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Thermodynamically consistent perturbation theory for molecular fluids

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New conditions for the reference system in a generalized Andersen-Weeks-Chandler approximation $y(12)=g(12)\exp[\beta\phi(12)]\approx y_0(12)$ are derived which minimize an approximate free energy functional and lead to improved internal thermodynamic consistency for molecular fluids.

1. INTRODUCTION

In order of increasing computational exactness, and generally also exactness, the tools available for the statistical mechanical study of classical fluids, simple or molecular, are perturbation theories, integral equations, and computer simulations [1]. Because they are significantly more complex to work with, molecular fluids have particularly attracted the use of perturbation theory, so that a fair number of different formulations have by now been examined [2-13]. The logical reference model for such theories should itself be a molecular system ; some work in this direction has been carried out [11-13], but lack of a convenient analytic molecular model analogous to the solution of the Percus-Yevick equation for hard spheres [14] has channelled most efforts towards spherically symmetric reference systems [2-10].

In these formulations, little or no attention has been paid to the question of internal thermodynamic consistency, long the bane of approximate theories. As a result, several different numerical values are generally obtainable for the same physical quantity, with an *a posteriori* selection of the best of these sometimes used to judge the merits of an approximation.

This work deals with the attainment of (at least partial) thermodynamic consistency in perturbation theory for molecular fluids. No new formulation of a perturbation theory itself is put forward, however. Instead, we shall work with an obvious generalization of the Andersen-Weeks-Chandler (AWC) [15] approximation widely used for simple fluids [16] and (with spherically symmetric reference potential) for molecular fluids as well [9, 10].

A discussion of the free energy lends itself best to the derivation of the desired results. In the next section, we show that minimizing an approximate expression for the free energy yields not only the generalized AWC approximation but also a set of constraints that affords a significant improvement in the internal thermodynamic consistency of this approximation.

2. THEORY

Let

$$\phi(12) = \phi(\mathbf{r}_{12}, \omega_1, \omega_2), \quad (1)$$

and

$$\phi_0(12) = \phi_0(\mathbf{r}_{12}, \omega_1, \omega_2) \quad (2)$$

denote respectively the intermolecular potential of interest and a chosen reference potential; here, ω_1 and ω_2 are the Euler angles specifying molecular orientations with respect to an arbitrary frame. We define a potential intermediate between ϕ_0 and ϕ by

$$\phi(12; \lambda) = \phi_0(12) + \lambda \Delta \phi(12), \quad (3)$$

with

$$\Delta \phi(12) = \phi(12) - \phi_0(12) \quad (4)$$

and

$$0 \leq \lambda \leq 1. \quad (5)$$

Then by the familiar charging artifice, the free energy difference between the system of interest ($\lambda = 1$) and the reference system ($\lambda = 0$) can be written as

$$\beta(A - A_0)/N = \frac{1}{2}\rho \int d\mathbf{r}_{12} \int_0^1 d\lambda \langle g(12; \lambda) \beta \Delta \phi(12) \rangle, \quad (6)$$

where the angular brackets denote an orientational average over ω_1 and ω_2 and

$$g(12; \lambda) = \exp [-\beta \phi(12; \lambda) + S(12; \lambda) + B(12; \lambda)] \quad (7)$$

is the pair distribution function for the intermediate potential (3). In (7), S and B are the corresponding generalizations of the series (or nodal) and bridge (or elementary) functions [1]. It is simple to verify from (7) that the integrand in (6) can be written

$$g(12; \lambda) \beta \Delta \phi(12) = -\frac{\partial}{\partial \lambda} \{g(12; \lambda) - g(12; \lambda) \ln g(12; \lambda) \exp [\beta \phi(12; \lambda)]\} \\ - [S(12; \lambda) + B(12; \lambda)] \frac{\partial g(12; \lambda)}{\partial \lambda}, \quad (8)$$

so that (6) becomes

$$\beta A/N = \beta A_0/N - \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle g(12) - g(12) \ln g(12) \exp [\beta \phi(12)] - g_0(12) \\ + g_0(12) \ln g_0(12) \exp [\beta \phi_0(12)] \rangle - \frac{1}{2}\rho \int d\mathbf{r}_{12} \int_0^1 d\lambda \\ \times \left\langle [S(12; \lambda) + B(12; \lambda)] \frac{\partial g(12; \lambda)}{\partial \lambda} \right\rangle. \quad (9)$$

The key approximation is now to be made in the second integral of (9), namely, we shall assume that S and B are relatively insensitive to the change in potential

from ϕ_0 to ϕ and may be approximated to their reference system values for all λ . The integral over λ is then trivial and we have

$$\begin{aligned}\beta A/N &\approx \beta A_0/N - \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle g(12) - g(12) \ln g(12) \exp [\exp \beta \phi(12)] - g_0(12) \\ &\quad + g_0(12) \ln g_0(12) \exp [\beta \phi_0(12)] \rangle - \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle [g(12) - g_0(12)] \\ &\quad \times \ln g_0(12) \exp [\beta \phi_0(12)] \rangle \\ &= \beta A_0/N - \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle g(12) - g_0(12) \\ &\quad - g(12) \ln \{g(12) \exp [\beta \phi(12)] / g_0(12) \exp [\beta \phi_0(12)]\} \rangle. \quad (10)\end{aligned}$$

This is the desired functional for the free energy. (We remark that it is not necessary to approximate the term involving $S(12; \lambda)$ in (9). Exact evaluation of this term, leaving only $B(12; \lambda)$ to be approximated by $B_0(12)$, leads to the Reference-Hypernetted Chain integral equation [17]. Equation (10) sacrifices this more exact possibility in exchange for the much greater simplicity of the results of (10).)

The equilibrium condition for the canonical ensemble is that the free energy be minimum. Viewing (10) as a functional of

$$y(12) = g(12) \exp [\beta \phi(12)] \quad (11)$$

and the corresponding $y_0(12)$, we may vary these to get

$$\begin{aligned}\beta \delta A/N &= \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle \delta g(12) \ln [y(12)/y_0(12)] \\ &\quad - \delta y_0(12) [g(12) - g_0(12)] / y_0(12) \rangle, \quad (12)\end{aligned}$$

which will satisfy the prescribed extremal condition if

$$y(12) = y_0(12) \quad (13)$$

and

$$\rho \int d\mathbf{r}_{12} \langle \delta y_0(12) [g(12) - g_0(12)] / y_0(12) \rangle = 0. \quad (14)$$

Equivalently, these may be written as

$$g(12) = y_0(12) \exp [-\beta \phi(12)] \quad (15)$$

and

$$\rho \int d\mathbf{r}_{12} \langle \{\exp [-\beta \phi(12)] - \exp [-\beta \phi_0(12)]\} \delta y_0(12) \rangle = 0. \quad (16)$$

Equation (15) will be recognized as a straightforward generalization of the AWC approximation [15], based now on an arbitrary reference potential $\phi_0(12)$. The second equation, (16), is a constraint on this potential, needed to minimize the free energy. We shall see below that it also produces a significant improvement in thermodynamic consistency.

The constraint is implemented as follows. A typical molecular reference potential will contain an energy parameter ϵ_0 and several distance parameters $d_0, d_1, \dots, d_n$. (A heteronuclear diatomic molecule, e.g., could have three distance scales.) The condition (16) is satisfied by varying these parameters until

$$\rho \int d\mathbf{r}_{12} \left\langle \Delta e(12) \frac{\partial y_0(12)}{\partial d_j} \right\rangle = 0 \quad (17)$$

for $j=0, 1, \dots, n$ and

$$\rho \int d\mathbf{r}_{12} \left\langle \Delta e(12) \frac{\partial y_0(12)}{\partial \epsilon_0} \right\rangle = 0, \quad (18)$$

where

$$\Delta e(12) = \exp[-\beta\phi(12)] - \exp[-\beta\phi_0(12)]. \quad (19)$$

Finally, with the use of (13) the free energy in the present approximation becomes

$$\beta A/N = \beta A_0/N - \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle \Delta e(12) y_0(12) \rangle. \quad (20)$$

The equation of state obtained by differentiation of the free energy is now explicitly, from (20),

$$\begin{aligned} \frac{\beta p}{\rho} &= \rho \frac{\partial(\beta A/N)}{\partial \rho} \\ &= \frac{\beta p_0}{\rho} - \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle \Delta e(12) y_0(12) \rangle - \frac{1}{2}\rho \int d\mathbf{r}_{12} \left\langle \Delta e(12) \rho \frac{\partial y_0(12)}{\partial \rho} \right\rangle. \end{aligned} \quad (21)$$

But $y_0(12)$ is a dimensionless function of lengths, in the form, say, $f(r/d_0, \rho d_0^3, d_1/d_0, \dots, d_n/d_0)$, so that

$$d_0 \frac{\partial y_0(12)}{\partial d_0} = -r \frac{\partial y_0(12)}{\partial r} + 3\rho \frac{\partial y_0(12)}{\partial \rho} - \sum_{j=1}^n d_j \frac{\partial y_0(12)}{\partial d_j} \quad (22)$$

and (21) becomes

$$\begin{aligned} \frac{\beta p}{\rho} &= \frac{\beta p_0}{\rho} - \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle \Delta e(12) y_0(12) \rangle - \frac{1}{8}\rho \int d\mathbf{r}_{12} \left\langle \Delta e(12) r \frac{\partial y_0(12)}{\partial r} \right\rangle \\ &\quad - \frac{1}{8}\rho \sum_{j=0}^n \int d\mathbf{r}_{12} \left\langle \Delta e(12) d_j \frac{\partial y_0(12)}{\partial d_j} \right\rangle, \\ &= 1 - \frac{1}{8}\rho \int d\mathbf{r}_{12} \left\langle y_0(12) \exp[-\beta\phi(12)] r \frac{\partial \beta\phi(12)}{\partial r} \right\rangle \\ &\quad - \frac{1}{8}\rho \sum_{j=0}^n \int d\mathbf{r}_{12} \left\langle \Delta e(12) d_j \frac{\partial y_0(12)}{\partial d_j} \right\rangle, \end{aligned} \quad (23)$$

after an integration by parts, and finally

$$\frac{\beta p}{\rho} = 1 - \frac{1}{8}\rho \int d\mathbf{r}_{12} \left\langle g(12) r \frac{\partial \beta\phi(12)}{\partial r} \right\rangle, \quad (24)$$

after using (15) and (17).

Similarly, since $y_0(12)$ will depend on temperature only through the dimensionless combination $\beta\epsilon_0$, we have for the potential energy, from (20),

$$\begin{aligned} \frac{\beta U}{N} &= \beta \frac{\partial}{\partial \beta} [\beta(A - A_{\text{ideal}})/N] \\ &= \frac{\beta U_0}{N} + \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle y_0(12) \{ \exp[-\beta\phi(12)] \beta\phi(12) \\ &\quad - \exp[-\beta\phi_0(12)] \beta\phi_0(12) \} \rangle - \frac{1}{2}\rho \int d\mathbf{r}_{12} \left\langle \Delta e(12) \epsilon_0 \frac{\partial y_0(12)}{\partial \epsilon_0} \right\rangle \\ &= \frac{1}{2}\rho \int d\mathbf{r}_{12} \langle g(12) \beta\phi(12) \rangle, \end{aligned} \quad (25)$$

after using (15) and (18).

Thus, differentiation of the free energy and the usual quadratures will, by construction, produce the same results. This guarantees, e.g., that the consistency test proposed by Hiroike [18], namely,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p, \quad (26)$$

will be satisfied when p and U are obtained from the quadratures (24) and (25), even though we are working with an approximate $g(12)$.

As written above, the principal equations of this work, namely (15), (17), (18) and (20), are premised on the availability of an explicit solution $y_0(12)$ for the molecular reference potential $\phi_0(12)$. For simple liquids, the analytic solution of the Percus-Yevick equation [14] and its empirical improvements [19] satisfy this need. No such analytic model is yet available for a molecular liquid and the present alternative, solving an integral equation by iteration, undermines the whole point of a simple perturbation approach. Thus, until such an analytic model is devised, the full scope of the scheme described above cannot be realized and one must, in the interim, fall back upon spherically symmetric reference systems. In this case, the relevant equations for an isotropic potential $\phi_0(r)$ become

$$g(12) = y_0(r_{12}) \exp [-\beta\phi(12)], \quad (27)$$

$$\rho \int d\mathbf{r} \Delta e(r) \frac{\partial y_0(r)}{\partial d_0} = 0, \quad (28)$$

$$\rho \int d\mathbf{r} \Delta e(r) \frac{\partial y_0(r)}{\partial \epsilon_0} = 0, \quad (29)$$

and

$$\beta A/N = \beta A_0/N - \frac{1}{2}\rho \int d\mathbf{r} \Delta e(r) y_0(r), \quad (30)$$

where now

$$\Delta e(r_{12}) = \langle \exp [-\beta\phi(12)] \rangle - \exp [-\beta\phi_0(r_{12})]. \quad (31)$$

Equation (27), with the hard sphere potential for $\phi_0(r)$, has already been studied [9, 10], but with a different condition for the diameter d_0 , namely [15]

$$\rho \int d\mathbf{r} \Delta e(r) y_0(r) = 0, \quad (32)$$

instead of (28). Equation (28) not only improves the internal consistency of the calculation but was found in a recent paper [20] to improve as well the actual computed results for repulsive potentials. (Equation (29) is of course not relevant for the hard sphere potential.)

Finally, we note that the choice [2-6]

$$\beta\phi_0(r_{12}) = -\ln \langle \exp [-\beta\phi(12)] \rangle, \quad (33)$$

or $\Delta e(r) = 0$, automatically produces thermodynamic consistency within the present approximation for A .

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