Solution of the Ornstein-Zernike equation in a hard-sphere Yukawa liquid containing an arbitrary-size hard sphere: a simple mean-spherical-approximation solution and free energy of forming a cavity

1994 J. Phys.: Condens. Matter 6 1439

(http://iopscience.iop.org/0953-8984/6/8/003)

J. Phys.: Condens. Matter 6 (1994) 1439–1448. Printed in the UK

Solution of the Ornstein–Zernike equation in a hard-sphere Yukawa liquid containing an arbitrary-size hard sphere: a simple mean-spherical-approximation solution and free energy of forming a cavity

M Ginoza

Department of Physics, College of Science, University of the Ryukyus, Nishihara-Cho, Okinawa 903-01, Japan

Received 8 June 1993, in final form 12 October 1993

Abstract. The simple mean-spherical-approximation solution of the Ornstein–Zernike equation in a hard-sphere Yukawa liquid containing an arbitrary-size sphere is presented. The surface density of liquid particles on the sphere is expressed in terms of a simple function of a set of parameters. On the basis of this density expression, the work of forming a cavity from the point cavity in the liquid is calculated, and expressions for the pressure, the surface tension and the Tolman length are obtained.

1. Introduction

In this paper, we consider a liquid containing an arbitrary-size hard sphere. By regarding the diameter of this solute hard sphere as a scaling parameter, many statistical mechanical studies on the system have been made.

The scaled particle theory (SPT), for example, starts calculations with an expression for the work of forming a cavity in the liquid using the fact that the cavity affects the remainder of the liquid in the same way as the solute hard sphere. The SPT was devised by Reiss *et al* (1959) (see also Lebowitz *et al* (1965) and Reiss (1965)) and has been extended to various cases (e.g., to the case of the non-spherical hard particle (Gibbons 1969, 1970)). The SPT has been extensively used to analyse thermodynamic features of liquids.

As for works on the structural aspects of the system, there have been many studies attempting to solve the Ornstein–Zernike (OZ) equation; once we obtain the solution, this gives us information about thermodynamic aspects as well. Henderson, Abraham and Barker (HAB) (1976) and Percus (1976) calculated the OZ equation for a liquid in contact with a structureless surface; this system corresponds to our system in which the diameter of the solute hard sphere is infinite (Perram and White 1975). HAB formulated the OZ equation for the system and calculated the density profile of the hard-sphere liquid from the solution of the OZ equation obtained by Lebowitz (1964). Using the HAB formulation, Blum and Stell (1976) obtained a formal solution of the mean-spherical-approximation (MSA) equation with a somewhat general closure for the direct correlation functions. The case in which the solute hard sphere has an arbitrary diameter was considered by Waisman *et al* (1976). They solved the MSA equation in the case when, outside the cores, the direct correlation functions are zero between liquid particles and Yukawa like between the solute hard sphere and the liquid particles. As far as the present author is aware, however, the full solution of the MSA equation for the system under consideration has not yet been extended further, in an explicit manner; this extension may be an interesting problem.

Now, the system is a limiting mixture in the sense that the partial packing fraction of a component (the solute component) vanishes. For a general n-component hard-core system, Blum and Hoye (1978) and Blum (1980) gave the formal solution of the OZ equation with MSA closure consisting of n Yukawa terms. In the case of the Yukawa terms with factorizable coefficients, the present author (Ginoza 1985, 1986a, b) showed that the system of non-linear algebraic equations defining the coefficients of the Blum–Hoye solution can be simplified markedly, and in the single-Yukawa-term case, in particular, a full solution can be found. Recently, Blum *et al* (1992) generalized the n-Yukawa term case. In the next section, we shall discuss the above problem in the context of this research background.

The aims of this paper are firstly to generalize the full MSA solution of Waisman *et al* (1976) to the case in which the direct correlation functions outside cores are Yukawa like between liquid particles as well as between the solute hard sphere and the liquid particles and secondly to present expressions for the surface density of liquid particles on the sphere and the work needed to create a spherical cavity in the liquid.

This paper is organized as follows: in section 2, we present the simple MSA solution of the OZ equation. Then, it is applied to the calculation of the surface density of liquid particles on the sphere in section 3. In section 4, the work of forming a cavity from the point cavity in the liquid is calculated on the basis of the expression for the surface density. The paper concludes with a summary and discussion in section 5.

2. Simple MSA solution of the OZ equation

Let us consider a liquid consisting of two kinds of hard sphere; the numbers of the two types of sphere in volume V are N_1 and N_2, respectively. The static structure is described by the total correlation function $h_{ij}(r)$ and the direct correlation function $c_{ij}(r)$ which are related to each other via the OZ equation. This equation in the Baxter (1970) formalism is

$$2\pi r c_{ij}(r) = -\frac{\mathrm{d}}{\mathrm{d}r}[Q_{ij}(r)] + \rho \sum_l c_l \int_{\lambda_{lj}}^{\infty} \mathrm{d}t \, \frac{\mathrm{d}}{\mathrm{d}r}[Q_{il}(t+r)]\, Q_{jl}(t) \tag{1a}$$

$$2\pi r h_{ij}(r) = -\frac{\mathrm{d}}{\mathrm{d}r}[Q_{ij}(r)] + 2\pi\rho \sum_l c_l \int_{\lambda_{jl}}^{\infty} \mathrm{d}t \, h_{il}(|t-r|)(r-t)\, Q_{lj}(t) \tag{1b}$$

where $\rho = (N_1+N_2)/V$, $c_i = N_i/(N_1+N_2)$ and $\lambda_{ji} = \frac{1}{2}(\sigma_j - \sigma_i)$ with sphere diameters σ_1 and σ_2. Equation (1a) defines the Baxter function $Q_{ij}(r)$, while equation (1b) is equivalent to the OZ equation under the condition of non-singularity of the Baxter (1970) matrix.

To these equations, we shall apply the following closure relations:

$$g_{ij}(r) = h_{ij}(r) + 1 = 0 \qquad r < \sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \tag{2a}$$

$$c_{ij}(r) = (K_{ij}/r)\exp[-z(r-\sigma_{ij})] \qquad r > \sigma_{ij} \tag{2b}$$

where K_{ij} and z are parameters either given by the MSA condition or determined from other physical criteria in the case of the generalized MSA (Waisman 1973). Equations (1a) and (1b) with equations (2a) and (2b) have been solved (Blum and Hoye 1978, Blum 1980). In fact, the solution is given by the single-Yukawa-term case of the Blum–Hoye solution:

$$Q_{ij}(r) = Q_{ij}^{0}(r) + D_{ij}\exp(-zr) \tag{3a}$$

where

$$Q_{ij}^{0}(r)=\begin{cases}\frac{1}{2}A_j(r-\sigma_{ij})(r-\lambda_{ji})+\beta_j(r-\sigma_{ij}) & \\ \qquad +C_{ij}[\exp(-zr)-\exp(-z\sigma_{ij})] & \text{for } \lambda_{ji}<r<\sigma_{ij} \\ 0 & \text{otherwise.}\end{cases} \tag{3b}$$

The coefficients defining these equations are given by a number of equations related to the acceptable solution of the system of non-linear equations, and we do not quote them here because of their length.

Now, our goal is to discuss the static structure of the mixture in the thermodynamic limit as

$$N_1/V \to \rho \qquad N_2/V \to 0 \qquad \text{as } V \to \infty. \tag{4}$$

In this limit, the system under consideration may be equivalent to a liquid containing one hard sphere of diameter σ_2; therefore, the resultant structure of the liquid does not depend on K_{22}. Without any loss of physical meaning, we can choose K_{22} to be defined by $K_{22}=K_{12}^2/K_{11}$. Now, let us define Z_1 and Z_2 by $Z_1=1$ and $Z_2=K_{12}/K$ with $K=K_{11}$. Thus,

$$K_{ij}=KZ_iZ_j \qquad (i,j=1,2). \tag{5}$$

It has been shown that, in the factorizable case such as equation (5), the expressions for the coefficients in equations (3*a*) and (3*b*) can be extremely simple and the system of non-linear equations can be reduced to the non-linear equation for a single parameter Γ (Ginoza 1985, 1986a, b).

The result in the thermodynamic limit given by equation (4), which can be obtained from the work of Ginoza (1986a, b) with the replacement of d_i in that work by $Z_i\exp(\frac{1}{2}z\sigma_i)$ and some straightforward calculations, is specified by a set of five parameters: $\eta\,(=\frac{1}{6}\pi\rho\sigma_1^3)$, $\theta\,(=KZ_1^2\eta/\sigma_1)$, $z\sigma_1$, σ_1/σ_2 and σ_1Z_2/σ_2Z_1. The explicit expression for the acceptable Γ will be given in the appendix, while the expressions for the coefficients in equations (3*a*) and (3*b*) are as follows:

$$A_j=(2\pi/\Delta)(1+3\eta\sigma_j/\Delta\sigma_1)+(\pi/\Delta)P_N\sigma_j \tag{6a}$$

$$\beta_j=(\pi/\Delta)\sigma_j+\Delta_N\sigma_j \tag{6b}$$

$$D_{ij}=-Z_i\sigma_j\exp(z\sigma_{ij}) \tag{6c}$$

$$C_{ij}=[Z_i-(B_i/z)\exp(-\tfrac{1}{2}z\sigma_i)]\sigma_j\exp(z\sigma_{ij}) \tag{6d}$$

where $\Delta=1-\eta$,

$$\sigma_1^2P_N=(12\eta/\pi z\sigma_1)(1+z\sigma_1+\Gamma\sigma_1+3\eta/\Delta)X_1 \tag{6e}$$

$$\sigma_1\Delta_N=-[12\eta/\Delta(z\sigma_1)^2](1+\tfrac{1}{2}z\sigma_1+\Gamma\sigma_1+3\eta/\Delta)X_1 \tag{6f}$$

$$\sigma_j/\sigma_1^2=\pi\Gamma\sigma_1X_j/3\eta X_1^2 \tag{6g}$$

$$\sigma_1B_i\exp(\tfrac{1}{2}z\sigma_i)=-\Gamma\sigma_1X_i-(1+\tfrac{1}{2}z\sigma_i)\sigma_1\Delta_N-(3\eta\sigma_i/\Delta\sigma_1)X_1 \tag{6h}$$

with

$$\frac{X_1}{Z_1} = \frac{1}{\Phi_0(z\sigma_1, \eta, 1) + \Gamma\sigma_1\Phi_1(z\sigma_1, \eta, 1)} \tag{7a}$$

$$\frac{X_2}{Z_2} = \frac{1}{1 + \Gamma\sigma_1\phi_0(z\sigma_1, \sigma_1/\sigma_2)} + \frac{X_1\sigma_2}{Z_2\sigma_1}\left[\frac{\sigma_1}{\sigma_2} - \frac{\Phi_0(z\sigma_1, \eta, \sigma_1/\sigma_2) + \Gamma\sigma_1\Phi_1(z\sigma_1, \eta, \sigma_1/\sigma_2)}{1 + \Gamma\sigma_1\phi_0(z\sigma_1, \sigma_1/\sigma_2)}\right]. \tag{7b}$$

The functions used above are defined as follows:

$$\Phi_0(z, y, x) = x + f(y)\phi_0(z, x) - 4f(y)\psi_1(z, x)[1 + \tfrac{1}{2}z + f(y)]$$

$$\Phi_1(z, y, x) = x\phi_0(z, x) - 4f(y)\psi_1(z, x)$$

$$\phi_0(z, x) = (1/z)[1 - \exp(-z/x)]$$

$$\psi_1(z, x) = (1/z^3)[x - \tfrac{1}{2}z - (x + \tfrac{1}{2}z)\exp(-z/x)]$$

with

$$f(y) = 3y/(1 - y).$$

3. Surface density of liquid particles

The surface density of liquid particles on the sphere is given by $\rho\sigma_1 g_{12}(\sigma_{12}^+)$, where σ_{12}^+ is σ_{12} plus a positive infinitesimal. It is easy to prove that the second term on the right-hand side of equation (1*b*) is a continuous function of r at $r = \sigma_{12}$; $g_{12}(\sigma_{12}^+)$ is determined by the jump in the derivative of $Q_{ij}(r)$ at $r = \sigma_{12}$, and from equations (3*a*) and (3*b*) we obtain (Blum and Hoye 1978, Blum 1980)

$$2\pi\sigma_{ij}g_{ij}(\sigma_{ij}^+) = \tfrac{1}{2}\sigma_i A_j + \beta_j - zC_{ij}\exp(-z\sigma_{ij}).$$

This equation, equations (6) and the use of equation (A1) yield the following:

$$g_{1j}(\sigma_{1j}^+) = g_{1j}^{\mathrm{HS}} + c_{1j}(\sigma_{1j}^+)(X_1/Z_1)(X_j/Z_j) \tag{8a}$$

where

$$g_{1j}^{\mathrm{HS}} = [1 + f(\eta)/(1 + \sigma_1/\sigma_j)]/\Delta \tag{8b}$$

and $c_{1j}(\sigma_{1j}^+)$ is the direct correlation function at $r = \sigma_{1j}^+$, given by equation (2*b*).

Because of the assumption given by equation (5), it may be meaningful to check the above result by comparing it with the limiting results of Waisman *et al* (1976) and Blum and Stell (1976).

Now, Waisman *et al* (1976) solved the OZ equation with the closure given in equations (2) in the case of $K_{11} = 0$ and $K_{12} \neq 0$ and gave an explicit result as follows:

$$g_{12}(\sigma_{12}^+) = g_{12}^{\mathrm{HS}} + c_{12}(\sigma_{12}^+)f(z\sigma_1, \eta)(1 - \eta)^2\exp(z\sigma_1) \tag{8c}$$

where $f(s,\eta) = s^3/[L(s,\eta) + S(s,\eta)\exp(s)]$ with $L(s,\eta) = 12\eta[1 + 2\eta + s(1 + \frac{1}{2}\eta)]$ and $S(s,\eta) = (1-\eta)^2 s^3 + 6\eta(1-\eta)s^2 + 18\eta^2 s - 12\eta(1+2\eta)$.

The above case corresponds to the following choice of parameters in this paper: $\theta \to 0$ (therefore, $\Gamma \to 0$) and $\sigma_2 Z_1/\sigma_1 Z_2 \to 0$. According to equations (7), this limit gives $Z_1/X_1 = \Phi_0(z\sigma_1, \eta, 1)$ and $Z_2/X_2 = 1$. On the other hand, it is straightforward to show that

$$f(z\sigma_1, \eta)(1-\eta)^2 \exp(z\sigma_1) = 1/\Phi_0(z\sigma_1, \eta, 1).$$

Therefore, equation (8*a*) in the limit is equivalent to equation (8*c*).

Next, Blum and Stell (1976) gave the formal solution to the MSA equation by using the HAB formulation of the OZ equation in a multicomponent liquid in contact with a wall. In the case of the closure given in equation (2*b*), the *k*-integration in their formal solution can be carried out by consideration of the contribution of the pole at $k = -\mathrm{i}z$, and the solution gives

$$g_{12}(\sigma_{12}^+) = 1 - \rho\tilde{Q}_{11}(0) + c_{12}(\sigma_{12}^+)/[1 - \rho\tilde{Q}_{11}(\mathrm{i}z)] \tag{8d}$$

where

$$\tilde{Q}_{11}(\mathrm{i}z) = \int_0^\infty \mathrm{d}r\ \exp(-zr)Q_{11}(r)$$

with $Q_{11}(r)$ given by equation (3*a*).

Now, in the limit $\sigma_1/\sigma_2 \to 0$, after somewhat lengthy but straightforward calculation, we obtain

$$1 - \rho\tilde{Q}_{11}(0) = [1 + f(\eta)]/\Delta - (2KX_1^2/\sigma_1)[\Phi_0(z\sigma_1, \eta, 0) + \Gamma\sigma_1\Phi_1(z\sigma_1, \eta, 0)]/[1 + \Gamma\sigma_1\phi_0(z\sigma_1, 0)]$$

$$1 - \rho\tilde{Q}_{11}(\mathrm{i}z) = [1 + \Gamma\sigma_1\phi_0(z\sigma_1, 0)]Z_1/X_1.$$

These equations guarantee that equation (8*a*) in this limit is equivalent to equation (8*d*).

4. Free energy of forming a cavity in the liquid

Let us consider the problem of forming a cavity in a liquid; we shall calculate the reversible work $W(r)$ required to produce a spherical cavity of radius r in the liquid. In the case when the cavity is macroscopic, thermodynamics give (Reiss *et al* 1959)

$$W(r) = \tfrac{4}{3}\pi r^3 p + 4\pi r^2\sigma(1 - 2\delta/r) + K_0 \tag{9}$$

where p is the pressure and σ is the planar surface tension. The factor in parentheses in the surface work term represents the asymptotic dependence of the surface tension upon curvature. The quantity K_0 is related to the work of introducing the point cavity and has no counterpart in the macroscopic situation.

Statistically, $W(r)$ can be calculated on the basis of the fact that the cavity affects the remainder of the liquid in the same way as the solute hard sphere in the system under consideration, and it is obtained by use of the following formula (Reiss *et al* 1959):

$$W(r) = k_B T \int_{\sigma_1/2}^{r+\sigma_1/2} \mathrm{d}s\, 4\pi s^2 \rho g_{12}(s) + K_0 \tag{10}$$

where $g_{12}(s)$ is the value of the radial distribution function $g_{12}(r)$ at the contact point $(r = s)$, which is regarded as a function of s.

Now, we shall employ the result of the previous section; $g_{12}(s)$ in the above integrand is given by equation (8a) with $\sigma_{12} = s$ and $\sigma_2 = 2s - \sigma_1$. Here, we may neglect the σ_2-dependences such as $\exp(-z\sigma_2)$ in the functions Φ_0, Φ_1 and ϕ_0 since r is macroscopic. In this case, from equation (8a) we obtain the following with the use of equations (7a) and (A1):

$$g_{12}(s) = G_0 + G_1\sigma_1/s \tag{11}$$

where

$$G_0 = \frac{1}{\Delta}\left(1 + \frac{3\eta}{\Delta}\right) + \frac{2\Gamma}{\Delta z}\left[1 + z\sigma_1 + \frac{3\eta}{\Delta} + \Gamma\sigma_1 - \frac{(z\sigma_1)^2 \Delta Z_1}{12\eta X_1} D_0\right] \tag{11a}$$

$$G_1 = -\frac{3\eta}{2\Delta^2} + \frac{\Gamma}{\Delta z}\left[1 - \left(1 + \frac{2}{z\sigma_1}\right)\left(1 + z\sigma_1 + \frac{3\eta}{\Delta} + \Gamma\sigma_1\right)\right] \tag{11b}$$

with

$$D_0 \equiv \sigma_1 Z_2/\sigma_{12} Z_1. \tag{11c}$$

It should be emphasized that equation (11) is the result of an σ_1/s expansion of equation (8a) and it consists of just two terms.

Following Waisman *et al* (1976) and Blum and Stell (1976), we assume that D_0 is a finite constant for $\sigma_2/\sigma_1 \gg 1$ (see also next section). Now, it is easy to integrate equation (10) using equation (11), and we obtain the following:

$$W(r) = 4\pi\rho k_B T\{\tfrac{1}{3}G_0[(r + \tfrac{1}{2}\sigma_1)^3 - (\tfrac{1}{2}\sigma_1)^3] + \tfrac{1}{2}G_1\sigma_1[(r + \tfrac{1}{2}\sigma_1)^2 - (\tfrac{1}{2}\sigma_1)^2]\} + K_0. \tag{12}$$

Now, comparing equation (12) with equation (9), we obtain

$$p = \rho k_B T G_0 \tag{13}$$

$$\sigma = \tfrac{1}{2}\rho k_B T (G_0 + G_1)\sigma_1 \tag{14}$$

$$\delta = -\tfrac{1}{4}\sigma_1 (G_0 + 2G_1)/(G_0 + G_1). \tag{15}$$

5. Summary and discussion

The simple MSA solution of the OZ equation in the liquid containing the arbitrary-size hard sphere is obtained from the MSA solution of the OZ equation in the two-component hard-sphere Yukawa mixture. The solution is expressed in terms of explicit functions of the set of five parameters: η, θ, $z\sigma_1$, σ_1/σ_2 and $\sigma_1 Z_2/\sigma_2 Z_1$; in particular, the acceptable solution of equation (A1) is obtained, explicitly. The simple result here is based on equation (5). It should be emphasized, however, that the assumption of equation (5) introduces no loss of physical meaning in the case of the thermodynamic limit given by equation (4).

The expression for the surface density of liquid particles on the sphere is obtained as a simple function of the parameters; the first term on the right-hand side of equation (8*a*) is the effect of the hard-sphere interactions, while the second term is related to the Yukawa interaction. It may be interesting that the latter term is expressed in terms of the direct correlation function in which the parameters Z_1 and Z_2 are replaced by X_1 and X_2, respectively, where X_1 and X_2 are given by equations (7*a*) and (7*b*), respectively. It is proved that the result given by equation (8*a*) gives the results of Waisman *et al* (1976) and Blum and Stell (1976) in each limiting case. This shows only the validity of the assumption of equation (5).

On the basis of the expression for the surface density, the free energy of forming the cavity in the hard-sphere Yukawa system is calculated, and then expressions for the pressure, the planar surface tension and the Tolman length are obtained. In the calculation, it is assumed that D_0 defined by equation (11*c*) is a finite constant when σ_2 varies in the region of $\sigma_2/\sigma_1 \gg 1$. Physically, this may be acceptable (Blum and Stell 1976, Waisman *et al* 1976) because D_0 is such a microscopic quantity that $D_0 = c_{12}(\sigma_{12}^+)/c_{11}(\sigma_1^+)$.

According to the SPT (Lebowitz *et al* 1965),

$$p = \rho k_B T(1+\eta+\eta^2)/\Delta^3$$

$$\sigma = 3k_B T\eta(2+\eta)/(2\pi\sigma_1^2\Delta^2)$$

$$\delta = -\tfrac{1}{2}\sigma_1\Delta/(2+\eta)$$

$$K_0 = -k_B T\log(1-\eta).$$

When we choose $K = 0$ in our above result, equations (11) give $G_0 = (1+2\eta)/\Delta^2$ and $G_1 = -3\eta/2\Delta^2$; σ and δ in the SPT agree with the values given by equations (14) and (15), respectively. With the same choice, however, p given by equation (13) does not agree with the pressure in the SPT. In general, the MSA has the familiar thermodynamic inconsistency, but it is well known that the generalized MSA solves this difficulty and leads to better agreement with the results of, for example, machine computations (Waisman 1973, Waisman *et al* 1976).

Acknowledgment

The author would like to express his sincere thanks to one of the referees for his significant suggestion on the SPT.

Appendix. The explicit expression for the acceptable solution Γ

In the thermodynamic limit given by equation (5), Γ is defined by the following equation (Ginoza 1986a, b):

$$\Gamma^2 + z\Gamma + K\pi\rho X_1^2 = 0 \tag{A1}$$

where X_1, defined by equation (8*a*), is a function of Γ. Equation (A1) can be written as

$$x(x+1)(x+a)^2 = b \tag{A2}$$

where

$$x = \Gamma/z$$

$$a = \Phi_0(z\sigma_1, \eta, 1)/z\sigma_1\Phi_1(z\sigma_1, \eta, 1)$$

$$b = -6\theta/[(z\sigma_1)^2\Phi_1(z\sigma_1, \eta, 1)]^2.$$

The left-hand side of equation (A2) is shown in figure A1 as a function of x in the typical case with $z\sigma_1 = 1$ and $\eta = 0.4$. Points B and C in the figure are (x_+, b_+) and (x_-, b_-), respectively, where

$$x_\pm = \tfrac{1}{2}\left(-\tfrac{1}{2}a - \tfrac{3}{4} \pm \sqrt{\tfrac{3}{8} - p}\right)$$

$$b_\pm = \tfrac{1}{2}(p^2 + \tfrac{3}{2}p + \tfrac{9}{64}) \pm \tfrac{1}{2}(p - \tfrac{3}{8})\sqrt{(p - \tfrac{3}{8})(p + \tfrac{1}{8})}$$

with

$$p = -\tfrac{1}{4}(a^2 - a + \tfrac{3}{4}).$$

As is obviously understood from the figure, equation (A2) has a variety of solutions depending on the value of b. In previous work (Ginoza 1990), we discussed the manifold solutions and the acceptable solution of the equation, on the basis of the non-singularity of the Baxter matrix (Pastore 1988). According to the result given there, the acceptable solution is in the region of $x > x_+$.

In the present case, we can obtain the explicit expression for this solution by the classical method. It depends on the sign of D defined as follows:

$$D = (\tfrac{1}{2}\beta)^2 + (\tfrac{1}{3}\alpha)^3 = (\tfrac{1}{12})^3 b(b - b_+)(b - b_-)$$

where

$$\alpha = -\tfrac{1}{48}[(a^2 - a)^2 - 12b]$$

and

$$\beta = -\tfrac{1}{864}[(a^2 - a)^3 - 9b(2a^2 - 2a + \tfrac{3}{2})].$$

The acceptable solution of equation (A2) is given as follows.

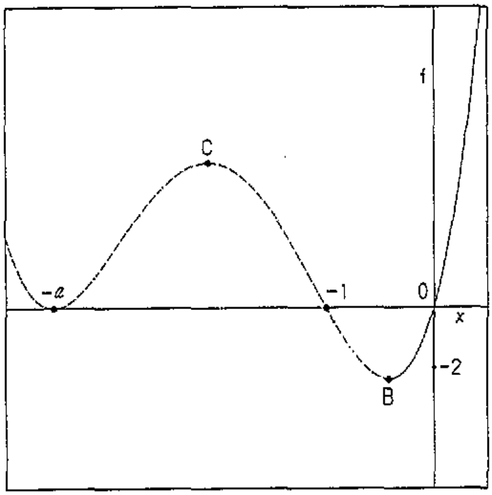

Figure A1. Plot of f (the left-hand side of equation (A2)) as a function of x in a typical case of a liquid: $z\sigma_1 = 1$ and $\eta = 0.4$. Points B and C are the minimum point and the local maximum point, respectively. For a given value of b, the solutions of equation (A2) correspond to the intersections of the curve and the horizontal line given by the ordinate value of b.

(1) If $b > b_-$ or $0 > b > b_+$,

$$x = [\{(K_+ + K_- + \tfrac{2}{3}p)^2 + 3(K_+ - K_-)^2\}^{1/2} - (K_+ + K_- + \tfrac{2}{3}p)]^{1/2} + (K_+ + K_- - \tfrac{1}{3}p)^{1/2} - \tfrac{1}{2}(a + \tfrac{1}{2}) \qquad \text{(A3)}$$

where

$$K_\pm = (-\tfrac{1}{2}\beta \pm \sqrt{D})^{1/3}.$$

(2) If $b_- > b > 0$,

$$x = (2R\cos\phi - \tfrac{1}{3}p)^{1/2} + (-R\cos\phi - \sqrt{3}R\sin\phi - \tfrac{1}{3}p)^{1/2} + (-R\cos\phi + \sqrt{3}R\sin\phi - \tfrac{1}{3}p)^{1/2} - \tfrac{1}{2}(a + \tfrac{1}{2}) \qquad \text{(A4)}$$

where

$$R = \sqrt{-\tfrac{1}{3}\alpha}$$

and

$$\phi = \tfrac{1}{3}\cos^{-1}(-\beta/2R^3).$$

(3) If $b_+ > b$, there is no real solution.

It should be pointed out, however, that the Baxter matrix is singular in the vicinity of point B, where the solution is unacceptable (Pastore 1988).

References

Baxter R J 1970 *J. Chem. Phys.* **52** 4559
Blum L 1980 *J. Stat. Phys.* **22** 661
Blum L and Hoye J S 1978 *J. Stat. Phys.* **19** 317
Blum L and Stell G 1976 *J. Stat. Phys.* **15** 439
Blum L, Vericat F and Herrera-Pacheco J N 1992 *J. Stat. Phys.* **66** 249
Gibbons R M 1969 *Mol. Phys.* **17** 81
—— 1970 *Mol. Phys.* **18** 809
Ginoza M 1985 *J. Phys. Soc. Japan* **54** 2783
—— 1986a *J. Phys. Soc. Japan* **55** 95
—— 1986b *J. Phys. Soc. Japan* **55** 1782
—— 1990 *Mol. Phys.* **71** 145
Henderson D, Abraham F F and Barker J A 1976 *Mol. Phys.* **31** 1291
Lebowitz J L 1964 *Phys. Rev.* A **133** 895
Lebowitz J L, Helfand E and Praestgaard E 1965 *J. Chem. Phys.* **43** 774
Pastore G 1988 *Mol. Phys.* **63** 371
Percus J K 1976 *J. Stat. Phys.* **15** 423
Perram J W and White L R 1975 *Discuss. Faraday Soc.* **59** 29
Reiss H 1965 *Adv. Chem. Phys.* **9** 1
Reiss H, Frisch H and Lebowitz J L 1959 *J. Chem. Phys.* **31** 369
Waisman E 1973 *Mol. Phys.* **25** 45
Waisman E, Henderson D and Lebowitz J L 1976 *Mol. Phys.* **32** 1373