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SOLUTION OF THE PERCUS-YEVICK EQUATION FOR THE WIDOM-ROWLINSON MODEL ☆

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The Percus-Yevick equation for the Widom-Rowlinson model is solved exactly in one and three dimensions. In one dimension the direct correlation function is obtained explicitely. In three dimensions only the thermodynamic properties have been obtained so far implicitely in terms of elliptic integrals, and there is a maximum density beyond which the P.Y. equation has no solution and that before that density is 'critical density' at which the homogenous state becomes unstable.

Widom and Rowlinson [1] have studied the properties of a model fluid which is isomorphic to a two component system in which there are no interactions between particles of the same species and a hard core of diameter R between particles of different species. This model, and some generalizations of it, were proven [2, 3] to undergo phase transitions (in two and higher dimensions) corresponding to a separation of the components when the density is sufficiently high. These results follow from very general arguments and do not give any other information about this system. Such information, apart from its inherent symmetry so nicely exploited by Widom and Rowlinson, has so far been obtained either from simple mean field theory or from low density expansions [4, 5] (via Padè approximations) and from some machine computations on related systems [6]. (Some rigorous inequalities on the correlation functions of this system have also been obtain recently [7].) In this note we give the results of the Percus-Yevick (P.Y.) approximation for this system which can be thought of as a mixture of hard spheres with (extremely) non-additive diameters, a type of system we have studied earlier [8, 9]. On the basis of experience with the P.Y. equation with additive diameters we may expect the results of this approximation to be quite accurate at low and moderate densities.

The P.Y. equations for the radial distribution function $g_{ij}(r)$, $i,j,=1,2$, in this system are [8]

$$[g_{ij}(r)-1] = C_{ij}(r) + \sum_{l=1}^{2} \rho_l \int [g_{il}(\mathbf{r}')-1]\, C_{lj}(\mathbf{r}-\mathbf{r}')\, \mathrm{d}\mathbf{r}', \tag{1}$$

$$C_{11}(r) = C_{22}(r) = 0; \qquad C_{12}(r) = C_{21}(r) = 0 \quad \text{for } r > R; \tag{2}$$

$$g_{12}(r) = g_{21}(r) = 0 \qquad \text{for } r < R. \tag{3}$$

The $C_{ij}(r)$, *defined* by eq. (1), are the direct correlations of Ornstein and Zernike, ρ_i is the density of species i, assumed spacially uniform, and the P.Y. approximation consist in setting, $C_{ij}(r) = 0$, for all values of r at which the interaction between a particle of species i and one of species j vanishes, as expressed in eq. (2). We look for a solution of (1–3) such that $g_{ij}(r) \to 1$ as $r \to \infty$ making $\int_0^\infty r|g_{ij}(r)-1|\,\mathrm{d}r < \infty$.

Given the solution of the P.Y. equation for C_{ij} and g_{ij} there are different ways of obtaining thermodynamic quantities from these correlation functions. These ways would all be equivalent *if* we had the exact functions. They are generally not equivalent for the P.Y. solution. Thus we may 'get' a thermodynamics from the virial theorem which relates the pressure to the 'contact' value of the distribution function. For the model considered here this has the form

$$\beta p^{\mathrm{V}}(\rho_1, \rho_2) = \rho_1 + \rho_2 + \tfrac{4}{3}\pi R^3 \rho_1 \rho_2 g_{12}(R) \tag{4}$$

where $\beta = (kT)^{-1}$ (we shall set $\beta = 1$ from now on) and

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$$g_{12}(R) = \lim_{r\to R-} g_{12}(r) = -\lim_{r\to R+} C_{12}(r) \quad (5)$$

the last equality being a consequence of (1) and (2).

Another way of obtaining thermodynamics from the $C_{ij}(r)$ is to use the 'compressibility' relations

$$\rho_j \frac{\partial \mu_i^c(\rho_1,\rho_2)}{\partial \rho_j} = \delta_{ij} - \rho \int C_{ij}(r)\,\mathrm{d}r, \qquad i,j = (1,2), \quad (6)$$

$$1 - \sum_{i=1}^{2} \rho_i \int C_{ij}(r)\,\mathrm{d}r = \sum_{i=1}^{2} \rho_i \frac{\partial \mu_i^c}{\partial \rho_j} = \frac{\partial p^c(\rho_1,\rho_2)}{\partial \rho_j} \quad (7)$$

where μ_i^c and p^c are respectively the chemical potential of the ith species and the pressure, both obtained from the compressibility relations.

For the case of hard spheres with additive diameters it has been found that both the virial and compressibility relations give quite accurate agreement (2–3%) with machine computations up to fairly high densities.

Taking Laplace transforms of (1), using the methods developed in references [8] and [9] the solution of the P.Y. equation reduces to the solution of a single non-linear functional equation in the complex s-plane (s is a Laplace transform variable). When applied to the Widom-Rowlinson model the results are as follows:

One dimension. Using units in which $2R = 1$ we obtain the following expression for $C_{12}(r)$,

$$C_{12}(r) = -qJ_0\{q(1-4r^2)^{1/2}\}/\eta, \quad (8)$$

$$r \leqslant \tfrac{1}{2},\ \eta \equiv (\rho_1\rho_2)^{1/2}$$

J_0 is the Bessel of zero argument, and $q = \eta g_{12}(R)$ is the solution of the equation $q = \eta \cos q$. This equation for q will have a unique solution for low densities, $\eta \leqslant \eta_0 \approx 2.80$. For $\eta > \eta_0$ there is more than one solution for q. It is however always possible, and the physics of the situation (continuity of the pressure) dictates that we simply continue with the low density solution. The free energy obtained from this solution remains stable for all value of η. We compared the values of pressures along the line of symmetry, i.e. $\rho_1 = \rho_2 = \rho/2$ obtained from the P.Y. equation with the exact result, $p/\rho = 1 + (\rho/2)/[1 + \exp(\rho/2)]$ [8]. For values of $\rho \leqslant 2$, in units in which $2R=1$, the agreement is very good. However as $\rho \to \infty$ the exact $p/\rho \to 1$ while the P.Y. equation gives $p^v/\rho \to 1 + \pi/4$ and $p^c/\rho \to 2$.

Three dimensions. In this case we have not yet obtained the complete solution for $C_{12}(r)$ but the quantities $g_{12}(R)$ and $\int C_{12}(r)\,\mathrm{d}r$ which are relevant for the thermodynamics are related to the densities ρ_1 and ρ_2 by the following relations: (using units in which $\frac{4}{3}\pi R^3 = 1$).

$$g_{12}(R) = 2\cos I_1/(\sqrt{z_0}\, I_2), \quad (9)$$

$$\int C_{12}(r)\,\mathrm{d}r = -\sin I_1/(\rho_1\rho_2)^{1/2}$$

where I_1 and I_2 are elliptic integrals depending on a parameter z_0.

$$I_1 = \int_1^\infty \mathrm{d}z/z(z_0^3 z^3 + 4z - 4)^{1/2}, \quad (10)$$

$$I_2 = \int_1^\infty z_0\,\mathrm{d}z/(z_0^3 z^3 + 4z - 4)^{1/2},$$

and z_0 has to be obtained from the solution of the equation $\eta \equiv 3(\rho_1\rho_2)^{1/2} = I_2^3/8 \cos I_1$ so that $\eta = 0$ when $z_0 = \infty$. As z_0 decreases η at first increases monotomically reaching a maximum value $\eta_{max} \approx 3.0$ at $z_0 = 0.094$ and then decreases to the value $\eta_0 \approx 1.72$ at $z_0 = 0$. For $\eta \geqslant \eta_0$ there is thus, as in one dimension, more than one solution of the P.Y. equation but again the reasonable thing seems to be to follow the low density branch as far as it will go. (The existence of a maximum density beyond which there are no solution to the integral equations is very similar to that found by Waisman [10] in the solution of the MSM for a similar system.

We find that before η reaches η_{max} there is a critical value η_c, such that for $\eta \geqslant \eta$ the free energy obtained from the P.Y. equation on the assumption that the system is uniform is no longer thermodynamically stable. The value of η_c obtained from the compressibility and virial equations are respectively $\eta_c^c = 1.6736 \pm 0.0005$, $\eta_c^v = 1.7876 \pm 0.005$. These values are remarkably close to the value $\eta_c^R = 1.674 \pm 0.003$ obtained by Melnyk, Rowlinson and Sawford [4] from a Padè approximation calculation based on the first ten virial coefficients obtained from the P.Y. compressibility pressure.

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