_{z2}(r) \). We have not so far been able to prove the connection between the decay of the correlation functions and the root of the auxiliary equation, but present some numerical evidence to support the idea in § 3.

3. CORRELATIONS IN THE BULK STICKY SPHERE SYSTEM

In figures 2, 3 and 4 we present graphs of the correlation functions on a supercritical, the critical and a subcritical isotherm. The numerical data for these graphs was produced by the method developed by Perram [18]. That is, we use (2.9) for a starting solution for (2.8 a), do the integrals in (2.8 a) by
the trapezoidal rule and solve the resulting algebraic equations for $h_{22}(r)$. For $r > R = 1.0$, $h_{22}$ is the solution of the equation

$$h_{22}(r) = 2\pi \rho_2 \int_0^1 q_{22}(t)(r-t)h_{22}(r-t) \, dt$$

(3.1)

and we know (cf. equation (2.9)) that on $0 < r \leq 1$,

$$h_{22}(r) = -1 + \frac{\lambda_{22}}{12} \delta(r-1).$$

(3.2)
Figure 4. (a) Graphs of $h_{22}(r)$ at $T/T_C = 0.933$ on gas side of transition. $\cdots \cdots$ : $\eta = 0.02$, $\cdots$ : $\eta = 0.04$, $\cdots$ : $\eta = 0.06$. (b) Graphs of $h_{22}(r)$ at $T/T_C = 0.933$ on liquid side of transition. $\cdots \cdots$ : $\eta = 0.24$, $\cdots$ : $\eta = 0.51$. 
In the figures the delta function is represented by a vertical line, and the amplitude of the delta function ($\lambda_{22}/12$) is represented by a horizontal bar on the vertical line. The discontinuity in $h_{22}(r)$ at $r=2$ arises from the fact that for $r>2$, the range of $(r-t)$ in the integral (3.1) does not include the delta function at $r=1$, while for $r<2$, the delta function is included. The discontinuity in the derivative of $h_{22}(r)$ at $r=3.0$ is similarly related to the discontinuity in $h_{22}(r)$ at $r=2.0$. Notice that in the region $r-1.0 < 1.0$, $h_{22}(r)$ increases monotonically at low densities, while at high densities, $h_{22}(r)$ displays well-developed fluctuations characteristic of liquid structure. As the density approaches $(6/\pi)r_0^3$ from below, $\lambda_{22}$ increases, so that the system has an increasing tendency to cluster. For $\eta_0 < \eta_L(\tau_{22})$, $\lambda_{22}$ decreases as the density increases, and the system develops the less tightly clustered 'ordered' liquid structure. At very high densities, $(\eta \gtrsim 0.6)$ we again see, of course, that $\lambda_{22}$ increases.

The other feature of the correlation functions is the behaviour at (and near) the classical critical point. Figure 3 shows the long-range nature of the correlation function at the critical point quite clearly. Since the critical point in the Percus–Yevick approximation is classical we try to fit the results for $h_{22}(r)$ to the form $A/r$. For $11.0 < r < 12.0$, we find that $1.04501 < A < 1.04633$. Close to a classical critical point, the correlation function has the form $A \exp(-\frac{r_1}{r})/r$. Using this form we find, for $\tau = 0.976311$ and $\eta = 0.12$, we find $\xi \approx 0.025$ for $19.0 < r < 12.0$. The solution of the auxiliary equation to equation (2.19) which is real, negative and close to zero is $\xi_1 \approx -0.025$. The numerical coincidence lends support to the idea of the connection of the roots of the auxiliary equation to the exponential decay of the correlation function discussed at the end of § 2.

4. Structure about a large sticky particle

The main reason for studying the structure of the sticky gas about a large isolated sticky particle is that the large isolated particle can be considered as a model of a condensation nucleus. In this section we consider the function $h_{12}(r)$ mainly at subcritical temperatures at densities $\eta$ close to but less than $\eta_0$.

In figures 5 and 6 we plot $h_{22}(r)$ and $h_{12}(r)$ at $T/T_c = 0.936$ with $\epsilon_{22}/kT_c = 0.312$ and $\epsilon_{21}/kT_c = 1.248$ so that $\tau_{22} \approx 0.90$. The horizontal axes, are, of course, different for the two functions. Figure 5 is for $\eta = 0.02$ and figure 6 for $\eta = 0.04$. We present $h_{12}(r)$ for two different values of $R_1$: $R_1 = 10R$ and $R_1 = 50R$. At fixed temperature, as $\eta$ approaches its value on the spinodal curve from below, the tendency of the bulk system to condense is shown by

(i) $\lambda_{22}$ increases as $\eta \rightarrow \eta_0(\tau_{22})$,

(ii) the range of the correlation function increases as $\eta \rightarrow \eta_0(\tau_{22})$ and (partly as a result of (i)),

(iii) the peak in $h_{22}(r)$ at $r = 2R$ becomes much more pronounced.
Figure 5. Graphs of $h_{22}(r)$ and $h_{12}(r)$ at $T/T_c = 0.936$ for $\eta = 0.02$ (i.e. in gas state). $\cdots$: $h_{22}(r)$, $\cdots$: $h_{12}(r)$ with $R_1 = 50$, $\cdots$: $h_{12}(r)$ with $R_1 = 10$. The horizontal axis is $x = r - S_{12}$ or $r$. The amplitude of the delta functions in $h_{12}(r)$ are 24.65 for $R_1 = 10$ and 88.11 for $R_1 = 50$. They are thus off scale.

Figure 6. Graph of $h_{22}(r)$ and $h_{12}(r)$ at $T/T_c = 0.936$ for $\eta = 0.04$ (i.e. in gas state). $\cdots$: $h_{12}(r)$, $\cdots$: $h_{12}(r)$ with $R_1 = 50$, $h_{12}(r)$ with $R_1 = 10$ is off scale. The horizontal axis is again $x = r - S_{12}$ or $r$. The amplitude of the delta functions in $h_{12}(r)$ are 57.36 for $R_1 = 10$ and 154.55 for $R_1 = 50$. 
The function $h_{12}(r)$ shows the following properties as $\eta \to \eta_G(\tau_{22})$:

(i) the value of $\lambda_{12}$ increases sharply;
(ii) the range of correlation increases;
(iii) the peak at $r = R_{12} + R$ becomes much more pronounced.

Further, these properties are much more marked than they are in $h_{22}(r)$, so that $h_{12}(r)$ looks like $h_{22}(r)$ but for $\eta$ much closer to $\eta_G(\tau_{22})$. As $\eta \to \eta_E(\tau_{22})$, the structure of $h_{22}(r)$ indicates that dense droplets form in the gas as a precursor to the condensation. About a sticky nucleus, we see a strongly accentuated version of this behaviour. Notice that as the radius of the sticky nucleus increases, the nucleus becomes less efficient at creating droplets, if we measure this tendency by the height of the peak in $h_{12}(r)$ at $r = R_{12} + R$.

In figures 7 and 8 we plot $h_{22}(r)$ and $h_{12}(r)$ for $\eta > \eta_G(\tau_{22})$ at $T/T_c = 0.936$. In the liquid state the function $h_{22}(r)$ shows less clustering and displays a more long-range ordered structure characteristic of a liquid. For $\eta = 0.6$ we see the oscillations in $h_{22}(r)$ characteristic of dense liquid structure. In the function $h_{12}(r)$, we see that the liquid structure is strongly accentuated by the presence of the nucleus.

It should be noticed, however, that the presence of a nucleus in the condensing gas does not lead to a local structure about the nucleus which might be called liquid-like. An interesting feature of the behaviour of $h_{12}(r)$ for $\eta < \eta_G(\tau_{22})$, is that for $\eta$ close enough to $\eta_G(\tau_{22})$, $\lambda_{12}$ diverges to $+\infty$ and then becomes negative, thus giving negative values of $g_{12}(r) = h_{12}(r) + 1$. As $\lambda_{12} \to +\infty$, we can no longer take the limit $\rho_1 \to 0$ as used in §2. The divergence of $\lambda_{12}$ as $\eta$
increases means that for \( \eta \) greater than the value at which \( \lambda_{12} \) diverges, we cannot define \( h_{12}(r) \) until \( \eta \) is large enough for the bulk system to be liquid. The divergence of \( \lambda_{12} \) indicates that the density of species 2 about the nucleus becomes very large. Since the problem then passes through a natural boundary in \( \eta \), we suggest that this corresponds to the nucleus seeding the condensation of a metastable state. To confirm this suggestion we would need to show that the phenomenon occurs at values of \( \eta \) for which the condensing gas was metastable. This would require a proper numerical construction of the compressibility free energy and generation of the co-existence curve by a double tangent construction [19] which we have not yet been able to perform.

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