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Progress in thermodynamic perturbation theory and self-consistent Ornstein–Zernike approach relevant to structural-arrest problems

Fernando O Raineri¹, George Stell^{1,3} and Dor Ben-Amotz²

¹ Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400, USA

² Department of Chemistry, Purdue University, West Lafayette, IN 4790, USA

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Abstract

We discuss the derivation and use of a key feature of a new version of thermodynamic perturbation theory (TPT) that Ben-Amotz and Stell have developed recently—the choice of a hard-core diameter to be used in modelling soft-core systems. We go on to show the way the new version of TPT can be used as input for the self-consistent Ornstein–Zernike approach (SCOZA) of Høye and Stell to obtain highly accurate static structure factors and thermodynamics for fluids and glasses. In obtaining quantitatively useful results for the structural arrest and other dynamic features in colloidal systems with pair potentials that include strong short-range attraction, accurate structure factors are a necessity.

1. Introduction

For Hamiltonian models with hard-core pair potentials, first-order thermodynamic perturbation theory (TPT) has been shown to become more and more accurate at any fixed temperature as the density approaches close packing [1, 2]. TPT has consequently become a valuable tool in the study of high-density liquid–liquid, liquid–solid and solid–solid transitions as well as other high-density thermodynamic effects in such models [3–7]. In studying such effects in colloids in which the colloid–colloid interactions include soft-core repulsion and strong short-range attraction, existing TPT recipes must be generalized in a fundamental way. We have made much progress in this connection recently, as set forth in a sequence of three articles [8–10]. Our contribution to these proceedings represents a fourth article in this series.

An integral part of modern TPT is the use of a hard-sphere reference system in modelling potentials that do not have a hard core, and typically one introduces an effective hard-core diameter that depends on the thermodynamic state in order to mimic the thermodynamic

³ Author to whom any correspondence should be addressed.

effects of the softness of the actual repulsive core [11–17]. In earlier TPT treatments, the resulting thermodynamics has proven to be extremely sensitive to the precise recipe used to determine the state dependence of the core diameter. We have developed a highly accurate version of TPT that is also highly robust and exceedingly simple to implement analytically, with a core diameter given by a recipe first developed by Boltzmann. It is the derivation and use of this recipe that we shall be primarily concerned with in this paper.

The version of TPT we have developed seems especially pertinent to the sort of colloid–colloid interactions that are being used to model and understand structural–arrest transitions. Here one is typically using an effective pair potential with a hard core to model an interaction with a repulsive core that in fact is not at all hard, and the issue of how to determine the core diameter in such a model seems crucial to the task of making quantitatively accurate contact with experimental results.

In addition to being of direct use in describing thermodynamics, our version of TPT can also be used as input for the self-consistent Ornstein–Zernike approach (SCOZA) that Stell and co-workers have developed. The SCOZA has already been shown to be of great value as a method for determining highly accurate structure factors and thermodynamic properties of colloid–fluid models with pair potentials that have strong short-range attraction and hard-core repulsion [18, 19]. An outstanding challenge has been to extend SCOZA modelling to potentials that have soft-core repulsion. Our recent TPT results provide an effective way of meeting this challenge, as we shall discuss in section 4 of this paper.

The thermodynamic perturbation theory of liquids traces its roots back to ideas developed by van der Waals [20] and Boltzmann [21], who suggested that the structure of a liquid is dictated primarily by repulsive intermolecular interactions, while cohesive interactions determine its energy. This implies that repulsive and attractive portions of an intermolecular pair-potential contribute more-or-less independently to fluid thermodynamics, and may each best be described using different types of approximation strategies. In particular, the structure and entropy of a fluid may be equated with that of an appropriately chosen repulsive reference fluid, while cohesive interactions may be treated as a perturbation, evaluated by averaging over the reference structure fluid structure. This fundamental understanding has held up remarkably well over the intervening years and has in fact played a central role in the later evolution of fluid statistical mechanics [11–17, 22–27], culminating in the liquid perturbation theory of Barker and Henderson (BH) and of Weeks, Chandler and Andersen (WCA). In our recent work [10] we revisited the WCA theory and showed that it may be viewed as a special case of a family of perturbation theories which differ in subtle but significant ways from either the WCA treatment or other previous formulations of liquid perturbation theory [11–17, 22–27]. Our work was focused on demonstrating the fundamental soundness and exceptional accuracy of this new formulation, as well as its significant practical advantages.

The original WCA theory extended previous perturbation theories by introducing two key refinements: the first involves the way in which the intermolecular potential is separated into repulsive and attractive contributions, and the second pertains to the method used to relate the thermodynamic properties of a soft-repulsive reference fluid to that of a hard-sphere (HS) fluid [14–17, 23]. The combination of these features produced a firmly grounded theory of unrivalled elegance and accuracy. The new theory of Ben-Amotz and Stell (BAS) described in [10] retains the essential features of the WCA theory, but introduces a subtle change in the way these are combined.

The original WCA theory may be viewed as a perturbation theory with a soft-repulsive reference fluid, whose properties are in turn approximated using a HS fluid. The new formulation differs from the WCA theory only in that it is better described as a HS perturbation theory, with a WCA correction introduced to represent the influence of soft repulsive

interactions. Thus, the difference between the two theories is almost a matter of semantics—but not quite. Predictions of the new formulation reduce exactly to those of WCA theory when the reference HS diameter is defined as prescribed by WCA theory. However, the two theories differ in the way the perturbation free energy is evaluated. As a result, the BAS formulation proves to be more forgiving with regard to the selection of the HS diameter. This feature is of significant practical importance, as it implies that one may use any one of several trivially simple prescriptions for defining an appropriate reference HS diameter, rather than having to numerically minimize the solution of an integral equation, as required by earlier formulations of the WCA theory [14–17].

While the WCA HS diameter is necessarily a function of both temperature and density, $\sigma_{\text{HS}}(T, \rho)$, the new theory can accommodate diameters which are functions of temperature only, $\sigma_{\text{HS}}(T)$, without loss of predictive accuracy. For example, we find that we can use a simple Boltzmann factor criterion (BFC) [28–30] to equate $\sigma_{\text{HS}}(T)$ with that value of the intermolecular separation at which the interaction potential is equal to kT (or RT if one prefers using molar units). For many types of pair potential, including those of Lennard-Jones or generalized-Lennard-Jones (GLJ) form [8, 9], this prescription reduces $\sigma_{\text{HS}}(T)$ to an algebraic function. Thus, determining $\sigma_{\text{HS}}(T)$ becomes even easier than it is when implementing the perturbation theory of Barker and Henderson [11–13], which requires numerically integrating over the repulsive potential to determine $\sigma_{\text{HS}}(T)$, and whose first order predictions are not as accurate as those of WCA or our new variant thereof [10, 14–17].

The fundamental basis of the BAS theory, and other variants of the WCA theory, are described in section 2. In section 3 we consider the origin of the Boltzmann factor criterion for the effective HS diameter from kinetic theory and thermodynamic standpoints. In section 4 we show the way the BAS results can be used as input for our SCOZA. Finally in section 5 we point out why this work has special relevance to colloidal-fluid modelling and to structural–arrest problems in particular.

2. TPT: quantitative details

The starting point of many thermodynamic perturbation theories is the decomposition of a spherically symmetric intermolecular pair-potential, $v(r)$, into the sum of a repulsive, $v_0(r)$, and a perturbative, $v_1(r)$, potential

$$v(r) = v_0(r) + v_1(r). \quad (1)$$

Although various separations are possible, a particularly appealing general method was suggested by WCA [14–17] who, for a potential with a repulsive core and an attractive tail, defined $v_0(r)$ as the potential associated with the repulsive part of the interparticle force (such that $dv(r)/dr < 0$) and $v_1(r)$ as that associated with the attractive force (such that $dv(r)/dr > 0$). More specifically, $v_0(r)$ is shifted up in energy by ϵ , the well-depth, and $v_1(r)$ is extended into the core region so as to render both $v_0(r)$ and $v_1(r)$ and their derivatives continuous over all r :

$$v_0(r) = \begin{cases} v(r) + \epsilon & \text{for } r \leq r_0 \\ 0 & \text{for } r > r_0 \end{cases} \quad (2)$$

$$v_1(r) = \begin{cases} -\epsilon & \text{for } r \leq r_0 \\ v(r) & \text{for } r > r_0 \end{cases}, \quad (3)$$

where r_0 is the position of the potential minimum (at which $dv(r)/dr = 0$).

In developing their perturbation theory WCA assumed that the reference fluid is one composed of soft-repulsive particles with pair potentials identical to $v_0(r)$. Thus the excess

Helmholtz free energy of the full fluid, $\tilde{A} \equiv A^\times/NkT$, may be expressed as the following sum of the reference fluid free energy, $\tilde{A}^{(0)} \equiv A^{(0)}/NkT$, plus a remainder, $\Delta\tilde{A}^{(1)} \equiv [A^\times - A^{(0)}]/NkT$:

$$\tilde{A} = \tilde{A}^{(0)} + \Delta\tilde{A}^{(1)}. \quad (4)$$

If it is assumed that the structural and thermodynamic properties of the reference fluid are known in advance, then the following first order (mean-field) approximation may be invoked to calculate $\Delta\tilde{A}^{(1)}$, where $g_0(r)$ is the radial distribution function of the soft repulsive reference fluid and $\beta = 1/kT$

$$\Delta\tilde{A}^{(1)} = 2\pi\beta\rho \int_0^\infty g_0(r)v_1(r)r^2 dr. \quad (5)$$

However, since the required reference fluid properties are not in general known, WCA proposed some additional approximations in order to complete their perturbation theory. In particular, WCA approximated $g_0(r)$ by assuming that the cavity function of the soft repulsive fluid is identical to that of an appropriately chosen HS fluid, $y_0(r) = y_{\text{HS}}(r)$ [14–17]. Since the radial- and cavity-distribution functions associated with a given pair potential are fundamentally related by $g_0(r) = y_0(r) \exp[-\beta v_0(r)]$, the above approximation implies that

$$g_0(r) \simeq y_{\text{HS}}(r) \exp[-\beta v_0(r)]. \quad (6)$$

Furthermore, by functionally differentiating $A^{(0)}$ with respect to $\exp[-\beta v_0(r)]$, WCA obtained the following first order expression for $A^{(0)}$ in terms of the excess Helmholtz free energy of the HS fluid [14–17]

$$\tilde{A}^{(0)} = \tilde{A}^{\text{HS}} + 2\pi\rho \int_0^\infty [g_{\text{HS}}(r) - g_0(r)]r^2 dr. \quad (7)$$

WCA showed that the above expression for $\tilde{A}^{(0)}$ (which may also be derived by other means [31, 32]) is accurate through third order in a parameter ξ , representing the length scale over which the ‘blip function’, $g_{\text{HS}}(r) - g_0(r)$, has a magnitude that is appreciably larger than zero. On the other hand, the WCA predictions for $\Delta\tilde{A}^{(1)}$ are only accurate to first order in ξ [33]. Thus, one should expect equation (7) to remain valid over a wider range of σ_{HS} values than equation (5). Moreover, WCA suggested a criterion for determining $\sigma_{\text{HS}}(T, \rho)$ by requiring that the integral on the right-hand side of equation (7) vanishes. This amounts to assuming that the soft-repulsive reference fluid and the HS fluid have the same compressibility [10]. Notice that the entire WCA construct hinges on this approximation, as it assures the accuracy of both $g_0(r)$ and $A^{(0)}$, as long as σ_{HS} is determined by iteratively minimizing the integral in equation (7) at each temperature and density.

On the other hand, Verlet and Weis [33] showed that the thermodynamic self-consistency of the WCA theory may be improved by using $\sigma_{\text{HS}}(T, \rho)$ values that differ slightly from those obtained using the equal-compressibility criterion. Lado proposed an elegant analytical implementation of this refinement of the WCA theory, which retains equations (1)–(7) but replaces the equal-compressibility assumption by a self-consistency criterion that requires iterative minimization of a slightly different integral equation in order to determine $\sigma_{\text{HS}}(T, \rho)$ [22]. The resulting diameters are invariably slightly smaller than those obtained from the original WCA theory [8, 9, 22, 33]. The predictions of Lado’s theory are somewhat more accurate than the original WCA theory when applied to fluids with repulsive-core potentials that are softer than the Lennard-Jones $v_0(r)$ [9, 22]. However, when applied to a Lennard-Jones fluid the predictions of both variants of the WCA theory are virtually indistinguishable and in essentially perfect agreement with simulation results (except in the near-critical and

low-density regions, where the predictions of both theories deviate somewhat from simulation results).

The BAS theory differs from the above formulations primarily in that it takes from the beginning a HS fluid rather than a soft repulsive fluid to be the reference system with respect to which all perturbations are determined. This implies that the full fluid free energy may be expressed as follows:

$$\tilde{A} = \tilde{A}^{\text{HS}} + \Delta\tilde{A}^{(0)} + \Delta\tilde{A}^{(1)}, \quad (8)$$

where $\Delta\tilde{A}^{(0)}$ and $\Delta\tilde{A}^{(1)}$ are the first-order perturbation free energies associated with $v_0(r)$ and $v_1(r)$, respectively. We approximate $\Delta\tilde{A}^{(0)}$, as in WCA theory, using equation (7)

$$\Delta\tilde{A}^{(0)} = 2\pi\rho \int_0^\infty [g_{\text{HS}}(r) - g_0(r)] r^2 dr. \quad (9)$$

So, up to this point all of the WCA and BAS are functionally equivalent, except for the criterion used to define the optimal HS diameter. However, since the BAS theory assumes a HS reference fluid, the attractive perturbation free energy in this case becomes

$$\Delta\tilde{A}^{(1)} = 2\pi\beta\rho \int_0^\infty g_{\text{HS}}(r)v_1(r)r^2 dr. \quad (10)$$

This is again very similar to equation (5) except that $g_0(r)$ is replaced by the HS radial distribution function $g_{\text{HS}}(r)$. Note that if the WCA criterion is used to determine $\sigma_{\text{HS}}(T, \rho)$ then the integrals in equations (5) and (10) become identical. This is because the only region over which $g_{\text{HS}}(r)$ and $g_0(r)$ differ is when $r < r_0$; since $v_1(r)$ is constant over this region (see equation (3)), the WCA equal-compressibility approximation implies that the integrals over $g_0(r)$ and $g_{\text{HS}}(r)$ are identical. Thus, there is strictly speaking no difference at all between BAS and WCA predictions when the equal-compressibility criterion is used to define $\sigma_{\text{HS}}(T, \rho)$.

The BAS and WCA theory predictions only differ when the reference HS fluid diameter is varied from the value prescribed by the equal compressibility approximation, and this brings us to the main advantage of the BAS treatment. The results presented in [10] demonstrate that the BAS theory is less sensitive to the precise value of σ_{HS} than WCA theory. Because of this relative insensitivity there is no need to precisely optimize the value of σ_{HS} used at each temperature and density. One may, for example, use either the WCA or Lado prescriptions. However, one may equally effectively use other criteria, including some which express σ_{HS} as a function of temperature only. A particularly appealing method is based on a Boltzmann-factor criterion (BFC) introduced by Boltzmann himself, which in its simplest form sets σ_{HS} to the value of r at which $\beta v_0(r) = 1$. For a Lennard-Jones fluid (with the WCA potential separation, equation (2)) this BFC implies that

$$\sigma_{\text{HS}}(T) = \sigma \left[\frac{2\sqrt{\beta\epsilon}}{1 + \sqrt{\beta\epsilon}} \right]^{1/6}. \quad (11)$$

In a slightly generalized form one may set $\beta v_0(r) = \zeta$ to obtain the following expression for σ_{HS} , whose predictions are within about $\pm 2\%$ of those obtained with equation (11) when $0.7 \leq \zeta \leq 1.5$

$$\sigma_{\text{HS}}(T) = \sigma \left[\frac{2\sqrt{\beta\epsilon/\zeta}}{1 + \sqrt{\beta\epsilon/\zeta}} \right]^{1/6}. \quad (12)$$

Furthermore, similar expressions may be used to obtain σ_{HS} values associated with GLJ or inverse-power potentials [8, 9]. For a GLJ potential one need only replace in equations (11) and (12) the exponent of $1/6$ by $2/n_0$, where n_0 is the exponent which characterizes the steepness of the GLJ repulsive core [8]. For an inverse power potential, $v(r) = \epsilon(\sigma/r)^n$, the

BFC equations reduce to $\sigma_{\text{HS}}(T) = \sigma(\beta\epsilon)^{1/n}$ and $\sigma_{\text{HS}}(T) = \sigma(\beta\epsilon/\zeta)^{1/n}$, respectively. The accuracy of the predictions obtained using the simple and explicit BFC compared to the WCA equal compressibility criterion represent one of the main observations of the BAS treatment and one of its main advantages.

3. The Boltzmann-factor criterion and its variants

3.1. Boltzmann-factor criterion from the standpoint of kinetic theory

The BFC identifies the effective hard sphere diameter σ_{HS} as the intermolecular distance at which the repulsive pair potential energy v_0 is of the order of the thermal energy kT . More specifically, the effective hard sphere diameter is determined as the solution of the equation

$$v_0(\sigma_{\text{HS}}) = \zeta kT. \quad (13)$$

The effective HS diameter determined under the BFC is only a function of the temperature, $\sigma_{\text{HS}}(T)$. For more generality, we have incorporated on the right-hand side of equation (13) a numerical factor ζ of order of unity; it is the same parameter that appears in equation (12). In this section we outline the variety of values that ζ can take as different criteria based on kinetic theory are invoked.

Historically many of the attempts at specifying the effective hard-sphere diameter of a molecule, σ_{HS} , in a fluid resort to the concept of the distance of closest approach between molecules. The latter concept occurs naturally in the kinetic theory of gases when considering intermolecular collisions. Use of this concept was pioneered by Boltzmann himself [21], who identified the distance of closest approach between molecules in a gas with the intermolecular separation at which the potential energy of interaction between two molecules equals the average relative kinetic energy $\overline{E_r}$ of the molecules in a uniform system at equilibrium.

From Boltzmann's prescription, when the pair potential is $v_0(r)$ (defined in equation (2)) we have

$$v_0(\sigma_{\text{HS}}) = \overline{E_r}. \quad (14)$$

Based on this Boltzmann distance-of-closest-approach criterion we can examine several variants of the BFC to determine σ_{HS} , which differ in the value of the numerical factor ζ in equation (13).

A first realization of equation (13) may be recovered by retracing Boltzmann's arguments in section 55 of [21]. (Notice that the discussion in that section of [21] is concerned explicitly only with the distance of closest approach between molecules in a Maxwell gas, in which the repulsive potential is of the form $v_{\text{rep}}(r) = K/(4r^4)$, where K is a constant.) By straightforward application of the theorem of equipartition of energy for a gas in three dimensions we find $\overline{E_r} = (3/2)kT$. (Or, equivalently we may calculate $\overline{E_r}$ as the average of the two-particle relative kinetic energy with the probability density $P(E_r)$ corresponding to a three-dimensional gas in equilibrium. In such a case $P(E_r) = (2\beta^{3/2}/\pi^{1/2})E_r^{1/2} \exp(-\beta E_r)$.) We observe that with $\overline{E_r} = (3/2)kT$, Boltzmann's distance-of-closest-approach recipe, equation (14), leads to the BFC equation (13) with $\zeta = 3/2$.

Basically the same calculation was performed by Andrews [29] to characterize the effective hard-sphere diameter of the molecules in a two-dimensional gas. In this case the theorem of equipartition of energy gives $(\overline{E_r})_{2\text{D}} = kT$. This result, when replaced into equation (14), leads to the two-dimensional version of the BFC, equation (13) with the numeric factor $(\zeta)_{2\text{D}} = 1$.

Although in this work we are specifically concerned with three-dimensional systems, Andrews' result for two-dimensions is of some relevance for the present discussion, since

it is occasionally argued that σ_{HS} may be conveniently determined from equation (13) with $\zeta = (\zeta)_{2\text{D}} = 1$ [34, 35]. The reasoning is that for two molecules moving in three-dimensions to collide at some time (in the future or in the past), their velocity vectors must lie on the same plane (and not be parallel). This feature, it is argued, justifies using the two-dimensional result for $\overline{E_r}$. Although the three-dimensional version of this calculation appears to us to be the natural one to apply in three-dimensional space, the value $\zeta = 1$ is one that also results from several other approaches, as we shall see at the end of this subsection and in the next one.

More recently Speedy *et al* [30] invoked a somewhat different distance-of-closest-approach criterion to determine the effective hard-sphere diameter σ_{HS} . These authors identify the distance of closest approach between molecules with the intermolecular separation at which the potential energy of interaction between two molecules equals the average relative kinetic energy $\overline{E_r^{\text{col}}}$ of a pair of molecules in a uniform system at equilibrium *that will undergo a collision within the next unit of time*. Thus, instead of equation (14), these authors propose the criterion

$$v_0(\sigma_{\text{HS}}) = \overline{E_r^{\text{col}}}, \quad (15)$$

where

$$\overline{E_r^{\text{col}}} = \int_0^\infty dE_r E_r P^{\text{col}}(E_r), \quad (16)$$

in which $P^{\text{col}}(E_r)$ is the probability density that, starting from a typical phase-space configuration for a many-particle system at equilibrium, a pair of molecules with relative kinetic energy E_r will collide within the next unit of time. The expression for $P^{\text{col}}(E_r)$ may be extracted from several classical sources [36–38]:

$$P^{\text{col}}(E_r) = \beta^2 E_r e^{-\beta E_r}. \quad (17)$$

With this expression equations (15) and (16) give the formula used by Speedy *et al* [30] to determine σ_{HS}

$$v_0(\sigma_{\text{HS}}) = 2kT, \quad (18)$$

which agrees with the BFC, equation (13), with the numerical factor $\zeta = 2$.

We conclude this section by calling attention to still another kinetic-theory derivation of the BFC. Instead of the average relative kinetic energy $\overline{E_r^{\text{col}}}$ in equation (15) we may consider the most probable relative kinetic energy E_r^{mp} for pairs of molecules that will undergo a collision within the next unit of time

$$v_0(\sigma_{\text{HS}}) = E_r^{\text{mp}} = kT, \quad (19)$$

where the second equality is the value of E_r that maximizes $P^{\text{col}}(E_r)$ given by equation (17). Comparing this result with equation (13) we see that this new recipe based on kinetic theory leads to the BFC with $\zeta = 1$.

3.2. Boltzmann factor criterion from a thermodynamic standpoint

An alternative way to determine a temperature-dependent effective hard sphere diameter $\sigma_{\text{HS}}(T)$ is based on the one-dimensional integral, which follows from the use of the Barker–Henderson version of TPT [11–13, 23]

$$\sigma_{\text{HS}} = \int_0^\infty dr (1 - e^{-\beta v_0(r)}) = \int_0^{r_0} dr (1 - e^{-\beta v_0(r)}), \quad (20)$$

where in the second equality we have taken into account that $v_0(r)$ vanishes for $r > r_0$.

This expression of σ_{HS} , which involves the integral of the negative of the Mayer function of the modified repulsive potential $v_0(r)$, seems at first sight to be very different from the BFC recipe, equation (13). Nevertheless, as commented upon by Hsu *et al* [39], equation (20) leads to values of σ_{HS} that are close to those obtained from the BFC with $\zeta = 1$. The purpose of this section is to show how σ_{HS} determined with equation (20) can also be thought as approximately equivalent to the BFC.

To show this we first perform an integration by parts of equation (20). Noticing that $r(1 - e^{-\beta v_0(r)})$ vanishes both at $r = 0$ and at r_0 , integration by parts of equation (20) leads to the virial-like expression

$$\sigma_{\text{HS}} = \int_0^{r_0} dr r \{-\beta v_0'(r)\} e^{-\beta v_0(r)}, \quad (21)$$

where $v_0'(r)$ denotes the derivative of the modified repulsive potential with respect to the intermolecular separation.

We consider now the BFC, equation (13) when $\zeta = 1$. An alternative way of writing this criterion, $\beta v_0(\sigma_{\text{HS}}) = 1$, is as follows:

$$\sigma_{\text{HS}} = \sigma_{\text{HS}} \beta v_0(\sigma_{\text{HS}}) = \int_0^{r_0} dr \sigma_{\text{HS}} \{\beta v_0(r)\} \delta(r - \sigma_{\text{HS}}). \quad (22)$$

In the second equality $\delta(r - \sigma_{\text{HS}})$ is the Dirac delta function, and we have implicitly assumed that $0 < \sigma_{\text{HS}} < r_0$ is satisfied. Recalling that $\delta(r - \sigma_{\text{HS}}) = d\theta(r - \sigma_{\text{HS}})/dr$, where $\theta(r - \sigma_{\text{HS}})$ is the step function, we can integrate by parts to obtain

$$\sigma_{\text{HS}} = \lim_{\tau \rightarrow 0} I_1(\tau) + I_2, \quad (23)$$

where

$$I_1(\tau) = \int_{\tau}^{r_0} dr \frac{d}{dr} \{\sigma_{\text{HS}} \beta v_0(r) \theta(r - \sigma_{\text{HS}})\}, \quad (24)$$

$$I_2 = \int_0^{r_0} dr \sigma_{\text{HS}} \{-\beta v_0'(r)\} \theta(r - \sigma_{\text{HS}}). \quad (25)$$

The integral $I_1(\tau)$ is zero because the product $v_0(r)\theta(r - \sigma_{\text{HS}})$ vanishes both at $r = r_0$ and at $r = \tau < \sigma_{\text{HS}}$. We conclude that under the BFC σ_{HS} can be calculated with the integral I_2 , equation (25).

To complete this discussion we notice that $\theta(r - \sigma_{\text{HS}})$ vanishes for $r < \sigma_{\text{HS}}$ and that $r_0 - \sigma_{\text{HS}}$ is small, so to a good approximation we can replace the factor σ_{HS} in the integrand of I_2 by the variable r . Thence the BFC for σ_{HS} may be written in the integral form

$$\sigma_{\text{HS}} \simeq \int_0^{r_0} dr r \{-\beta v_0'(r)\} \theta(r - \sigma_{\text{HS}}). \quad (26)$$

This expression should be contrasted with the Barker and Henderson criterion, equation (21). Clearly the two estimates of σ_{HS} will be comparable when the Boltzmann factor $\exp[-\beta v_0(r)]$ is well approximated by the step function $\theta(r - \sigma_{\text{HS}})$. Consideration of the plot of $\exp[-\beta v_0(r)]$ as a function of r shows that this is not an unreasonable expectation, thus justifying the numerical observation [39] that σ_{HS} calculated with equation (20) is roughly equivalent to σ_{HS} calculated under the BFC criterion (13) with $\zeta = 1$. In the next section we examine numerically the approximate equivalence of the two criteria for the determination of $\sigma_{\text{HS}}(T)$.

Besides the Barker–Henderson integral (20), an alternative thermodynamically based criterion for associating a T -dependent HS diameter $\sigma_{\text{HS}}(T)$ to a given continuous repulsive potential $v_0(r)$ may be proposed by requiring that the HS- and the $v_0(r)$ -systems have the same second virial coefficient. We find that such a criterion gives $\sigma_{\text{HS}}(T)$ values that are similar to

those obtained with equation (12) when setting $\zeta \simeq 0.4$. Like the Barker–Henderson criterion, the equal-virial coefficient criterion predicts values for $\sigma_{\text{HS}}(T)$ that are somewhat too large for use as the HS reference system in the BAS theory [10].

3.3. Simple harmonic approximation for estimating σ_{HS}

In this section we consider the case in which the original interaction potential $v(r)$ between pairs of particles is of the Lennard-Jones type, and compare $\sigma_{\text{HS}}(T)$ calculated under the BFC with $\zeta = 1$ (equation (11)) and the Barker–Henderson integral (20). We also present an approximate analytical method for estimating σ_{HS} under the latter criterion.

The proposed analytical approximation is obtained by representing the modified repulsive potential $v_0(r)$ with a quadratic polynomial in the neighbourhood of r_0 :

$$v_0(r) \simeq a(r - r_0)^2, \quad r \leq r_0. \quad (27)$$

The constant a is adjusted to match the curvature of $v_0(r)$ to the left of the minimum; the result is $a = 72\epsilon/2^{1/3}\sigma^2$ for a Lennard-Jones potential (and $a = n_0^2\epsilon/2^{(n_0+4)/n_0}\sigma^2$ for the generalized Lennard-Jones potential). With approximation (27) for $v_0(r)$, equation (20) can be evaluated analytically; when $v(r)$ is the Lennard-Jones potential we obtain

$$\sigma_{\text{HS}}^* = 2^{1/6} \left[1 - \frac{1}{12} \left(\frac{\pi}{2\beta^*} \right)^{1/2} \text{erf}(\sqrt{72\beta^*}) \right], \quad (28)$$

where $\text{erf}(x)$ is the error function. For convenience we have introduced the reduced diameter $\sigma_{\text{HS}}^* \equiv \sigma_{\text{HS}}/\sigma$ and the reduced reciprocal temperature $\beta^* \equiv \beta\epsilon$, both defined in terms of the Lennard-Jones parameters σ and ϵ .

In figure 1 we compare the reduced effective hard-sphere diameter σ_{HS}^* for the Lennard-Jones potential as a function of the reduced reciprocal temperature β^* when calculated with the BFC (using $\zeta = 1$) and with the Barker–Henderson integral. The BFC (solid curve) is computed with equation (11). The BH integral is evaluated (i) numerically (dashed curve) and (ii) under the harmonic approximation to $v_0(r)$ in the argument of the integral (dashed–dotted curve).

The figure shows that, for a given reduced reciprocal temperature, the HS diameter σ_{HS}^* obtained with the Barker–Henderson integral is larger than the reduced diameter estimated with the BFC criterion with $\zeta = 1$. In fact, the Barker–Henderson estimate of $\sigma_{\text{HS}}(T)$ is approximately equal to the estimate obtained with the BFC with $\zeta \simeq 0.6$, as calculated with equation (12). The Barker–Henderson estimate of $\sigma_{\text{HS}}(T)$ is a bit too large for the corresponding HS system to be used as the reference in the BAS perturbation theory [10].

Figure 1 shows that equation (28), although a reasonable approximation to the Barker–Henderson integral, gives an even larger $\sigma_{\text{HS}}(T)$ when $\beta^* > 2$, thus deteriorating the quality of the HS reference system even more. A similar deterioration occurs for $\beta^* < 0.5$, when the harmonic approximation leads to much too small HS diameters. On the other hand, and because of the inaccuracy in the approximation, the estimate (28) for the HS diameter is in close agreement with $\sigma_{\text{HS}}(T)$ calculated with the $\zeta = 1$ BFC criterion (12) whenever $0.5 < \beta^* < 1.5$.

4. SCOZA

4.1. SCOZA for models with hard-core

Much of our SCOZA work has been done for systems with hard-core (HC) pair interactions $v(r)$ consisting of a repulsive HC (diameter σ_{HS}) and an adjacent attractive tail $w(r)$:

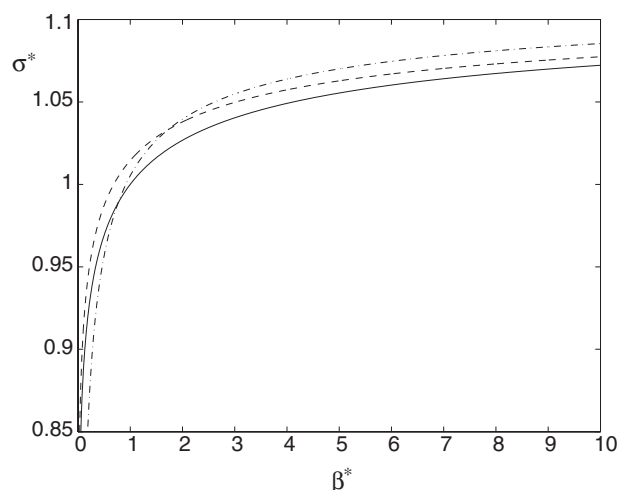


Figure 1. Comparison of the reduced hard-sphere diameter σ_{HS}^* as a function of the reduced inverse temperature β^* as estimated for the Lennard-Jones potential by the BFC and the Barker and Henderson integral. —: $\sigma_{\text{HS}}(T)$ calculated with the BFC, equation (11); ---: $\sigma_{\text{HS}}(T)$ calculated with the Barker–Henderson integral criterion, equation (20); — · —: $\sigma_{\text{HS}}(T)$ calculated with equation (28) bases on a harmonic approximation to $v_0(r)$ in the argument of the Barker–Henderson integral.

$$v(r) = \begin{cases} \infty & \text{for } r \leq \sigma_{\text{HS}} \\ w(r) & \text{for } r > \sigma_{\text{HS}}. \end{cases} \quad (29)$$

We shall begin by considering this case, and then go on to the soft-core extension. For convenience, we shall focus on pair interactions that are linear combinations of Yukawa tails (labelled by Greek indices), i.e.

$$w(r) = \sum_v \frac{K_v}{r} \exp[-z_v(r - \sigma_{\text{HS}})]. \quad (30)$$

Here we can allow $w(r)$ to be explicitly density dependent ($w(r) = w(r; \rho)$, ρ being the number density). To be more specific, we introduce a density-dependent inverse screening length $z_v(\rho)$.

The SCOZA is based on the Ornstein–Zernike relation

$$h(r) = c(r) + \rho \int d\mathbf{r}' c(r') h(|\mathbf{r} - \mathbf{r}'|) \quad (31)$$

supplemented by a MSA-type closure relation

$$g(r) = 0 \quad \text{for } r \leq \sigma_{\text{HS}} \quad (32)$$

$$c(r) = c_{\text{HC}}(r) + K(\rho, T)w(r) \quad \text{for } r > \sigma_{\text{HS}}. \quad (33)$$

Here $h(r)$ and $c(r)$ are the total and the direct correlation functions, $g(r) = h(r) + 1$ is the pair distribution function and T is the temperature. $c_{\text{HC}}(r)$ is the direct correlation function for the hard-core reference system for which we choose the Waisman parametrization [40], which is known to reproduce simulation results for the structural properties with high accuracy. For $r > \sigma_{\text{HS}}$, $c_{\text{HC}}(r) = (K_0/r) \exp[-z_0(r - \sigma_{\text{HS}})]$, where K_0 and z_0 are known functions of ρ (see the appendix of [41] for details). The state-dependent function $K(\rho, T)$ in equation (33) is not

fixed *a priori* and is determined by the requirement of thermodynamic consistency between the energy and the compressibility routes: let $\chi_{\text{red}} \equiv \rho kT \chi_T$ be the reduced (dimensionless) isothermal compressibility, given via the compressibility route by

$$(\chi_{\text{red}})^{-1} = 1 - \rho \hat{c}(q=0), \quad (34)$$

where the circumflex $\hat{}$ indicates the Fourier transform; furthermore, let u be the excess (over that of the ideal gas) internal energy per unit volume, given via the energy route by

$$u = 2\pi\rho^2 \int dr r^2 w(r)g(r); \quad (35)$$

if χ_{red} and u come from the unique Helmholtz free energy, then they are related via

$$\rho \frac{\partial^2 u}{\partial \rho^2} = \frac{\partial}{\partial \beta} \left(\frac{1}{\chi_{\text{red}}} \right). \quad (36)$$

For the special choice of the pair interaction $w(r)$ given by equation (30) along with the Waisman parametrization of $c_{\text{HC}}(r)$, the SCOZA benefits from the availability of the semi-analytic solution of the MSA. Two different approaches to this solution have been proposed in the literature: the (original) Laplace-transform route [42–45] and the Wiener–Hopf factorization technique introduced by Wertheim and Baxter [46, 47]. In the following we outline the formulation of the SCOZA for many-Yukawa potential tails using the Baxter approach, and refer the reader interested in a more detailed presentation to [48].

Under certain conditions [49], the solution of the OZ equation is equivalent to the solution of the following two integral equations:

$$2\pi r c(r) = -Q'(r) + \rho \int Q(t) Q'(r+t) dt \quad (37)$$

$$2\pi r h(r) = -Q'(r) + 2\pi\rho \int (r-t)h(|r-t|)Q(t) dt \quad (38)$$

introducing the so-called factor function $Q(t)$. For a system with n Yukawa tails the factor function is characterized by $(2n+2)$ as yet undetermined coefficients (a , b , C_v and D_v), i.e.

$$Q(r) = Q^0(r) + \sum_v \frac{1}{z_v} D_v e^{-z_v(r-\sigma_{\text{HS}})}, \quad (39)$$

with

$$Q^0(r) = \frac{a}{2}(r-\sigma_{\text{HS}})^2 + b(r-\sigma_{\text{HS}}) + \sum_v \frac{1}{z_v} C_v [e^{-z_v(r-\sigma_{\text{HS}})} - 1] \quad (40)$$

for $0 < r < \sigma_{\text{HS}}$ and $Q^0(r) = 0$ for $r > \sigma_{\text{HS}}$. Introducing further G_v via

$$G_v = z_v \int_{\sigma_{\text{HS}}}^{\infty} r e^{-z_v(r-\sigma_{\text{HS}})} g(r) dr \quad (41)$$

one can derive (along with the MSA closure relation) a set of $2n$ non-linear equations for the $2n$ unknowns G_v and D_v : n of these equations are linear in the D_v ; their solution gives $D_v = D_v(\rho, G_v)$. Finally one can also relate a to these unknowns, leading thus to an expression $a = a(G_v, D_v)$; the relations are summarized in [50].

The factorization formalism leads to

$$(\chi_{\text{red}})^{-1} = \left(\frac{a}{2\pi} \right)^2, \quad (42)$$

so that equation (36) now becomes

$$\rho \frac{\partial^2 u}{\partial \rho^2} = 2 \frac{a}{(2\pi)^2} \frac{\partial a}{\partial u} \frac{\partial u}{\partial \beta}. \quad (43)$$

Inserting $a = a(G_v, D_v)$ with $D_v = D_v(\rho, G_v)$ into the partial differential equation (43), one arrives at

$$\rho \frac{\partial^2 u}{\partial \rho^2} = 2 \frac{a}{(2\pi)^2} \left(\sum_v \frac{\partial a}{\partial G_v} \frac{\partial G_v}{\partial u} \right) \frac{\partial u}{\partial \beta} = B(\rho, u) \frac{\partial u}{\partial \beta} \quad (44)$$

once a , $\partial a / \partial G_v$ and $\partial G_v / \partial u$ have been expressed as functions of ρ and u . The required expressions are obtained by implicit differentiation of a set of nonlinear equations in the G_v and u that are summarized in [48]. Equation (44) is now a quasilinear partial differential equation of diffusion type which has to be solved numerically (as described in detail in [51]) on a (β, ρ) grid, $[0, \beta_f] \times [0, \rho_0]$, with a suitable initial condition (for $\beta = 0$) and suitable boundary conditions (here, the high-temperature approximation for the upper density limit $\rho_0 \sigma^3 = 1$). In contrast to conventional liquid-state theories, the SCOZA can be solved up to the critical point; special care has to be taken in the region of instability (characterized by a negative compressibility) which has to be excluded from the region of integration.

From the solution of the partial differential equation (44) we obtain the full information about the structure and the thermodynamic properties of the system. For instance, the pressure P and the chemical potential μ (i.e. two quantities required to determine the phase behaviour) are calculated from

$$\frac{\partial}{\partial \beta}(\beta P) = -u + \rho \frac{\partial u}{\partial \rho} \quad (45)$$

$$\frac{\partial}{\partial \beta}(\beta \mu) = \frac{\partial u}{\partial \rho} \quad (46)$$

via thermodynamic integration.

4.2. Soft-core extension

We now consider the case in which we have soft-core in the pair potential. One can still use SCOZA with a hard-reference potential of diameter σ_{HS} to describe a soft-core potential given in terms of a characteristic length σ , as long as the ratio $\sigma_{\text{HS}}/\sigma$ is allowed to be appropriately dependent on the thermodynamic state. This is already the standard procedure in applying existing versions of TPT to soft-core potentials, such as the LJ potential, and there is no problem in using SCOZA with a state-dependent $\sigma_{\text{HS}}/\sigma$. One need not change any of the equations that define the SCOZA, equations (31)–(36), as long as one includes in $\partial^2 u / \partial \rho^2$ in equation (36) the change in u resulting from any ρ -dependence of σ_{HS} that occurs in the version of TPT being used as SCOZA input.

One can also abandon the hard-core condition altogether in using the SCOZA. One sees from the derivation of the SCOZA critical exponents given in [52] that the SCOZA critical exponents are unchanged if one replaces the core-condition $g(r) = 0$ for $r < \sigma_{\text{HS}}$ by prescribing instead that $g(r)$ be given by some explicit function for $r < \sigma_{\text{HS}}$, or that $c(r)$ be prescribed for $r < \sigma_{\text{HS}}$ as well as for $r > \sigma_{\text{HS}}$. Thus one can treat a soft-core potential by setting $\sigma_{\text{HS}} = 0$ in equations (29) through (33) by replacing the $c_{\text{HS}}(r)$ in equation (33) by a prescribed reference-system $c^{\text{ref}}(r)$ appropriate to a soft potential. Integrals involving such a $c^{\text{ref}}(r)$ and the corresponding $h^{\text{ref}}(r)$ can then be treated using the analytic recipes developed in our earlier TPT papers [8–10].

An explicit recipe involving the combined use of the BAS theory and SCOZA is the following, which applies to the typical case of a potential that has a soft repulsive head and an attractive tail. One uses the WCA criterion to separate the full potential $v(r)$ into its soft repulsive $v_0(r)$ and attractive $v_1(r)$ contributions. Then one uses SCOZA to calculate the thermodynamic properties of a fluid with hard-core plus a tail, where the value of the

HS diameter is determined from the shape of the WCA soft-repulsive core potential using the BFC. Then, BAS theory is used to determine the difference between the thermodynamic properties of the soft- and hard-repulsive reference fluids (using the WCA correction integral as prescribed in the BAS theory). This procedure provides a quantitative method for correcting the hard-core SCOZA predictions to account for the softness of the true core potential.

5. Conclusions

Mode-coupling studies of glass transitions in colloid models with interactions that include strong short-range attraction yield quantitative estimates of transition locations that have proved to be extremely sensitive to the accuracy of the static structure factors that are used as input [53]. Unless structure factors for a given potential are of very high accuracy, this means that there will be uncertainty as to whether any disparity in transition behaviour between experimental and mode-coupling results are due to a poor choice of model potential, an intrinsic error in mode-coupling theory, or inaccuracy in the structure factor.

SCOZA results for the structure factors have already been shown to be of very high accuracy for simple Lennard-Jones-like potentials. The extension of those results to colloid models that include strong short-range attraction using TPT to implement the SCOZA evaluation promises similar accuracy for such models.

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