

Equivalent potentials for equations of state for fluids of nonspherical molecules

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We analyze the extent to which the equation of state and other thermodynamic properties of systems of hard nonspherical molecules can be obtained from a density independent hard sphere reference system. We conclude that the median and Barker–Henderson prescriptions effectively reproduce all data now available. We discuss the motivation for these two formulations in detail.

I. INTRODUCTION

The hard sphere fluid (HSF) is *the* basic reference system for classical equilibrium fluids.¹ The HSF properties are geometrically determined, independent of temperature, and a function only of the fluid density in sphere volume units

$$\eta = (\pi/6) R^3 \rho, \quad (1.1)$$

where R is the sphere diameter and $\rho = N/V$ is the particle number density. The usefulness of the HSF as a reference system is due in no small part to the excellent analytical approximations available for its structure function and equation of state from the solution of the Percus–Yevick (PY) equation and improvements thereon. The best of these, for $\eta \leq 0.5$, is provided by the Carnahan–Starling formula:

$$\frac{\beta P}{\rho} = \psi_{cs}(\eta) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (1.2)$$

In this paper, we examine the extent to which the conceptual simplicity of the HSF is retained when the component molecules remain hard but are instead nonspherical. In particular, we inquire whether the equation of state, and hence other thermodynamic properties, can be reasonably represented over a “wide range” of densities by an HSF with a density independent equivalent diameter R_{eqv} , i.e.,

$$(\beta P)/\rho = \psi_{cs}(\eta_{eqv}), \quad (1.3)$$

where

$$\eta_{eqv} = (\pi/6) R_{eqv}^3 \rho, \quad (1.4)$$

and where R_{eqv} is to be in some sense geometrically determined. We focus on the method of finding an optimal constant, and conclude that there are at least two prescriptions that effectively reproduce all data now available.

The next section will be devoted to an analysis of one of these two constructions as applied to two classes of hard nonspherical molecules. Results will be presented on the resultant equation of state and pair distribution functions. Section III will be a review of reference fluid perturbation theory.

II. EFFECTIVE SPHERICAL REFERENCE SYSTEM

There exists now a substantial body of Monte Carlo simulation data on uniform fluids of hard nonspherical molecules.^{2–4} Most of the data is for the basic dumbbell and spherocylinder models for homonuclear molecules with a variety of eccentricities γ , i.e., the ratio of the center-to-center distance to the diameter of the two spheres involved (Fig. 1). We will normalize by choosing the sphere diameter to be unity.

In light of the discussion above, the obvious way to present the data is in terms of that hard sphere diameter which, at a given density, reproduces the observed pressure of the system in question. If we introduce the inverse Carna-

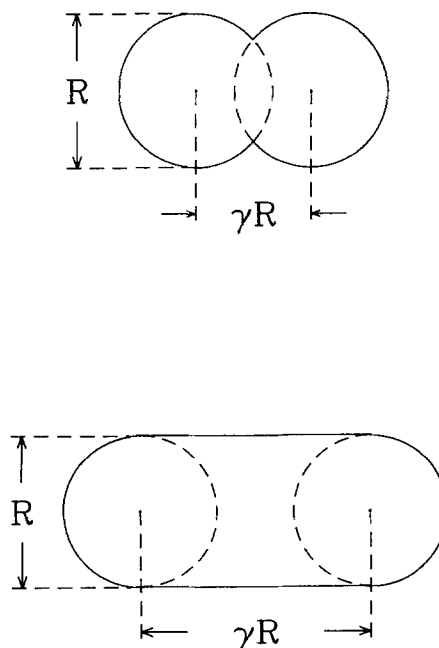


FIG. 1. Geometries of the two basic molecular configurations, dumbbells and spherocylinders.

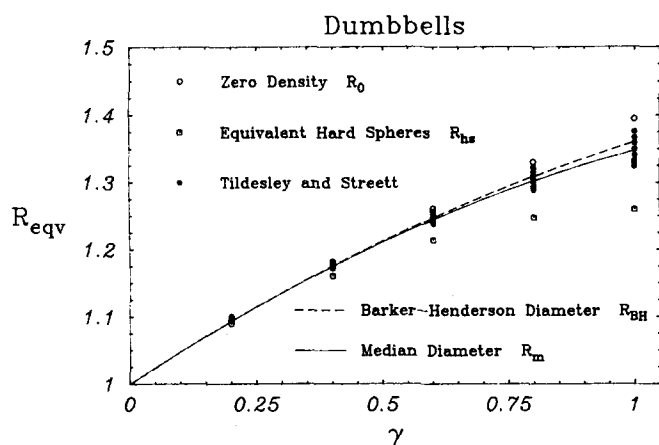


FIG. 2. Equivalent hard sphere diameters $R_{\text{eqv}}(\rho; \gamma)$ for dumbbells. Monte Carlo data is taken from Tildesley and Streett (Ref. 2). Also shown are the zero density and equivalent volume diameters, R_0 and R_{hs} , which are observed to bracket the simulation results. The solid curve is the median diameter R_m given by Eq. (2.9) and the dashed curve is the Barker-Henderson diameter R_{BH} , given by Eq. (3.27).

han-Starling function $\eta = \psi_{\text{cs}}^{-1}(\beta P / \rho)$, then, according to Eqs. (1.3) and (1.4),

$$R_{\text{eqv}}(\rho) = \left[\frac{6}{\pi \rho} \psi_{\text{cs}}^{-1}(\beta P / \rho) \right]^{1/3}. \quad (2.1)$$

In Figs. 2 and 3, we have plotted $R_{\text{eqv}}(\rho; \gamma)$ as a function of density and eccentricity for these two basic molecular shapes.^{2,3} The spread in values at each γ is remarkably small, with the nonconvex dumbbells having more dispersion, as might be anticipated. In all cases, R_{eqv} appears to decrease monotonically but very slowly as the density ρ increases from zero. Thus, the introduction of a density independent $R_{\text{eqv}, \gamma}$ is a sensible leading approximation.

Given the tight clustering of the data, one density independent choice for $R_{\text{eqv}, \gamma}$ which immediately suggests itself is the zero density value of R_{eqv} . From the virial expansion for the pressure and the expression for ψ_{cs}^{-1} one has

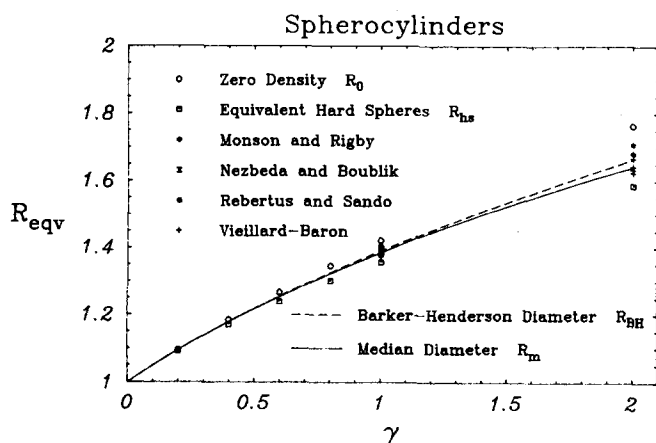


FIG. 3. Equivalent hard sphere diameters $R_{\text{eqv}}(\rho; \gamma)$ for spherocylinders. Monte Carlo data is from several sources (Ref. 3). Also shown are the zero density and equivalent volume diameters, R_0 and R_{hs} , which are observed to bracket the simulation results. The solid curve is the median diameter R_m given by Eq. (2.9) and the dashed curve is the Barker-Henderson diameter R_{BH} , given by Eq. (3.27).

$$R_0 = \left(\frac{3}{2\pi} B_2 \right)^{1/3}, \quad (2.2)$$

where the second virial coefficient B_2 is just half the mean excluded volume of a pair of molecules:

$$B_2 = \frac{1}{2\Omega^2} \int \epsilon [R(\omega_1, \omega_2) - r] d^3r d\omega_1 d\omega_2. \quad (2.3)$$

Here, $\Omega = 4\pi$, $\epsilon(x)$ is a Heaviside unit step function, and $R(\omega_1, \omega_2)$ is the distance of closest approach for two molecules at angular configurations ω_1 and ω_2 . R_0 has been indicated by open circles in Figs. 2 and 3 and serves as an upper bound to $R_{\text{eqv}}(\rho)$.

A simpler but perhaps less well motivated geometric characterization of R_{eqv} might be the diameter of a sphere whose volume is the same as that of the nonspherical body under study⁵:

$$R_{\text{hs}} = \left(\frac{6V}{\pi} \right)^{1/3} = \left\{ \frac{6}{\pi} \int \epsilon [r(\omega) - r] r^2 dr d\omega \right\}^{1/3}. \quad (2.4)$$

Here, V is the volume of the body under study, and $r(\omega)$ is its radius along the direction ω . One would expect this diameter to be more relevant at high densities, and indeed R_{hs} uniformly lies at the high density end of the simulation data (open squares in Figs. 2 and 3).

The estimates R_{hs} and R_0 are related for convex bodies by the second virial expression⁶

$$B_2 = 4V + (r_M S - 3V), \quad (2.5)$$

where S is the surface area and r_M the mean radius of curvature of the body. Thus

$$R_0 = \left[R_{\text{hs}}^3 + \frac{3}{2\pi} (r_M S - 3V) \right]^{1/3}. \quad (2.6)$$

Since $r_M > 3V/S$, it follows that $R_{\text{hs}} < R_0$.

Building upon a complex analysis of Shaw, Johnson, and Holian,⁷ Lebowitz and Percus⁸ have suggested the use of the median reference potential $\phi_0(r_{12})$, which is given by

$$\phi_0(r_{12}) = \text{Med}_{\omega_1, \omega_2} [\phi(r_{12}, \omega_1, \omega_2)]. \quad (2.7)$$

Here, $\phi(r_{12}, \omega_1, \omega_2)$ is the true molecular potential at intermolecular separation r_{12} and angular configurations ω_1 and ω_2 of the molecules. The motivation for this choice will be treated in Sec. III, but we note here that this prescription is particularly appropriate for hard interactions in that it preserves the hard, discontinuous nature of the potential. An equivalent bounded form of Eq. (2.7) which is generally more convenient is

$$\exp[-\beta\phi_0(r_{12})] = \text{Med}_{\omega_1, \omega_2} \{ \exp[-\beta\phi(r_{12}, \omega_1, \omega_2)] \}. \quad (2.8)$$

This form allows one to conclude at once that if ϕ is a hard potential, then ϕ_0 represents a spherical hard core of diameter R_m satisfying

$$\frac{1}{\Omega^2} \int \epsilon [R(\omega_1, \omega_2) - R_m] d\omega_1 d\omega_2 = \frac{1}{2}. \quad (2.9)$$

This median diameter for both hard dumbbells and spherocylinders is indicated by the solid curves in Figs. 2 and 3. It is seen to pass through the centers of the clusters of machine data points in each case and thus offers the possibility of being a particularly good leading approximation.

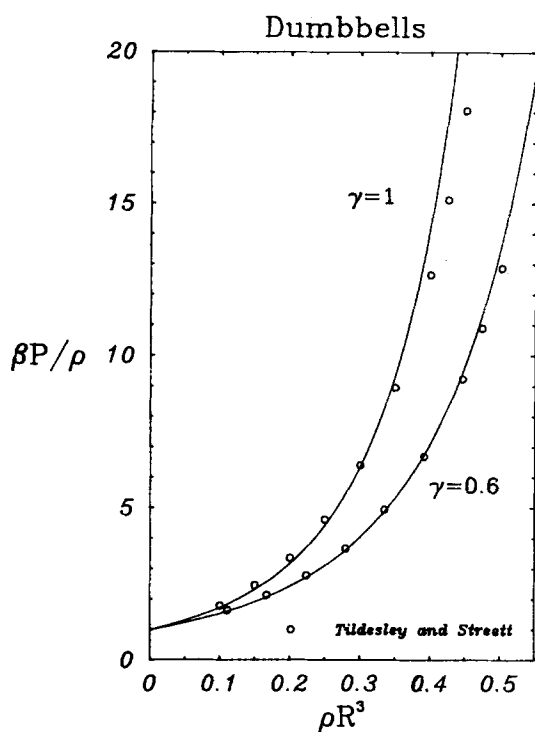


FIG. 4. Dumbbell equation of state for $\gamma = 0.6$ and $\gamma = 1$. Monte Carlo data is taken from Tildesley and Streett (Ref. 2). The solid curves are the Carnahan-Starling equation of state for hard spheres of diameter R_m .

The dashed curves in Figs. 2 and 3 represent an equivalent hard sphere radius due independently to Bellemans⁹ and to Barker and Henderson¹⁰ who extended an earlier suggestion by Rowlinson.¹¹ This formulation will be discussed in detail in Sec. III.

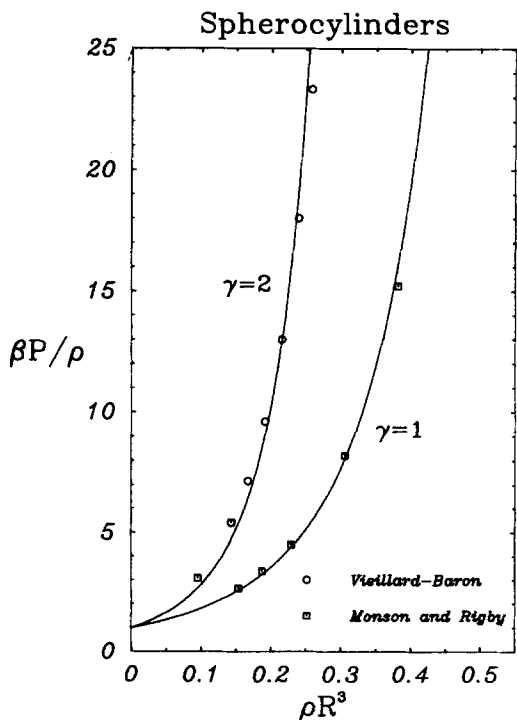


FIG. 5. Spherocylinder equation of state for $\gamma = 1$ and $\gamma = 2$. Monte Carlo data is taken from Monson and Rigby and Viellard-Baron (Ref. 3). The solid curves are the Carnahan-Starling equation of state for hard spheres of diameter R_m .

A. Median equation of state

A more direct evaluation of the validity the median potential is a comparison of the simulation equation of state with that predicted by the Carnahan-Starling equation for hard spheres of diameter R_m .

This is done for four separate systems in Figs. 4 and 5: dumbbells with $\gamma = 0.6$ and $\gamma = 1$,² and spherocylinders with $\gamma = 1$ and $\gamma = 2$.³ In all four of these systems the median reference system reproduces the equation of state to reasonable accuracy at all reported values of the density. Even in the stringent case of $\gamma = 2$ (a 3 : 1 aspect ratio) excellent agreement is observed, particularly at high density.

Since the above comparison is so favorable, it is natural to ask whether a further correction can be applied to produce greater accuracy. Alternatively, one may try to apply the median prescription in a somewhat more sophisticated way to improve the equation of state. One way of doing this is to use the relative insensitivity of the function $y(1,2) = g(1,2) \exp[\beta\phi(1,2)]$ (1 and 2, respectively, denote all the degrees of freedom of molecules 1 and 2) to changes of the potential, a point employed many times in the literature.¹² By approximating $y(1,2)$ by $y_0(r_{12})$ of the spherical reference system, one may obtain an approximation to the pair distribution functions $g(1,2)$ given by

$$g(1,2) = y_0(r_{12}) \exp[-\beta\phi(1,2)]. \quad (2.10)$$

There are two obvious ways of using the presumed relation (2.10) to obtain thermodynamics. First, one may consider the compressibility relation,

$$\frac{\partial p}{\partial \beta P} = 1 + \frac{\rho}{\Omega^2} \int [g(1,2) - 1] d^3 r_{12} d\omega_1 d\omega_2. \quad (2.11)$$

This is most conveniently written as

$$\frac{\partial p}{\partial \beta P} = \frac{\partial p}{\partial \beta P} \Big|_{\text{ref}} + \frac{\rho}{\Omega^2} \int [y_0(r_{12}) \exp[-\beta\phi(1,2)] - g_0(r_{12})] d^3 r_{12} d\omega_1 d\omega_2, \quad (2.12)$$

since the integrand now vanishes both outside the maximum and inside the minimum diameters of interaction. There remains the question of the proper form for y_0 to insert, and many options are available. Strangely, the best seems to be that of the PY approximation.¹³

Inserting the PY forms for y_0 and g_0 in Eq. (2.12) and integrating the resulting pressure-density relation, one obtains results which, while not bad, are generally poorer than those obtained by direct use of the reference hard core system. In the numerical procedure, one notes that the correction, which is small, is the result of near cancellation of large positive and negative parts and is thus very sensitive to the approximation used.

Similar comments apply to the second obvious choice, that of the virial theorem:

$$\frac{\beta P}{\rho} = 1 - \frac{\beta p}{6\Omega^2} \int g(1,2) r_{12} \cdot \nabla_{12} \phi(1,2) d^3 r_{12} d\omega_1 d\omega_2, \quad (2.13)$$

which is now approximated as

$$\begin{aligned}
\frac{\beta P}{\rho} &= 1 + \frac{\rho}{6\Omega^2} \int y_0(r_{12}) r_{12} \cdot \nabla_{12} \\
&\quad \times \exp[-\beta\phi(1,2)] d^3r_{12} d\omega_1 d\omega_2 \\
&= 1 + \frac{4\pi\rho}{6\Omega^2} \int R^3(\omega_1, \omega_2) y_0[R(\omega_1, \omega_2)] d\omega_1 d\omega_2 \\
&= \left. \frac{\beta P}{\rho} \right|_{\text{ref}} + \frac{4\pi\rho}{6\Omega^2} \int \{R^3(\omega_1, \omega_2) y_0[R(\omega_1, \omega_2)] \\
&\quad - R_m^3 y_0(R_m)\} d\omega_1 d\omega_2. \quad (2.14)
\end{aligned}$$

Again the choice of the PY y_0 yields the closest results, the cancellations in the correction term are very large, and the equation of state is not superior to that of the bare reference system.

We conclude that coupling another first order approximation, $y = y_0$, to the first order free energy approximation which gave rise to the original prescription (see Sec. III) is ineffective as a correction procedure. One must go to the next order in the free energy, with the obvious attendant difficulties, including its realistic density dependent corrections.

B. Angular correlations

The approximation (2.10) does have the virtue of introducing angular correlations into the leading order, and these are after all the hallmark of nonspherical interactions. Simulation data on such correlations is notably more sparse than that on thermodynamics¹⁴ and is generally presented in the form of the joint spherical harmonics¹⁵

$$g(1,2) = \frac{1}{4\pi} \sum g_{ll'm}(r_{12}) Y_{lm}(\omega_1) Y_{l'-m}(\omega_2). \quad (2.15)$$

Within the context of the approximation (2.10), the spherical harmonic coefficients $g_{ll'm}$ are given by

$$\begin{aligned}
g_{ll'm}(r_{12}) &= 4\pi y_0(r_{12}) \int \exp[-\beta\phi(1,2)] \\
&\quad \times Y_{lm}^*(\omega_1) Y_{l'-m}^*(\omega_2) d\omega_1 d\omega_2 \\
&= 4\pi y_0(r_{12}) e_{ll'm}(r_{12}). \quad (2.16)
\end{aligned}$$

Apart from the choice of reference system, Eq. (2.16) is identical with the lowest order RAM perturbation theory result, which is known to give reasonable, though not extremely accurate, results.¹⁶ We note that the reduced pair correlation function $g^*(1,2) = g(1,2)/g_{000}(r_{12})$ is in this approximation density independent. The reduced spherical harmonic coefficients are given by

$$g_{ll'm}^*(r_{12}) = \frac{e_{ll'm}(r_{12})}{e_{000}(r_{12})}, \quad (2.17)$$

and thus cannot be expected to produce realistic angular correlations over a wide range of densities.

III. REFERENCE FLUID PERTURBATION THEORY

A well established technique for selecting model fluids to simulate more realistic ones involves introducing a transformation from model to reality, demanding that leading order corrections vanish under this transformation. Particu-

larly convenient for assessing corrections in a canonical ensemble is the Helmholtz free energy F , which has the basic property that, under a change $\delta\phi$ in the potential energy,

$$\delta F = \langle \delta\phi \rangle. \quad (3.1)$$

In particular, for a change in a pair potential $\delta\phi(1,2)$,

$$\delta F = \frac{1}{2} \int n_2(1,2) \delta\phi(1,2) d1 d2, \quad (3.2)$$

where $n_2(1,2)$ is the pair distribution, and we have left unspecified the space to which the arguments 1 and 2 refer. A completely equivalent expression is

$$\begin{aligned}
-\beta\delta F &= \frac{1}{2} \int n_2(1,2) \exp[\beta\phi(1,2)] \\
&\quad \times \delta \exp[-\beta\phi(1,2)] d1 d2. \quad (3.3)
\end{aligned}$$

Equations (3.2) and (3.3) can both be regarded as beginnings of perturbation series, illustrating the fact that a perturbation series is not at all a unique concept. If one wants to go from a potential ϕ_0 to a potential ϕ , any path will do. This idea is illustrated in Fig. 6. In particular, the initial direction or first order perturbation is mathematically, and to some extent physically, arbitrary, as are initial higher derivatives. Intelligent physical input is, however, responsible for some of the more successful approximation methods in the area of simple fluids, and we would like to understand how fluids of hard nonspherical molecules can be similarly treated.

The object then is to arrive at a system with a nonspherical interaction potential $\phi(1,2) = \phi(r_{12}, \omega_1, \omega_2)$, where ω denotes the multidimensional internal state of a molecule, by perturbing a reference fluid with a spherically symmetric potential $\phi_0(1,2) = \phi(r_{12})$. This can be done quite generally via the path

$$\phi_\lambda(1,2) = \phi_0(r_{12}) + \lambda\Delta_\lambda(1,2), \quad 0 \leq \lambda \leq 1, \quad (3.4)$$

with $\phi_1(1,2) = \phi(1,2)$. This results, for example, in a first order free energy change

$$\Delta F = \frac{\lambda}{2} \int n_{2_0}(r_{12}) \Delta_0(1,2; \phi, \phi_0) d1 d2, \quad (3.5)$$

where n_{2_0} is the reference fluid pair distribution and

$$\Delta_0(1,2; \phi, \phi_0) = \left. \frac{\partial \phi_\lambda(1,2)}{\partial \lambda} \right|_{\lambda=0}, \quad (3.6)$$

and we have explicitly identified the ϕ, ϕ_0 dependence of Δ .

The observation has been made many times that the correction ΔF can be annulled if

$$\int \Delta_0(r_{12}, \omega_1, \omega_2) d\omega_1 d\omega_2 = 0, \quad (3.7)$$

independently of any knowledge of $n_{2_0}(r_{12})$.¹⁷ Equation (3.2) then corresponds to choosing

$$\Delta_0(1,2) = \phi(r_{12}, \omega_1, \omega_2) - \phi_0(r_{12}), \quad (3.8)$$

and is totally inappropriate for hard potentials. On the other hand, Eq. (3.3) suggests the choice

$$\beta\Delta_0(1,2) = \exp[-\beta\phi(r_{12}, \omega_1, \omega_2)] - \exp[-\beta\phi_0(r_{12})]. \quad (3.9)$$

Equation (3.7) then gives the form of the reference potential as

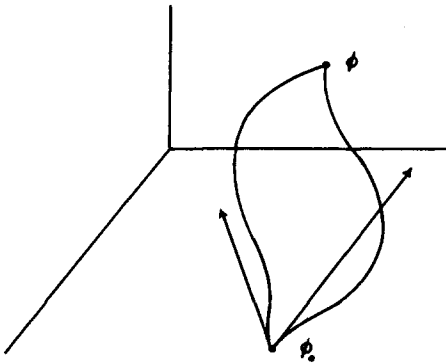


FIG. 6. Illustration of two paths from a potential ϕ_0 to a potential ϕ in an appropriate function space.

$$\exp[-\beta\phi_0(r_{12})] = \frac{1}{\Omega^2} \int \exp[-\beta\phi(r_{12}, \omega_1, \omega_2)] d\omega_1 d\omega_2, \quad (3.10)$$

where $\Omega = 4\pi$ or, more generally, is the volume of the internal space. The RAM¹⁸ potential defined by Eq. (3.10) does not give bad results, but it certainly does not convert hard potentials into hard spheres.

The median potential introduced in Sec. II, for which

$$\beta\Delta_0(1,2) = \text{sgn}[\phi(1,2) - \phi_0(r_{12})], \quad (3.11)$$

and

$$\phi_0(r_{12}) = \text{Med}_{\omega_1, \omega_2}[\phi(r_{12}, \omega_1, \omega_2)], \quad (2.7)$$

has the property that if f is any invertible function of ϕ , then $\text{Med}[f(\phi)] = f[\text{Med}(\phi)]$. This makes the median prescription particularly useful for hard interactions [cf. Eqs. (2.8) and (2.9)].

A. Other reference fluids

Although the median prescription offered by Eqs. (2.7) and (3.11) is a bit unusual, specific paths from ϕ_0 to ϕ may be constructed. For example, a quadratic fit to the boundary conditions on ϕ_λ and $\partial\phi_\lambda/\partial\lambda$ gives

$$\phi_\lambda(1,2) = (1-\lambda^2)\phi_0(r_{12}) + \lambda(1-\lambda)\Delta_0(1,2) + \lambda^2\phi(1,2). \quad (3.12)$$

More traditional paths are available however. One of the simplest is a generalization of an extension by Barker and Henderson¹⁰ of an earlier suggestion by Rowlinson.¹¹ In this formalism the spherical reference potential curve ϕ_0 is moved horizontally at each angular configuration to its desired location on ϕ :

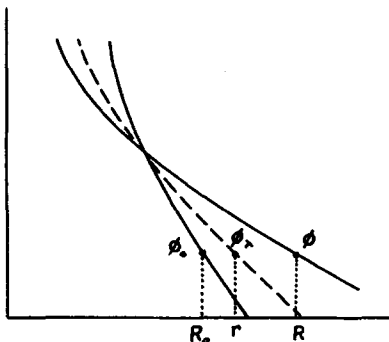


FIG. 7. Illustration of the parametrization of ϕ_λ defined by Eq. (3.13).

$$\phi_0(R_0) = \phi_\lambda(r) = \phi(R), \quad (3.13)$$

as shown in Fig. 7. Note that R_0 , r , and R are all variables and we have suppressed the explicit angular dependence. Thus, it is the inverse potential that is perturbed:

$$R_\lambda(\phi) = R_0(\phi) + \lambda [R(\phi) - R_0(\phi)]. \quad (3.14)$$

Combining Eqs. (3.13) and (3.14) yields

$$\begin{aligned} r &= R_\lambda[\phi_\lambda(r)] \\ &= R_0[\phi_\lambda(r)] + \lambda \{R[\phi_\lambda(r)] - R_0[\phi_\lambda(r)]\}. \end{aligned} \quad (3.15)$$

Applying $\partial/\partial\lambda$ to Eq. (3.15) and setting $\lambda = 0$ (we denote ordinary differentiation by a prime),

$$0 = R'_0[\phi_0(r)] \frac{\partial\phi_\lambda(r)}{\partial\lambda} \Big|_{\lambda=0} + R[\phi_0(r)] - R_0[\phi_0(r)], \quad (3.16)$$

or

$$\frac{\partial\phi_\lambda(r)}{\partial\lambda} \Big|_{\lambda=0} = \frac{R[\phi_0(r)] - r}{\partial r/\partial\phi_0} = \{\phi^{-1}[\phi_0(r)] - r\} \phi'_0(r). \quad (3.17)$$

The perturbation to the free energy then vanishes if

$$\int n_{2_0}(r) \{\phi_{\omega_1, \omega_2}^{-1}[\phi_0(r)] - r\} \phi'_0(r) d^3r d\omega_1 d\omega_2 = 0. \quad (3.18)$$

There are two limits in which explicit knowledge of the reference fluid pair distribution n_{2_0} is not needed. First, we can require the angular integral to vanish at each value of r :

$$\int \{\phi_{\omega_1, \omega_2}^{-1}[\phi_0(r)] - r\} d\omega_1 d\omega_2 = 0, \quad (3.19)$$

or

$$r(\phi_0) = \frac{1}{\Omega^2} \int \phi_{\omega_1, \omega_2}^{-1}(\phi_0) d\omega_1 d\omega_2. \quad (3.20)$$

If ϕ is a hard potential, then $\phi_{\omega_1, \omega_2}^{-1}(\phi_0)$ is just the distance of closest approach $R(\omega_1, \omega_2)$, independent of ϕ_0 . In this case, Eq. (3.18) produces a hard sphere potential with

$$R_{\text{eqv}} = \frac{1}{\Omega^2} \int R(\omega_1, \omega_2) d\omega_1 d\omega_2, \quad (3.21)$$

a formulation first used in this context by Bellemans.⁹

The second case is the approach of Rowlinson¹¹ and Barker and Henderson,¹⁰ in which ϕ_0 is required to be hard. To find the consequences of this requirement, we rewrite Eq. (3.18) as

$$\begin{aligned} \int y_0(r) \{\exp[-\beta\phi_0(r)]\}' \\ \times \{\phi_{\omega_1, \omega_2}^{-1}[\phi_0(r)] - r\} d^3r d\omega_1 d\omega_2 = 0. \end{aligned} \quad (3.22)$$

Using $R = \phi_{\omega_1, \omega_2}^{-1}[\phi_0(r)]$, Eq. (3.22) becomes

$$\begin{aligned} \int y_0 \{\phi_0^{-1}[\phi(R)]\} \{\exp[-\beta\phi(R)]\}' \{\phi_0^{-1}[\phi(R)]\}^2 \\ \times \{R - \phi_0^{-1}[\phi(R)]\} dR d\omega_1 d\omega_2 = 0. \end{aligned} \quad (3.23)$$

Since $\phi_0^{-1}[\phi(R)] = R_{\text{eqv}}$ for all R , then, on using the conditions that $\phi(0) = \infty$ and $\phi(\infty) = 0$, Eq. (3.23) reduces to

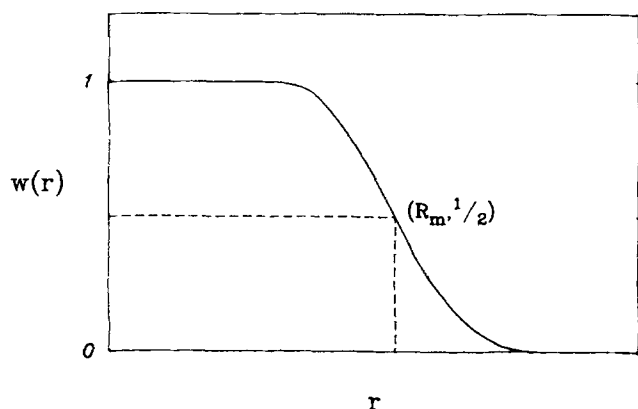


FIG. 8. Typical form of the function $w(r)$ given by Eq. (3.26).

$$R_{\text{eqv}} = \frac{\int R \{ \exp[-\beta\phi(R, \omega_1, \omega_2)] \}' dR d\omega_1 d\omega_2}{\int \{ \exp[-\beta\phi(R, \omega_1, \omega_2)] \}' dR d\omega_1 d\omega_2}$$

$$= \frac{1}{\Omega^2} \int \{ 1 - \exp[-\beta\phi(R, \omega_1, \omega_2)] \}' dR d\omega_1 d\omega_2. \quad (3.24)$$

In particular, if ϕ is a hard potential, Eq. (3.24) now reads instead

$$R_{\text{BH}} = R_{\text{eqv}} = \frac{1}{\Omega^2} \int R(\omega_1, \omega_2) d\omega_1 d\omega_2, \quad (3.25)$$

a result identical to Eq. (3.21).

The Barker-Henderson diameter is indicated by the dashed curves in Figs. 2 and 3, and is almost indistinguishable from the median result, Eq. (2.9). The reason for this is most easily seen in terms of the RAM potential of Eq. (3.10) which, for hard particles, reads

$$w(r) \equiv 1 - \exp[-\beta\phi_0(r)]$$

$$= \frac{1}{\Omega^2} \int \epsilon [R(\omega_1, \omega_2) - r] d\omega_1 d\omega_2. \quad (3.26)$$

In terms of this potential, we see that

$$R_{\text{BH}} = \int w(r) dr, \quad (3.27)$$

with

$$w(R_m) = \frac{1}{2}. \quad (3.28)$$

If $w(r) - 1/2$ is an odd function of $r - R_m$, then R_{BH} and R_m will coincide. Numerically, this is always nearly the case; a typical $w(r)$ is shown in Fig. 8.

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¹There are several excellent books which treat liquid state theory and contain the standard results quoted in this paper. Among these are J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976); T. M. Reed and K. E. Gubbins, *Applied Statistical Mechanics* (McGraw-Hill, New York, 1973); P. A. Eglestaff, *An Introduction to the Liquid State* (Academic, New York, 1967).

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