

Sphericalization of nonspherical interactions

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A density and temperature-independent spherically symmetric reference potential is constructed for an interacting classical fluid of nonspherical molecules. It annuls the first order correction to the free energy and, in special cases, the second as well. The potential is a limiting form of that used successfully for N_2 by Shaw *et al.*, and reproduces numerically the Y_4 approximation of Barboy and Gelbart for homonuclear dumbbell molecules.

I. INTRODUCTION

Equilibrium classical statistical mechanics of simple bulk fluids is a well-tilled field. An obvious extension is that of molecules with internal degrees of freedom, among which rigid rotations assume particular importance. These become meaningful when the molecule changes its aspect under such a rotation, i. e., is nonspherical. The increase in complexity resulting from the consequent use of angle-dependent interactions is not trivial, and even minor computations such as those of the low order virial coefficients become major undertakings.¹ Computer simulation of such fluids is much more burdensome, and analytic approximations harder to justify and harder to carry out.

But much of the real world is modeled by such fluids, and a good deal of effort has gone into treating them. A particularly appealing viewpoint is that of starting with a reference spherically symmetric molecular fluid, all of whose properties are reliably known, and then turning on the asphericity perturbationally.² Shaw, Johnson, and Holian³ have recently made the observation that for a realistic N_2 model that they consider, there exists a spherical reference system remarkably independent of density and temperature which is such an effective reference that the corresponding free energy reproduces that of the desired fluid to very high accuracy. We would like to point out in this note that their result may be simplified, that it then amalgamates several approaches, and that in special cases it may be extended to higher order without difficulty.

II. REFERENCE POTENTIAL

To start with, we consider a fluid with spherically symmetric interaction $\phi_0(r_{12})$ and canonical (Helmholtz) free energy F_0 . We then convert to the desired potential, say $\phi(r_{12}, \omega_1, \omega_2)$, for rotationally asymmetric molecules via a sequence $\phi_\gamma(r_{12}, \omega_1, \omega_2)$ which without loss of generality can be taken as

$$\phi_\gamma(r_{12}, \omega_1, \omega_2) = \phi_0(r_{12}) + \gamma \Delta_\gamma(r_{12}, \omega_1, \omega_2),$$

where

$$\Delta_1(r_{12}, \omega_1, \omega_2) = \phi(r_{12}, \omega_1, \omega_2) - \phi_0(r_{12}). \quad (1)$$

Since⁴

$$\frac{\partial F}{\partial \gamma} = \frac{1}{2} \int n_{2\gamma}(12) \frac{\partial \phi_\gamma(12)}{\partial \gamma} d1 d2, \quad (2)$$

this means that there will be no first order change in F_0 if

$$\int n_{20}(r_{12}) \Delta_0(r_{12}, \omega_1, \omega_2) d\omega_1 d\omega_2 dr_{12} = 0. \quad (3)$$

In fact, it is not even necessary to know the reference fluid pair distribution $n_{20}(r_{12})$ if

$$\int \Delta_0(r_{12}, \omega_1, \omega_2) d\omega_1 d\omega_2 = 0 \quad (4)$$

is satisfied. This criterion is not new. The obvious choice⁵

$$\phi_\gamma(12) = \phi_0(12) + \gamma [\phi(12) - \phi_0(12)] \quad (5)$$

identifies $\phi_0(12)$ as the mean over angles of $\phi(12)$. A more reasonable choice might be⁶

$$\exp[-\beta \phi_\gamma(12)] = \exp[-\beta \phi_0(12)] + \gamma (\exp[-\beta \phi(12)] - \exp[-\beta \phi_0(12)]), \quad (6)$$

so that the Boltzmann factor of ϕ_0 is the average of that of ϕ . But there is no obvious *a priori* way of distinguishing the various possibilities.

Our first point then is that one may ask for a formulation (4) such that $\Delta_0(r_{12}, \omega_1, \omega_2) = \Delta_0[\phi(12), \phi_0(12)]$ is unaltered under any 1:1 functional change: $\Delta_0[\phi(12), \phi_0(12)] = \Delta_0[f[\phi(12)], f[\phi_0(12)]]$, thereby making obsolete the question of the optimal function of ϕ to use. By taking $f(x) = \lambda x$ and then $f(x) = x^k$, $k \rightarrow \infty$, it is easily seen that, to within a constant multiple, Δ_0 must take the form

$$\Delta_0(\phi, \phi_0) = \text{sgn}(\phi - \phi_0), \quad (7)$$

with the accompanying criterion

$$\int \text{sgn}[\phi(r_{12}, \omega_1, \omega_2) - \phi_0(r_{12})] d\omega_1 d\omega_2 = 0. \quad (8)$$

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Thus, $\phi_0(r_{12})$ is no longer the mean of $\phi(r_{12}, \omega_1, \omega_2)$ over angle but rather the *median* interaction at each value of r_{12} . Indeed, one sees that Eq. (7) corresponds to the extreme limit, $B \rightarrow \infty$, of

$$\Delta_0(x) = \sinh^{-1} Bx, \quad x = \phi_1 - \phi_0, \quad (9)$$

the function used by Shaw *et al.*,³ who also observed numerically improved results as the parameter B grew large. We conclude that their excellent agreement with Monte Carlo simulations for N_2 is shared by Eq. (8).

III. DUMBBELL MODEL

Another simple check can be made. Suppose that each molecule is hard but nonspherical. Then the median $\phi_0(r_{12})$ of Eq. (8) is either 0 or ∞ , with a cross-over when $\phi(r_{12}, \omega_1, \omega_2)$ at fixed r_{12} is 0 half the time, ∞ half the time. Hence if the separation $r(\omega_1, \omega_2)$ at contact at fixed ω_1, ω_2 is uniquely defined (and it will be unless the bodies are highly nonconvex), the diameter R_0 of the reference hard sphere potential is given by

$$\int_{R_0 > r(\omega_1, \omega_2)} d\omega_1 d\omega_2 = \int_{R_0 < r(\omega_1, \omega_2)} d\omega_1 d\omega_2 = \frac{1}{2} \int d\omega_1 d\omega_2 \quad (10)$$

and the effective volume of course by

$$v_0 = \pi R_0^3 / 6. \quad (11)$$

Equation (10) is equivalent to a RAM potential⁶ hardened at the radius at which the Boltzmann factor becomes $\frac{1}{2}$. With no further corrections, the predicted equation of state would now be

$$\beta P / \rho = \Psi_{hc}(v_0 \rho), \quad (12)$$

where Ψ_{hc} is the $\beta P / \rho$ ratio for hard cores, a function of the product $v_0 \rho$ alone.

Consider for example the case of homonuclear dumbbell-shaped molecules, pairs of (overlapping) spheres of diameter a with centers separated by λa . Many simulations and approximations to such fluids have appeared in the literature, and we will focus on results reported by Barboy and Gelbart⁷ for the special values $\lambda = 0.6$, $\lambda = 0.2$. A direct numerical computation using Eq. (10) shows that

$$\begin{aligned} \lambda = 0.6: \quad v_0 &= 1.0056 a^3, \\ \lambda = 0.2: \quad v_0 &= 0.6846 a^3, \end{aligned} \quad (13)$$

(compared to the corresponding molecular volumes $v_a = 0.9383 a^3$, $0.6786 a^3$). Insertion into Eq. (12), using standard hard sphere equation of state data⁸ produces equations of state that are graphically indistinguishable from the numerically effective Y_4 approximation of Barboy and Gelbart.⁷ It must be pointed out however that, like RISA,⁹ this is a medium density approximation: the normalized second virial coefficient $B_2^* = B_2/v_a$ predicted by the low density behavior of Eq. (12) is obtained from the derivative of Eq. (12),

$$B_2^* = 4v_0/v_a, \quad (14)$$

and is not very accurate at all.

IV. FURTHER CORRECTIONS

Finally, let us examine briefly the second correction to the free energy, obtained from⁴

$$\begin{aligned} \frac{\partial^2 F}{\partial \gamma^2} &= \frac{1}{2} \int \frac{\partial^2 \phi_\gamma(12)}{\partial \gamma^2} n_{2\gamma}(12) d1 d2 - \beta \int \left(\frac{\partial \phi_\gamma(12)}{\partial \gamma} \right)^2 \\ &\times n_{2\gamma}(12) d1 d2 - \frac{1}{2} \beta \int \frac{\partial \phi_\gamma(12)}{\partial \gamma} \frac{\partial \phi_\gamma(34)}{\partial \gamma} \\ &\times [n_{4\gamma}(1234) - n_{2\gamma}(12)n_{2\gamma}(34)] d1 d2 d3 d4 \\ &- 2\beta \int \frac{\partial \phi_\gamma(12)}{\partial \gamma} \frac{\partial \phi_\gamma(13)}{\partial \gamma} n_3(123) d1 d2 d3. \end{aligned} \quad (15)$$

If Eq. (4) is retained, Eq. (15) cannot in general be made to vanish at $\gamma = 0$ independently of n_{20} , n_{30} , n_{40} . The requirements are now that in addition

$$\begin{aligned} \int \Delta_0(r_{12}, \omega_1, \omega_2) d\omega_2 &= 0, \\ \int [\Delta'_0(r_{12}, \omega_1, \omega_2) - \beta \Delta_0(r_{12}, \omega_1, \omega_2)^2] d\omega_1 d\omega_2 &= 0, \end{aligned} \quad (16)$$

where $\Delta'_0 = \partial \Delta / \partial \gamma |_{\gamma=0}$. However, the first of these is in fact implied by Eq. (4) whenever the interaction takes the form

$$\phi(r_{12}, \omega_1, \omega_2), \quad (17)$$

and the second, while affecting the computation of local quantities such as distributions, is invisible in free energy calculations. Moreover, it is comforting to note that even a form as simple as

$$\beta \Delta_\gamma(\phi - \phi_0) = (1 - \gamma) \operatorname{sgn}(\phi - \phi_0) + [\beta \gamma(\phi - \phi_0) + 1 - \gamma] \gamma \quad (18)$$

is consistent with Eqs. (1) and (8), and the second of Eq. (16). A Boltzmann factor version of Eq. (18) is readily obtained.

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