Thermodynamic consistency conditions for the reference-hypernetted chain equation with arbitrary molecular potential

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The free energy functional that characterizes the reference-hypernetted chain equation for molecular fluids is variationally minimized, leading to rules for the choice of reference system parameters that guarantee a significant improvement in internal thermodynamic consistency. This work generalizes a successful procedure developed recently for simple fluids.

I. INTRODUCTION

The reference-hypernetted chain (RHNC) integral equation, derived originally as a perturbation approximation for simple fluids,¹ was broadened in its scope by Rosenfeld and Ashcroft,² who treated the reference potential used in the equation as *adjustable*. Recently, it was shown³ that the parameters of the adjustable reference system could be conveniently chosen by minimizing the free energy functional that characterizes the RHNC approximation; this procedure has, further, the remarkable effect of significantly improving the internal consistency of the RHNC thermodynamics. Numerical tests of the method^{3,4} have confirmed that, for simple fluids, the results obtained in this way are in excellent agreement with simulation data for both the thermodynamics and structure. This note deals with a straightforward generalization of the method of Ref. 3 to arbitrary molecular fluids.

II. THEORY

The excess free energy of a molecular fluid at density ρ and temperature $T = 1/k_B \beta$ in RHNC approximation may be written⁵

$$\beta A/N = \beta A_1/N + \beta A_2/N + \beta A_3^{(0)}/N + \beta \Delta A_3/N, \quad (1)$$

where

$$\beta A_1/N = -\frac{1}{2}\rho \int d\mathbf{r} \langle \frac{1}{2}h^2(12) + h(12) - g(12) \times \ln g(12) - g(12)\beta\phi(12) \rangle, \quad (2)$$

$$\beta A_2/N = -\frac{1}{2\rho} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_m \{ \ln \det [I + (-1)^m \rho \tilde{h}_m(k)] - (-1)^m \rho \text{Tr} [\tilde{h}_m(k)] \}, \quad (3)$$

$$\beta A_3^{(0)}/N = -\frac{1}{2}\rho \int d\mathbf{r} \int_0^1 d\xi \left\langle B^{(0)}(12;\xi) \frac{\partial g^{(0)}(12;\xi)}{\partial \xi} \right\rangle, \quad (4)$$

$$\beta \Delta A_3/N = -\frac{1}{2}\rho \int d\mathbf{r} \langle [g(12) - g^{(0)}(12)] B^{(0)}(12) \rangle. \quad (5)$$

In these expressions,

$$g(12) \equiv g(\mathbf{r}_{12}, \omega_1, \omega_2) \quad (6)$$

is the pair distribution function for the molecular potential $\phi(12)$ which, along with the other functions, depends in general on the separation $\mathbf{r}_{12} \equiv \mathbf{r}$ between molecular centers and on the molecular orientations, expressed through the sets of Euler angles ω_1 and ω_2 . The angular brackets denote an

orientational average over ω_1 and ω_2 , while quantities with a superscript zero pertain to the reference system with potential $\phi^{(0)}(12)$. For simplicity, Eq. (3) is written in a notation appropriate to linear molecules,⁶ with $\tilde{h}_m(k)$ an infinite matrix whose elements are $\tilde{h}_{l_1 l_2 m}(k)$, $l_1, l_2 \geq m$, where

$$\tilde{h}(12) = 4\pi \sum_{l_1 l_2 m} \tilde{h}_{l_1 l_2 m}(k) Y_{l_1 m}(\omega_1) Y_{l_2 m}(\omega_2) \quad (7)$$

is the Fourier transform of $h(12) \equiv g(12) - 1$ expanded in spherical harmonics. The final results will not be restricted by this specialization, however.

The defining approximation of the RHNC equation occurs in Eq. (5), all others terms in A being exact. The properties of the reference system are of course assumed known.

Equation (1) is manifestly a functional of $g(12)$, $g^{(0)}(12)$, and $B^{(0)}(12)$, the last of these being the bridge function of the reference system. Proceeding as in Ref. 3, we will require that the free energy be minimal with respect to variations in these functions, which is a fundamental condition of the canonical ensemble. Successive variation of Eqs. (2)–(5) yields

$$\beta \delta A_1/N = -\frac{1}{2}\rho \int d\mathbf{r} \times \langle [h(12) - \ln g(12) - \beta\phi(12)] \delta h(12) \rangle, \quad (8)$$

$$\beta \delta A_2/N = \frac{1}{2}\rho \int d\mathbf{r} \langle C(12) \delta h(12) \rangle, \quad (9)$$

$$\beta \delta A_3^{(0)}/N = -\frac{1}{2}\rho \int d\mathbf{r} \langle B^{(0)}(12) \delta g^{(0)}(12) \rangle, \quad (10)$$

$$\beta \delta \Delta A_3 = -\frac{1}{2}\rho \int d\mathbf{r} \langle \{ [g(12) - g^{(0)}(12)] \times \delta B^{(0)}(12) + B^{(0)}(12) [\delta g(12) - \delta g^{(0)}(12)] \} \rangle. \quad (11)$$

The result in Eq. (9), which introduces the direct correlation function $C(12)$, is easily obtained by proceeding backwards through the steps leading to Eq. (88) in Ref. 6, while Eq. (10) follows from a standard integration by parts technique.⁷ Combining now Eqs. (8)–(11), we have finally

$$\begin{aligned} \beta \delta A/N = & \frac{1}{2}\rho \int d\mathbf{r} \langle [C(12) - h(12) + \ln g(12) \\ & + \beta\phi(12) - B^{(0)}(12)] \delta h(12) \rangle \\ & - \frac{1}{2}\rho \int d\mathbf{r} \langle [g(12) - g^{(0)}(12)] \delta B^{(0)}(12) \rangle. \end{aligned} \quad (12)$$

For Eq. (12) to satisfy the external condition $\delta A = 0$, we must have, first,

$$C(12) = h(12) - \ln g(12) - \beta\phi(12) + B^{(0)}(12), \quad (13)$$

which is the RHNC closure, in which the reference system bridge function $B^{(0)}(12)$ fills in for the exact but unknown $B(12)$. The second condition

$$\rho \int d\mathbf{r} [g(12) - g^{(0)}(12)] \delta B^{(0)}(12) = 0 \quad (14)$$

amounts to a constraint on the reference potential $\phi^{(0)}(12)$. For simple fluids, a typical potential $\phi^{(0)}$ will depend on energy and distance parameters, ϵ_0 and d_0 ; for molecular fluids, the evident extension is additional distance scales $d_1, d_2, \dots, d_n$. (A simple homonuclear molecule, e.g., requires two distance scales.) Equation (14) is satisfied by varying these parameters until

$$\rho \int d\mathbf{r} [g(12) - g^{(0)}(12)] \frac{\partial B^{(0)}(12)}{\partial d_j} = 0 \quad (15)$$

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

$$\rho \int d\mathbf{r} [g(12) - g^{(0)}(12)] \frac{\partial B^{(0)}(12)}{\partial \epsilon_0} = 0. \quad (16)$$

These constraints thus fix the optimum values for the reference system parameters.

As with simple fluids,³ conditions (15) and (16) turn out to be precisely those needed to enforce thermodynamic consistency. This is most easily demonstrated using functional derivatives, after first expressing the integrals of the free energy in terms of $\mathbf{x} = r\rho^{1/3}$. We have then

$$\begin{aligned} \frac{\beta p}{\rho} &= \rho \frac{\partial(\beta A/N)}{\partial \rho} \\ &= \rho \int d\mathbf{x} \left\langle \frac{\delta(\beta A/N)}{\delta h(12)} \frac{dh(12)}{d\rho} + \frac{\delta(\beta A/N)}{\delta g^{(0)}(12)} \frac{dg^{(0)}(12)}{d\rho} \right. \\ &\quad \left. + \frac{\delta(\beta A/N)}{\delta B^{(0)}(12)} \frac{dB^{(0)}(12)}{d\rho} + \frac{\delta(\beta A/N)}{\delta \phi(12)} \frac{d\phi(12)}{d\rho} \right\rangle \\ &= \rho \int d\mathbf{r} \left\langle \frac{1}{2} [g(12) - g^{(0)}(12)] \right. \\ &\quad \times \left[\frac{1}{3} r \frac{\partial B^{(0)}(12)}{\partial r} - \rho \frac{\partial B^{(0)}(12)}{\partial \rho} \right] \\ &\quad \left. - \frac{1}{6} g(12) \beta r \frac{\partial \phi(12)}{\partial r} \right\rangle, \end{aligned} \quad (17)$$

where the first three functional derivatives in Eq. (17) are obtained from Eq. (12) and the last one is evident from Eqs. (1) and (2). The derivative of $B^{(0)}(12)$ with respect to ρ yields

$$\begin{aligned} \rho \frac{dB^{(0)}(12)}{d\rho} &= \rho \frac{d}{d\rho} B^{(0)}(\mathbf{x}\rho^{1/3}, \omega_1, \omega_2; \rho, \beta, d_0, \dots, d_n, \epsilon_0) \\ &= -\frac{1}{3} r \frac{\partial B^{(0)}(12)}{\partial r} + \rho \frac{\partial B^{(0)}(12)}{\partial \rho} \end{aligned} \quad (18)$$

in the second equality of Eq. (17). But $B^{(0)}(12)$ is more generally a *dimensionless* function of distances and could be expressed, e.g., in the form $f(r/d_0; \rho d_0^3, d_1/d_0, \dots, d_n/d_0)$, so that

$$d_0 \frac{\partial B^{(0)}}{\partial d_0} = -r \frac{\partial B^{(0)}}{\partial r} + 3\rho \frac{\partial B^{(0)}}{\partial \rho} - \sum_{j=1}^n d_j \frac{\partial B^{(0)}}{\partial d_j}, \quad (19)$$

and Eq. (17) finally becomes

$$\begin{aligned} \frac{\beta p}{\rho} &= -\frac{1}{6} \rho \int d\mathbf{r} \left\langle g(12) \beta r \frac{\partial \phi(12)}{\partial r} \right. \\ &\quad \left. + [g(12) - g^{(0)}(12)] \sum_{j=0}^n d_j \frac{\partial B^{(0)}(12)}{\partial d_j} \right\rangle \\ &= -\frac{1}{6} \rho \int d\mathbf{r} \left\langle g(12) \beta r \frac{\partial \phi(12)}{\partial r} \right\rangle, \end{aligned} \quad (20)$$

by virtue of conditions (15). It is easy to show similarly that

$$\begin{aligned} \frac{\beta U}{N} &= \beta \frac{\partial(\beta A/N)}{\partial \beta} \\ &= \frac{1}{2} \rho \int d\mathbf{r} \left\langle g(12) \beta \phi(12) - [g(12) - g^{(0)}(12)] \epsilon_0 \right. \\ &\quad \left. \times \frac{\partial B^{(0)}(12)}{\partial \epsilon_0} \right\rangle \\ &= \frac{1}{2} \rho \int d\mathbf{r} \langle g(12) \beta \phi(12) \rangle, \end{aligned} \quad (21)$$

where we have used the fact that $B^{(0)}(12)$ is a dimensionless function of $\beta\epsilon_0$ and have imposed condition (16).

Thus, differentiation of the free energy yields, by construction, the same results for pressure and energy as do the usual quadratures, an internal consistency that is generally lacking in approximate theories of fluids.

If for simplicity an isotropic potential were chosen as the reference system, Eqs. (15) and (16) would reduce to

$$\rho \int d\mathbf{r} [\langle g(12) \rangle - g^{(0)}(r)] \frac{\partial B^{(0)}(r)}{\partial d_0} = 0, \quad (22)$$

$$\rho \int d\mathbf{r} [\langle g(12) \rangle - g^{(0)}(r)] \frac{\partial B^{(0)}(r)}{\partial \epsilon_0} = 0, \quad (23)$$

which involve only the center-to-center part of the molecular distribution function.

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