Structure and phase diagram of mixtures of hard spheres in the limit of infinite size ratio

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(Received 23 June 1997; accepted 12 September 1997)

[SO021-9606(97)52247-1]

The phase diagram of mixtures of hard spheres has received attention in the last years. In this work the phase diagram of a binary mixture of points (component 1) and hard spheres (component 2) is considered. The diameter of the spheres is given by \( \sigma \). The points cannot penetrate the spheres. This system can be regarded as the limiting case of a mixture of hard spheres when the diameter of one of them becomes arbitrarily large. The compressibility factor \( Z \), for this system is given exactly by the following expression:

\[
Z = \frac{p}{\rho kT} = \frac{x_1}{1 - y} + x_2 Z_{HS},
\]

where \( \rho \) is the total number density, \( x_1 \) and \( x_2 \) are the molar fractions of points and hard spheres respectively, \( y \) is the volume fraction of the mixture \( y = \rho x_2 (\pi/6) \sigma^3 \) and \( Z_{HS} \) is the compressibility factor of pure hard spheres at the same volume fraction. Equation (1) can be derived in a number of ways. The first one, proposed by McLellan and Alder\(^7\) uses the fact that the phase integral can be integrated with respect to the points for any hard sphere configuration. Another possibility (for the fluid phase) is to use the virial expansion. Diagrams containing only hard spheres yield the second term on the right-hand side of Eq. (1) whereas those containing hard spheres and one point particle yield the first one.\(^9\) By applying the virial theorem, the compressibility factor of the mixture can be written as:

\[
Z = 1 + \frac{2 \pi \rho}{3} \left( 2 x_1 x_2 \left( \frac{\sigma}{2} \right)^3 g_{12}(\sigma/2) + (x_2)^2 \sigma^3 g_{22}(\sigma) \right),
\]

where \( g_{22}(\sigma) \) and \( g_{12}(\sigma/2) \) are the contact values in the mixture for the sphere-sphere and point-sphere pair correlation functions respectively.\(^8\) Concerning the structure of the point-sphere mixture the following facts are of interest: i) The sphere-sphere pair correlation function in the mixture is identical to that in the pure hard sphere (at the same value of \( y \)). This can be easily proved by considering the graph expansion of \( g_{22} \) in the mixture.\(^11\) A consequence of that is that for this model, the binary mixture, and the quenched system\(^12–14\) present identical structure; ii) The point-point correlation function in the mixture is not identically one (as in a pure fluid made up of point particles) but it presents some structure.\(^8\) In fact, the point-point correlation function corresponds to the blocking part of the pair correlation function\(^13,8\); iii) The point-sphere correlation function also presents structure (for instance the contact value is not one).\(^8\) Taking into account these exact results Eq. (2) can be rewritten as:

\[
Z = x_1 (1 + y g_{12}(\sigma/2)) + x_2 Z_{HS}.
\]

By equating Eq. (1) and Eq. (3) the contact value\(^15\) for the point-sphere interaction \( g_{12}(\sigma/2) = 1/(1 - y) \) is obtained. This result is exact, and in fact it shows excellent agreement with simulation (see Fig. 9 of Ref. 8). The free energy of the mixture can now be obtained as:

\[
\frac{A}{NkT} = x_1 \ln(\rho x_1 \Lambda^3_1) + x_2 \ln(\rho x_2 \Lambda^3_2) - \frac{1}{2} x_2 A_{HS}^{res} N k T
\-
\frac{x_1}{1 - y},
\]

where \( \Lambda_1 \) and \( \Lambda_2 \) are the thermal wavelengths of components 1 and 2 respectively. Without loss of generality we will set \( \Lambda_1^3 = \Lambda_2^3 = (\pi/6) \sigma^3 \). In Eq. (4) \( A_{HS}^{res} \) is the residual part of the free energy of a pure hard sphere fluid at volume fraction \( y \). The number of hard spheres is denoted as \( N_2 \) and the total number of particles as \( N \). By using Carnahan-Starling expression for the residual free energy of pure hard spheres\(^16\) we computed the stability determinant\(^17\) for this mixture. The value of the determinat was always positive and this rule out the possibility of fluid-fluid equilibrium for this system (see also discussion later).

Now we shall consider the fluid-solid equilibrium. We shall assume that the stable solid corresponds to that formed by an fcc structure of hard spheres, with points filling the empty space left by the hard spheres. The key idea is that Eq. (4) is not only valid for the fluid phase but it is also correct and exact for the solid phase (although now the residual part of the free energy corresponds to that of the pure hard sphere...
solid). The fluid-solid equilibrium is obtained by solving the following set of equations:

$$\frac{\rho^*_1}{1 - y} = \frac{\rho^*_1'}{1 - y'},$$  \hspace{1cm} (5)

$$\frac{A^*_{HS}}{N_2 kT} + \ln(y) + Z_{HS} + \frac{\rho^*_1}{1 - y} = \frac{A^*_{HS}'}{N_2 kT} + \ln(y') + Z_{HS}' + \frac{\rho^*_1'}{1 - y'},$$  \hspace{1cm} (6)

$$\frac{\rho^*_1}{1 - y} + y Z_{HS} = \frac{\rho^*_1'}{1 - y'} + y' Z_{HS'},$$  \hspace{1cm} (7)

where in Eqs. (5)–(7) magnitudes without prime correspond to the fluid phase and with prime to the solid phase. Equations (5)–(7) represent the equalities of chemical potential of component 1, chemical potential of component 2 and pressure respectively, in fluid and solid phases. We have also defined $\rho^*_1$ as $\rho^*_1 = \rho x_1 (\pi \sigma^3 / 6)$. The meaning of Eq. (5) is clear, the density of points in the free volume left by the spheres should be the same in the fluid and in the solid phase. Once Eq. (5) is satisfied, Eq. (6) and Eq. (7) correspond just to the equality of chemical potential and pressure between a pure hard sphere fluid and a pure hard sphere solid. Using Hoover et al.’s estimate of the freezing properties of pure hard spheres one obtains $y = 0.4938$ and $y' = 0.5451$ for the freezing of the point-sphere mixture. At coexistence the contribution to the pressure arising from the hard spheres is $p^*_1 = p_l ((kT/\sigma^3) = 11.7$. The composition of the solid phase $x_1'$ in equilibrium with a fluid phase of composition $x_1$ is given by:

$$x_1' = \frac{ax_1}{b + x_1 (a - b)},$$  \hspace{1cm} (8)

where $a = (1 - y')/(1 - y)$ and $b = y'/y$. In Fig. 1 the reduced coexistence pressure is plotted as a function of the molar fraction of spheres. Recently Yau, Chan, and Henderson have studied by computer simulation a binary mixture of hard spheres with a size ratio of 1:20 and found the solid phase to be mechanically unstable for $y'$ less than 0.49 (approximately) regardless of the composition. For a pure hard sphere system Alder et al.\(^1\) found that the solid phase was not mechanically stable for $y'$ less than 0.49 (approximately). This coincidence suggests that for the size ratio 1:20, freezing occurs for volume fractions quite close to those of pure hard spheres, in agreement with the results of this work.

Let us return to the possibility of fluid-fluid phase separation for this system. To determine fluid-fluid equilibria Eqs. (5)–(7) should be solved (now the prime denotes a second fluid phase). By simple inspection it can be seen that searching for fluid-fluid separation in the point-sphere system is equivalent to searching for fluid-fluid separation in the pure hard sphere system. No fluid-fluid phase separation exists for pure hard spheres. Therefore, this work shows that fluid-fluid separation is not possible in the limit of infinite size ratio. From the results of this note it can be inferred that the “effective pair potential” between spheres in the point-sphere mixture is the hard sphere potential! Although the point-hard sphere system has been considered by other authors\(^5\)–\(^8\) leading to Eq. (1), some of its implications as presented in this note have not been presented before (to the best of our knowledge).

This project has been financially supported by project PB94-0285 of the Spanish DG-ICYT (Direccion General de Investigacion Cientifica y Tecnica). Helpful discussions with Dr. E. Enciso are gratefully acknowledged.

\(^10\) The term containing $\xi_{11}$ is not included since the distance at contact is zero.
\(^15\) The contact value, $\xi_{11}(\pi \sigma^3 / 6)$, depends only on $y$ and not on the structure presented by the spheres (fluid or solid).