Inequalities for penetrable sphere model systems*

James Monroe† and Joel L. Lebowitz

Belfer Graduate School of Science, Yeshiva University, New York, New York 10033
(Received 21 January 1974)

We make use of certain inequalities derived for mixtures with a nonnegative interaction between particles of different species and no interaction between particles of the same species to derive bounds on the thermodynamic functions of these systems and of their one component, "penetrable sphere model," analogs.

I. INTRODUCTION

Recently there has been interest in a class of binary fluid mixture models with repulsive interactions between unlike molecular pairs of particles and no interaction between like molecular pairs.[1-8] The total potential energy of such a mixture of N_A particles of type A and N_B particles of type B has the form

$$U\binom{N_A}{N_B} = \sum_{i=1}^{N_A}\sum_{j=1}^{N_B} u(|x_i - y_j|), \quad u(r) \geq 0 , \tag{1.1}$$

where the x_i's are the positions of the A particles and the y_j's are the B particle positions. These mixtures can be related to thermodynamically equivalent pure fluid systems which have become collectively known as "penetrable sphere models."

In a recent paper[9] we have shown that certain inequalities which are analogous to the FKG inequalities[10] for lattice systems are valid for these two component systems. In particular inequalities between the average joint densities for the A and B particles were derived. In this note we shall combine these inequalities with various known relations between the thermodynamic parameters and the pair distribution functions to derive some bounds on the former. Some of the resulting inequalities have been previously derived by Widom,[2] for a particular form of the pair potential, on the basis of purely thermodynamic arguments.

II. INEQUALITIES FOR TWO COMPONENT SYSTEMS

Using the standard definition[11] to relate the correlation functions $g_{l,k}(\mathbf{x}_1, \cdots, \mathbf{x}_l, \mathbf{y}_1, \cdots, \mathbf{y}_k) = g_{l,k}(\mathbf{x}^l, \mathbf{y}^k)$ to the average joint density of having l A particles at positions $\mathbf{x}_1, \cdots, \mathbf{x}_l$ and k B particles at positions $\mathbf{y}_1, \cdots, \mathbf{y}_k$

$$n_{l,k}(\mathbf{x}^l, \mathbf{y}^k) \equiv \rho_A^l \rho_B^k g_{l,k}(\mathbf{x}^l, \mathbf{y}^k) , \tag{2.1}$$

where ρ_A and ρ_B are the average densities of the A and B particles. We have the following inequalities between the correlation functions[9];

$$g_{l+k,0}(\mathbf{x}^{l+k}) \geq g_{l,0}(\mathbf{x}^l) g_{k,0}(\mathbf{x}^k) \geq 1 , \tag{2.2}$$

$$g_{l,k}(\mathbf{x}^l, \mathbf{y}^k) \leq g_{l,0}(\mathbf{x}^l) g_{0,k}(\mathbf{y}^k) , \tag{2.3}$$

$$g_{0,l+k}(\mathbf{y}^{l+k}) \geq g_{0,l}(\mathbf{y}^l) g_{0,k}(\mathbf{y}^k) \geq 1 . \tag{2.4}$$

For the (pair) radial distribution functions we have

$$\begin{aligned} g_{2,0}(r) &= g(r; A, A) \geq 1 , \\ g_{1,1}(r) &= g(r; A, B) \leq 1 , \\ g_{0,2}(r) &= g(r; B, B) \geq 1 , \end{aligned} \tag{2.5}$$

where r is the distance between the two particles.

These radial distribution functions can be related to various thermodynamic quantities, for example, one has the compressibility relations[11]

$$\beta^{-1}(\partial\rho_i/\partial\mu_j) = \rho_i\delta_{ij} + 4\pi\rho_i\rho_j \int [g(r; i, j) - 1] r^2 \, dr, \tag{2.6}$$

where $i = A, B$ and $j = A, B$, β is the reciprocal temperature, $\beta = (kT)^{-1}$, and we have assumed we are dealing with a three dimensional system. From (2.5) and (2.6) we obtain

$$\beta^{-1}\frac{\partial\rho_A}{\partial\mu_A} \geq \rho_A, \; \beta^{-1}\frac{\partial\rho_B}{\partial\mu_B} \geq \rho_B , \text{ and } \frac{\partial\rho_A}{\partial\mu_B} = \frac{\partial\rho_B}{\partial\mu_A} \leq 0 . \tag{2.7}$$

The last of these inequalities can also be obtained directly from the FKG inequalities.

We shall now present some additional results obtained from the radial distribution function inequalities for the two specific systems studied in detail, the Widom–Rowlinson model[1] and the Gaussian mixture model.[6,7] In the Widom–Rowlinson model the potential between unlike pairs is

$$\begin{aligned} u(r) &= \infty, \quad r < R \\ &= 0, \quad r \geq R \end{aligned} \tag{2.8}$$

giving a hard core of radius R between A–B pairs. The Gaussian mixture model is constructed so that the Mayer f function is a Gaussian, $-e^{-\alpha r^2}$, therefore the potential is

$$\beta u(r) = -\ln[1 - \exp(-\alpha r^2)] , \tag{2.9}$$

where α is some positive constant, and $\beta = (kT)^{-1}$.

Using the virial theorem one can obtain the following equation for the pressure of these two-component mixtures:

$$\beta p = \rho_A + \rho_B - \frac{4\pi\beta}{3}\rho_A\rho_B \int_0^\infty r^3 \frac{du(r)}{dr} g(r; A, B) \, dr \tag{2.10}$$

and more specifically $\beta p = \rho_A + \rho_B + \frac{4}{3}\pi\rho_A\rho_B R^3 g(R; A, B)$ for the Widom–Rowlinson model. Using this equation and the center inequality of (2.5) we have

$$\beta p \leq \rho_A + \rho_B + v_0\rho_A\rho_B , \quad v_0 = \tfrac{4}{3}\pi R^3 \tag{2.11}$$

for the Widom–Rowlinson model. For this case, only the contact value, $g(R; A, B)$ contributes to the integral. For the Gaussian mixture model we have

$$\beta p \leq \rho_A + \rho_B + (\pi/\alpha)^{3/2}\rho_A\rho_B\,\xi(5/2, 1) \tag{2.12}$$

where $\xi(5/2, 1)$ is the generalized zeta function.[12] For this model we also have a bound on the interaction energy per unit volume.

$$E \leq \tfrac{1}{2}\rho_A \rho_B 4\pi \int r^2 u(r)\, dr . \qquad (2.13)$$

III. ONE COMPONENT SYSTEM INEQUALITIES

To obtain the one component image of the two component system the integrations in the grand partition function of the mixture are carried out for the B particle positions giving

$$\Xi(\beta, z_A, z_B) = \exp[\beta p \Lambda]$$

$$= \sum_{N_A=0}^{\infty} \frac{(z_A)^{N_A}}{N_A!} \int_\Lambda d\mathbf{x}_1 \int \circ\circ\circ \int_\Lambda dx_{N_A} \times \exp[z_B W(\mathbf{x}_1, \circ\circ\circ, \mathbf{x}_{N_A})] , \qquad (3.1)$$

where

$$W(\mathbf{x}_1, \cdots, \mathbf{x}_{N_A}) = \int_\Lambda d\mathbf{y} \exp\left[-\beta \sum_{i=1}^{N_A} (\mathbf{x}_1 - \mathbf{y})\right]$$

and Λ is the volume of the system. It can be shown that (3.1) can be written as a single component fluid grand partition function

$$\Xi'(\beta, z) = \exp[\beta p' \Lambda]$$

$$= \sum_{N=0}^{\infty} \frac{(z)^N}{N!} \int_\Lambda d\mathbf{x} \int \circ\circ\circ \int_\Lambda d\mathbf{x}_N \exp[-\beta\Phi_N(\mathbf{x}_1, \cdots, \mathbf{x}_N)], \qquad (3.2)$$

where the prime indicates quantities for the single component system. The correspondences between the two systems are given by

$$v_0(\beta) = -\int_\Lambda d\mathbf{s} \{\exp[-\beta u(\mathbf{s} - \mathbf{x})] - 1\} , \qquad (3.3)$$

$$p' = p - z_B/\beta , \quad z = z_A \exp[-z_B v_0(\beta)], \qquad (3.4)$$

$$\Phi_n(\mathbf{x}_1, \circ\circ\circ, \mathbf{x}_n) = \frac{\epsilon}{v_0(\beta)} \left(n v_0(\beta) - \int_\Lambda d\mathbf{y} \left\{ \exp\left[-\beta \sum_{i=1}^{n} (\mathbf{x}_1 - \mathbf{y})\right] - 1 \right\} \right), \qquad (3.5)$$

where $\epsilon = z_B v_0(\beta)/\beta$. Note that the many body potentials Φ_n depend explicitly on β and implicitly also on Λ. In addition v_0 also depends implicitly on x near the boundaries. These implicit dependences disappear however in the thermodynamic limit, $\Lambda \to \infty$.

It is easily seen that there is the following correspondence between the distribution functions of the two systems

$$n_{l,0}(\mathbf{x}_1, \cdots, \mathbf{x}_l) = n'_l(\mathbf{x}_1, \cdots, \mathbf{x}_l) \qquad (3.6)$$

and therefore from (2.2) we have that for the one-particle system there is a positive correlation between particle positions, i.e., $g'_l(x_1, \cdots, x_l) \geq 1$. This is in marked contrast to the behavior of the radial distribution functions in a system with pair potentials $v(r)$ (which are positive for small values of r) where $g(r)$ oscillates about the value one.

It follows now from (2.7) [or directly from the analog of (2.6) for a one component system] that, for fixed β,

$$\partial\rho/\partial z \geq \rho/z , \quad \text{or } \rho \geq z , \qquad (3.7)$$

where ρ is the density in the one component system. Equation (3.7) is the "inverse" of the relation, $\rho \leq z$, which is known to hold for a one component system with nonnegative interaction potentials.[13]

The bounds on the pressure (2.11) and (2.12) can be transcribed into bounds for the one component system giving, respectively,

$$\pi \leq -\phi\theta + (1 + \theta - \theta e^{-\theta} - \phi\theta)\gamma - \theta e^{-\theta}\gamma^2 \qquad (3.8)$$

for the Widom–Rowlinson model and

$$\pi \leq -\phi\theta + [1 + \theta\xi(5/2, 1) - \theta e^{-\theta} - \phi\theta\xi(5/2, 1)]\gamma - \theta e^{-\theta}\xi(5/2, 1)\gamma^2 \qquad (3.9)$$

for the Gaussian mixture model. Here the following dimensionless quantities have been used,

$$\gamma = \rho v_0, \quad \theta = \beta\epsilon, \quad \phi = v_0 \langle U \rangle/\epsilon, \quad \pi = \beta p' v_0, \qquad (3.10)$$

and $\langle U \rangle$ is the one-component interaction energy per unit volume.

*Supported in part by AFOSR-73-2430.

†Present address: Dept. of Physics, Northwestern University, Evanston, IL.

[1]B. Widom and J. S. Rowlinson, J. Chem. Phys. **52**, 1670 (1970).

[2]B. Widom, J. Chem. Phys. **54**, 3950 (1971).

[3]D. Ruelle, Phys. Rev. Lett. **27**, 1040 (1971).

[4]J. Lebowitz and E. Lieb, Phys. Lett. A **39**, 98 (1972).

[5]T. J. Lie, J. Chem. Phys. **56**, 332 (1972).

[6]F. H. Stillinger, Jr., and E. Helfand, J. Chem. Phys. **41**, 2495 (1964).

[7]E. Helfand and F. H. Stillinger, Jr., J. Chem. Phys. **49**, 1232 (1968).

[8]B. Widom and F. H. Stillinger, J. Chem. Phys. **58**, 616 (1973).

[9]J. L. Lebowtiz and J. L. Monroe, Commun. Math. Phys. **28**, 301 (1972).

[10]C. M. Fortuin, P. W. Kasteleyn, and J. Ginibre, Commun. Math. Phys. **22**, 89 (1971).

[11]T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).

[12]W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Springer, New York, 1966).

[13]J. Groeneveld, Phys. Lett. **3**, 50 (1962).