

# Spherical Reference Systems for Nonspherical Hard Interactions

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We investigate the applicability of the median and Barker-Henderson prescriptions for obtaining spherical reference systems for three models: hard linear triatomics, hard heteronuclear dumbbells, and two-component mixtures of hard dumbbells. We propose an empirical method for determining the median potential for systems lacking a high degree of symmetry. For mixtures of hard molecules, we find that both the median and Barker-Henderson prescriptions give rise to approximately additive hard-sphere reference potentials.

## I. Introduction

The statistical mechanics of molecular fluids was one of Debye's abiding interests and is a subject to which he made enormous contributions. We are therefore pleased to commemorate him with this article, which contains some new results for model fluids obtained via some old and some recently developed "sphericalizations" of angle-dependent intermolecular potentials.

The motivation for this work comes from the fact that there now exist well-developed approximation methods for obtaining the thermodynamic properties and structure functions of fluids whose particles interact via spherical potentials. Nonspherical molecules are still quite difficult to treat directly. The increase in complexity resulting from the angle-dependent interactions causes even minor computations, such as low-order virial coefficients, to become major undertakings.

The median procedure, recently proposed by Lebowitz and Percus,<sup>1</sup> was motivated by the work of Shaw, Holian, and Johnson.<sup>2</sup> It proposes that the thermodynamic properties of a fluid of symmetric molecules interacting through an angle-dependent pair potential  $\phi(r, \omega_1, \omega_2)$  be approximated by those of a fluid with a spherical pair potential  $\phi_0(r)$  equal to the angular median of  $\phi$ . Here,  $r = |\mathbf{r}|$  is the distance between the centers of symmetry of the two molecules, while the (multidimensional) variables  $\omega_1$  and  $\omega_2$  define the orientations of the molecules relative to  $\mathbf{r}$ .  $\phi_0(r)$  may be defined by the relation<sup>1</sup>

$$\int d\omega_1 \int d\omega_2 \operatorname{sgn} [\phi(r, \omega_1, \omega_2) - \phi_0(r)] = 0 \quad (1.1)$$

Since it is well-known that the median minimizes the sum of absolute deviations, we may also define  $\phi_0(r)$  to be that  $\Phi(r)$  which minimizes

$$\int d\omega_1 \int d\omega_2 |\phi(r, \omega_1, \omega_2) - \Phi(r)| \quad (1.2)$$

A property of the median which is particularly convenient for hard interactions is that  $f(\cdot)$

$$\phi_0 = \operatorname{Med} \phi \leftrightarrow f(\phi_0) = \operatorname{Med} f(\phi) \quad (1.3)$$

is a monotone function of its argument. In particular, by letting  $f(\phi) = \exp(-\beta\phi)$  we find that for hard potentials, where  $\phi(r, \omega_1, \omega_2) = \infty$  or 0 depending on whether or not the particles overlap,  $\phi_0$  is also a hard potential independent of  $\beta$ . Thus, the spherical reference fluid interacting via  $\phi_0$  is a hard-sphere system with diameter  $R_m$  determined by the relation

$$[1/(4\pi)^2] \int d\omega_1 \int d\omega_2 \exp[-\beta\phi(R_m, \omega_1, \omega_2)] = 1/2 \quad (1.4)$$

The median prescription has been seen to work extremely well for dense fluids composed of either symmetric hard dumbbells

or spherocylinders.<sup>1,3</sup> Similar results were obtained for the pressure of symmetric diatomics interacting via Lennard-Jones, exponential-six, or  $1/r^n$  site-site potentials.<sup>4-6</sup> In order to obtain realistic internal energies at low temperatures (near the triple point), it appears<sup>6</sup> to be best if the site-site Lennard-Jones potential is first divided into its  $r^{-12}$  and  $r^{-6}$  parts and the reference potential taken as the sum of the medians separately obtained for each part.

In this paper, we present results on three more complex systems of hard molecules: linear triatomics, heteronuclear dumbbells, and two-component mixtures of dumbbells. In addition to studying the equation of state generated by the median potential, we also investigate the Barker-Henderson<sup>7</sup> reference system, which was seen to give results nearly indistinguishable from those obtained from the median system.<sup>3</sup> We find that both reference systems continue to reproduce the bulk thermodynamics of the true systems moderately well. We also find that both reference potentials are approximately additive when applied to mixtures. These results continue to suggest that either of these two reference systems may form the basis of a successful perturbation theory for fluids of nonspherical molecules.

## II. Linear Triatomics

Streett and Tildesley<sup>8</sup> have carried out limited Monte Carlo simulations of hard linear triatomic molecular fluids (Figure 1). Holding the diameter of the two outer spheres  $R_B$  fixed, they have varied the diameter of the inner sphere  $R_A$ , considering three systems:  $T_1$ ,  $R_A/R_B = 0.857$ ;  $T_2$ ,  $R_A/R_B = 1.0$ ; and  $T_3$ ,  $R_A/R_B = 1.2$ . In each case, the separation of the two outer spheres  $l$  was set to  $0.897R_B$ , and simulations were performed at a single reduced density  $\rho^* = 0.897 = (6/\pi) \rho V_m$ , where  $\rho = N/V$  is the particle number density, and  $V_m$  is the molecular volume.

We compare the median and Barker-Henderson reference systems with the experimental systems in two ways. First, we ask what diameter hard spheres at the same density  $\rho$  give rise to the experimentally observed compressibility factor  $\beta P/\rho$ . To do this, we invert the Carnahan-Starling equation<sup>9</sup>

$$\frac{\beta P}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (2.1)$$

where the packing fraction  $\eta$  is given by

$$\eta = (\pi/6) R_{\text{eqv}}^3 \rho \quad (2.2)$$

and  $R_{\text{eqv}}$  is the desired equivalent hard-sphere diameter. The Carnahan-Starling equation is known to reproduce the equation

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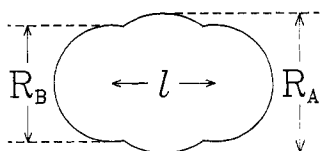


Figure 1. Geometry of the hard linear triatomics studied by Streett and Tildesley.<sup>8</sup> They simulated three models: T<sub>1</sub>,  $R_A/R_B = 0.857$ ; T<sub>2</sub>,  $R_A/R_B = 1$ ; and T<sub>3</sub>,  $R_A/R_B = 1.2$ . In each case,  $l = 0.897R_B$ .

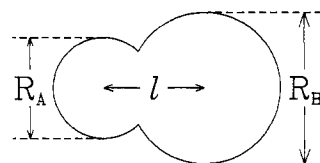


Figure 2. Geometry of the hard heteronuclear dumbbells studied by Jolly, Freasier, and Bearman.<sup>11</sup> See Table III for a summary of the systems studied.

TABLE I: Equivalent Hard-Sphere Diameters for Hard Linear Triatomics

molecule	$R_{eqv}^a$	$R_m^b$	$R_{BH}^c$
T <sub>1</sub>	1.325	1.323	1.331
T <sub>2</sub>	1.337	1.345	1.349
T <sub>3</sub>	1.409	1.396	1.408

<sup>a</sup>  $R_{eqv}$  is obtained by applying the inverse Carnahan-Starling equation to Monte Carlo data.<sup>8</sup> <sup>b</sup>  $R_m$  is the median diameter. <sup>c</sup>  $R_{BH}$  is the Barker-Henderson diameter.

TABLE II: Compressibility Factors for Hard Linear Triatomics at a Reduced Density  $\rho^* = (6/\pi)\rho V_m = 0.897^a$

molecule	$\beta P/\rho$		
	MC	m	BH
T <sub>1</sub>	14.84	14.55	15.54
T <sub>2</sub>	12.84	13.61	14.04
T <sub>3</sub>	12.88	11.79	12.83

<sup>a</sup> MC denotes Monte Carlo data,<sup>8</sup> and m and BH, respectively, denote values obtained by applying the Carnahan-Starling equation for hard spheres of diameters  $R_m$  and  $R_{BH}$ .

of state for a hard-sphere system to a very high degree of accuracy for  $\eta \lesssim 0.5$ .<sup>10</sup>

The resulting density-dependent  $R_{eqv}$  may then be compared to the density-independent median and Barker-Henderson diameters  $R_m$  and  $R_{BH}$ . For hard molecules,  $R_m$  is that distance at which exactly half of the possible orientations of two molecules result in overlap and half do not, and  $R_{BH}$  is the average distance of closest approach and is not expected to deviate markedly from  $R_m$ .<sup>3</sup> These results are presented in Table I.

The second way of comparing these two reference potentials with experimental data is to directly compute the equation of state, applying the Carnahan-Starling equation to spheres of diameter  $R_m$  and  $R_{BH}$  at the same density  $\rho$  as the simulated systems. This comparison is less meaningful here since data are available at only a single density, although we note that this is a moderately high density, and so provides a not unrealistic test of the applicability of both the median and Barker-Henderson reference potentials, which are seen in Table II to give compressibility factors that agree with experimental data to within 10%.

### III. Heteronuclear Dumbbells

Jolly, Freasier, and Bearman<sup>11</sup> have performed Monte Carlo simulations of five separate hard heteronuclear dumbbells (Figure 2). The geometries of these five systems are summarized in Table III. The diameter of the smaller sphere was held fixed, and simulations were carried out at two densities for each system,

TABLE III: Geometries of the Five Heteronuclear Dumbbells<sup>a</sup>

molecule	$R_B/R_A$	$l/R_A$
H <sub>1</sub>	1.5	0.75
H <sub>2</sub>	1.5	0.5
H <sub>3</sub>	1.5	1.0
H <sub>4</sub>	1.8	0.9
H <sub>5</sub>	1.2	0.6

<sup>a</sup> See ref 11. See Figure 2 for definitions of  $R_A$ ,  $R_B$ , and  $l$ .

TABLE IV: Compressibility Factors for Heteronuclear Dumbbells<sup>a</sup>

molecule	$\rho R_{chs}^3$	$\beta P/\rho$		
		MC	m	BH
H <sub>1</sub>	0.4	2.75	2.66	2.68
	0.7	6.45	6.38	6.48
H <sub>2</sub>	0.4	2.66	2.56	2.57
	0.7	6.04	5.92	5.95
H <sub>3</sub>	0.4	2.93	2.81	2.85
	0.7	7.13	7.15	7.38
H <sub>4</sub>	0.4	2.68	2.64	2.66
	0.7	6.34	6.29	6.39
H <sub>5</sub>	0.4	2.78	2.67	2.68
	0.7	6.51	6.43	6.49

<sup>a</sup> MC denotes Monte Carlo data,<sup>11</sup> and m and BH, respectively, denote values obtained by applying the Carnahan-Starling equation for hard spheres of diameters  $R_m(\lambda_{maxm})$  and  $R_{BH}(\lambda_{maxBH})$ .

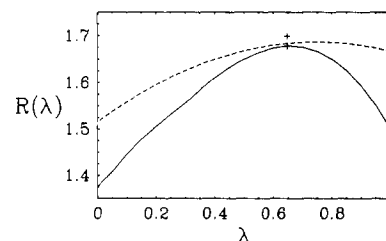


Figure 3. Median diameter  $R_m(\lambda)$  (solid curve) and Barker-Henderson diameter  $R_{BH}(\lambda)$  (dashed curve) as a function of the location of the fixed point for molecule H<sub>3</sub> ( $R_B/R_A = 1.5$ ,  $l/R_A = 1.0$ ). The plus signs indicate  $R_{eqv}(\rho)$ .

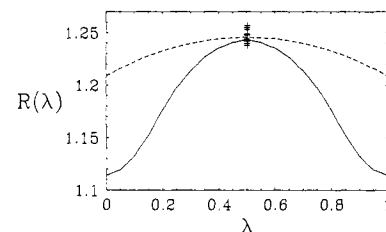


Figure 4. Median diameter  $R_m(\lambda)$  (solid curve) and Barker-Henderson diameter  $R_{BH}(\lambda)$  (dashed curve) as a function of the location of the fixed point for a symmetric dumbbell of length  $l/R = 0.6$ . The plus signs indicate  $R_{eqv}(\rho)$ .

$\rho R_{chs}^3 = 0.4$  and  $0.7$ , where  $R_{chs}$  is the diameter of that hard sphere whose volume is the same as that of the molecule under study.

The computations of  $R_m$  and  $R_{BH}$  both involve integrations over the internal angular degrees of freedom of two molecules. For objects which possess a high degree of symmetry, such as symmetric dumbbells, spherocylinders, and symmetric linear triatomics, it is natural to perform the indicated rotations about the center of volume of the given molecule. For less symmetric objects, this choice may not be the most natural. For example, one may choose the fixed point in each molecule which will form the center of the equivalent hard sphere to lie anywhere along the line segment joining the centers of the two spheres which make up the heteronuclear dumbbells we consider here.

If we parameterize the location of this fixed point by  $\lambda$ , so that for  $\lambda = 0$  it is positioned on the center of the smaller of the two spheres and for  $\lambda = 1$  it is positioned on the center of the larger one, we may then compute both  $R_m(\lambda)$  and  $R_{BH}(\lambda)$ . Results for molecule H<sub>3</sub> ( $R_B/R_A = 1.5$ ,  $l/R_A = 1.0$ ) are shown in Figure 3.

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TABLE V: Median and Barker-Henderson Diameters for Like ( $R^{AA}$  and  $R^{BB}$ ) and Unlike ( $R^{AB}$ ) Species, together with  $R^+ = (R^{AA} + R^{BB})/2^a$ 

$(l_A^*, l_B^*)$	$R_B/R_A$	$R_m^{AA}$	$R_m^{BB}$	$R_m^{AB}$	$R_m^+$	$R_{BH}^{AA}$	$R_{BH}^{BB}$	$R_{BH}^{AB}$	$R_{BH}^+$
(0.4,0.2)	1	1.175	1.093	1.133	1.134	1.175	1.094	1.134	1.135
(0.6,0.2)	1	1.244	1.093	1.164	1.169	1.246	1.094	1.168	1.170
(0.6,0.0)	1	1.244	1	1.116	1.122	1.246	1	1.119	1.123
(1.0, 0.0)	1	1.345	1	1.151	1.173	1.352	1	1.162	1.176
(0.6,0.3)	1	1.244	1.135	1.186	1.190	1.246	1.136	1.190	1.191
(1.0,0.6)	1	1.345	1.244	1.288	1.294	1.352	1.246	1.299	1.299
(0.6,0.0)	1.215	1.244	1.215	1.227	1.229	1.246	1.215	1.230	1.231
(1.0,0.0)	1.260	1.345	1.260	1.294	1.303	1.352	1.260	1.303	1.306
(0.6,0.3)	1.076	1.244	1.213	1.226	1.228	1.246	1.213	1.229	1.230
(1.0,0.6)	1.037	1.345	1.287	1.308	1.314	1.352	1.285	1.319	1.319
(0.6,0.0)	1.061	1.244	1.061	1.147	1.152	1.246	1.061	1.151	1.154
(1.0,0.0)	1.101	1.345	1.101	1.207	1.223	1.352	1.101	1.217	1.227
(0.6,0.3)*	0.928	1.244	1.062	1.149	1.153	1.246	1.063	1.153	1.155
(1.0,0.6)	0.906	1.345	1.144	1.235	1.244	1.352	1.147	1.247	1.250

<sup>a</sup> All values in units of  $R_A$ . If additivity were strictly obeyed, then one would expect  $R^{AB} = R^+$ .  $R_B/R_A$  is the ratio of component sphere diameters for the two species, and  $l^* = l/R$ . The first grouping is the models studied by Aviram and Tildesley,<sup>13</sup> while the remaining three are those studied by Wojcik and Gubbins.<sup>14</sup> The second of these latter three corresponds to  $V_A = V_B$ , while the third corresponds to  $V_A = 2/3 V_B$ . For the pair marked by the asterisk,  $V_A \approx 0.64 V_B$ .

Superimposed on these curves are the experimental values of  $R_{eq}(\rho)$ , which are seen to approximate the maximum values for  $R_m(\lambda)$  and  $R_{BH}(\lambda)$ , which themselves roughly correspond.

For comparison, in Figure 4 we present similar results for symmetric dumbbells with sphere separation  $l = 0.6R$ , where  $R = R_A = R_B$ . Data, taken from an extensive survey by Tildesley and Streett,<sup>12</sup> are available for a wide range of densities and are found to bracket the maxima of  $R_m(\lambda)$  and  $R_{BH}(\lambda)$  with relatively small dispersion. As expected, these maxima are located at  $\lambda = 1/2$ .

It appears, then, that the appropriate choice for the location of the fixed point is at that value of  $\lambda$  which maximizes  $R_m(\lambda)$  or  $R_{BH}(\lambda)$ . In an effort to formalize this observation, one may instead seek that value of  $\lambda$  which minimizes the integral of the absolute value of the deviation of the median reference potential from the true potential.

Following the discussion centering around 1.3, we seek that value of  $\lambda$  which minimizes

$$S_\mu(\lambda) = \int |\exp[-\beta\phi_\lambda(r, \omega_1, \omega_2)] - \exp[-\beta\phi_0(r)]| d\omega_1 d\omega_2 d\mu \quad (3.1)$$

where  $\phi_\lambda(r, \omega_1, \omega_2)$  is the true intermolecular potential at internal angular configurations  $\omega_1$  and  $\omega_2$ ,  $\phi_0(r)$  is the median reference potential, and  $r$  is the distance of separation of the fixed points of the two molecules.  $d\mu$  is the measure for the  $r$ -space integration, and its choice is again not obvious. Two reasonable candidates are  $d\mu = dr$  and  $d\mu = r^2 dr$ , for which we shall denote the left-hand side of eq 3.1 by  $S_0$  and  $S_2$ , respectively.

In Figure 5 we show  $S_0(\lambda)$  and  $S_2(\lambda)$  for molecule  $H_2$ . The arrow indicates that value  $\lambda_{max_m}$  for which  $R_m(\lambda)$  is a maximum. The minima of  $S_0(\lambda)$  and  $S_2(\lambda)$  are seen to be broad and to correspond roughly to  $\lambda_{max_m}$ .

In Table IV are given the compressibility factors obtained by applying the Carnahan-Starling equation to hard spheres of diameter  $R_m(\lambda_{max_m})$  and  $R_{BH}(\lambda_{max_{BH}})$  together with the Monte Carlo data for each of the systems considered. Agreement is in all cases within 5%, although we note that these systems are at relatively low pressures.

#### IV. Mixtures

Multicomponent mixtures offer an important test of any reference potential, and to that end we investigate here the effectiveness of the median and Barker-Henderson prescriptions at reproducing the equation of state for dumbbell-dumbbell and sphere-dumbbell two-component mixtures. Such systems have been investigated by Aviram and Tildesley<sup>13</sup> and, more recently, by Wojcik and Gubbins.<sup>14</sup> These studies treated two species, A

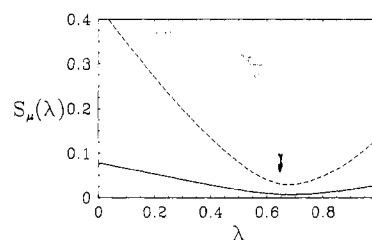


Figure 5. Functions  $S_0(\lambda)$  (solid curve) and  $S_2(\lambda)$  (dashed curve) for molecule  $H_2$ . The arrow indicates the location of the maximum of  $R_m(\lambda)$ .

and B, of symmetric dumbbells characterized by component sphere diameters  $R_A$  and  $R_B$  and sphere separations  $l_A = l_A^* R_A$  and  $l_B = l_B^* R_B$ , respectively.

Aviram and Tildesley investigated two equimolar mixtures, with  $(l_A^*, l_B^*)$  of (0.4,0.2) and (0.6,0.2), both with  $R_A = R_B$ . Wojcik and Gubbins investigated three classes of systems, one for which  $R_A = R_B$ , one for which  $V_A = V_B$  ( $V_A$  is the volume of molecular species A), and one for which  $V_A = 2/3 V_B$ . Each of these systems was studied for  $(l_A^*, l_B^*)$  of (0.6,0.0), (1.0,0.0), (0.6,0.3), and (1.0,0.6). (A dumbbell with  $l^* = 0.0$  is a sphere.)

We begin by asking to what extent the median and Barker-Henderson prescriptions obey additivity. That is, how accurately can one represent a mixture of nonspherical molecules by a mixture of hard spheres corresponding to the respective pure fluids? We compute the median diameters for the pure fluids of each species,  $R_m^{AA}$  and  $R_m^{BB}$ , and additionally compute the median diameter for the interaction of two unlike species,  $R_m^{AB}$ . In Table V are presented the results of these computations, together with values for  $R_m^+ = (R_m^{AA} + R_m^{BB})/2$ . In each case, additivity is obeyed within 1.5%, with  $R_m^+$  always greater than  $R_m^{AB}$ .

One may also perform the same computations for the corresponding Barker-Henderson diameters; these data are also given in Table V. In each case, results similar to those obtained by the median prescription are obtained, with additivity even more closely obeyed.

In view of the nearly additive behavior of both the median and Barker-Henderson diameters, we have applied the Carnahan-Starling equation for two-component mixtures of hard spheres with diameters  $R_\alpha$  and  $R_\beta$ <sup>9</sup>

$$\frac{\beta P}{\rho} = \frac{1}{\xi_0} \left( \frac{\xi_0}{1 - \xi_3} + \frac{3\xi_1\xi_2}{(1 - \xi_3)^2} + \frac{3\xi_2^2}{(1 - \xi_3)^3} - \frac{\xi_3\xi_2^3}{(1 - \xi_3)^3} \right) \quad (4.1)$$

where

$$\xi_i = \rho(R_\alpha^i + R_\beta^i) \quad (4.2)$$

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**TABLE VI: Compressibility Factors for the Equimolar Mixtures Studied by Aviram and Tildesley<sup>a</sup>**

$(l_A^*, l_B^*)$	$\eta$	$\beta P/\rho$		
		MC	m	BH
(0.4,0.2)	0.075	1.410	1.375	1.376
	0.150	2.022	1.935	1.936
	0.226	2.940	2.787	2.791
	0.301	4.580	4.126	4.134
	0.376	7.536	6.308	6.325
(0.6,0.2)	0.451	12.776	10.049	10.086
	0.088	1.475	1.466	1.469
	0.176	2.224	2.222	2.230
	0.264	3.391	3.491	3.511
	0.352	5.500	5.727	5.775
	0.440	9.342	9.939	10.055

<sup>a</sup>See ref 13.  $l^* = l/R$  and  $R = R_A = R_B$ .  $\eta = \rho(V_A + V_B)/2$ , where  $V$  is the molecular volume. MC denotes Monte Carlo data, while m and BH, respectively, denote results obtained from the Carnahan-Starling equation of mixtures.

**TABLE VII: Compressibility Factors for the Mixtures Studied by Wojcik and Gubbins<sup>a</sup>**

$(l_A^*, l_B^*)$	$\eta$	$x_A$	$\beta P/\rho$		
			MC	m	BH
(0.6,0.0)	0.30	0.50	4.20	4.21	4.23
		0.45	9.78	9.95	10.01
	0.45	0.25	10.15	10.51	10.62
		0.75	10.76	11.06	11.22
(1.0,0.0)	0.30	0.50	4.88	4.86	4.95
		0.35	5.95	5.97	6.05
	0.43	0.75	7.26	7.40	7.65
		0.25	9.74	10.07	10.27
(0.6,0.3)	0.30	0.50	11.06	11.82	12.24
		0.75	12.31	13.55	14.20
	0.45	0.30	4.31	4.28	4.31
		0.50	10.52	10.77	10.89
(1.0,0.6)	0.45	0.25	10.58	12.26	13.03
		0.50	13.33	14.58	15.16
	0.75	0.50	14.46	16.29	17.14
		0.75	14.46	16.29	17.14

<sup>a</sup>See ref 14.  $l^* = l/R$  and  $R = R_A = R_B$ .  $\eta = \rho(V_A x_A + V_B x_B)$ , where  $V$  is the molecular volume and  $x$  is the mole fraction ( $x_B = 1 - x_A$ ). MC denotes Monte Carlo data, while m and BH denote results obtained from the Carnahan-Starling equation for mixtures.

to compute the compressibility factors for both the median and Barker-Henderson reference systems. These results are summarized in Tables VI-IX.

Moderate agreement (within 15%) is obtained for the systems under study, with the exception of the (1.0,0.6) systems where the reference system compressibility factors lie 15-30% above the simulation results.

## V. Conclusions

The median and Barker-Henderson reference potentials have been seen to accurately reproduce bulk thermodynamics for a variety of potentials, both hard and soft.<sup>3-6</sup> We have extended these results to more complicated systems, and we have presented an empirical procedure for computing the reference potential for

**TABLE VIII: Compressibility Factors for the Mixtures Studied by Wojcik and Gubbins<sup>a</sup>**

$(l_A^*, l_B^*)$	$\eta$	$x_A$	$\beta P/\rho$		
			MC	m	BH
(0.6,0.0)	0.30	0.50	4.25	4.21	4.23
		0.45	9.76	9.89	9.93
	0.45	0.50	10.27	10.43	10.51
		0.75	10.82	11.00	11.14
(1.0,0.0)	0.30	0.50	4.83	4.72	4.79
	0.43	0.50	10.71	11.11	11.40
(0.6,0.3)	0.30	0.50	4.30	4.20	4.22
	0.45	0.50	10.52	10.37	10.47
(1.0,0.6)	0.45	0.25	12.14	12.40	12.76
		0.50	13.27	14.02	14.58
	0.75	0.75	14.37	15.93	16.75

<sup>a</sup>See ref 14. For these mixtures,  $V_B = V_A$ . Symbols are defined in Table VII.

**TABLE IX: Compressibility Factors for the Mixtures Studied by Wojcik and Gubbins<sup>a</sup>**

$(l_A^*, l_B^*)$	$\eta$	$x_A$	$\beta P/\rho$		
			MC	m	BH
(0.6,0.0)	0.30	0.50	4.19	4.22	4.25
		0.45	9.63	9.96	10.01
	0.45	0.25	10.06	10.52	10.63
		0.75	10.60	11.08	11.23
(1.0,0.0)	0.30	0.50	4.63	4.82	4.91
	0.43	0.50	10.24	11.60	11.97
(0.6,0.3)*	0.30	0.50	4.27	4.35	4.38
	0.45	0.50	10.25	11.09	11.23
(1.0,0.6)	0.45	0.25	10.29	11.86	12.67
		0.50	12.92	15.86	16.65
	0.75	0.50	13.94	17.03	18.00
		0.75	13.94	17.03	18.00

<sup>a</sup>See ref 14. For these mixtures,  $V_A = 2/3 V_B$ , except for the pair marked by the asterisk, for which  $V_A \approx 0.64 V_B$ . Symbols are defined in Table VII.

systems lacking a high degree of symmetry. For mixtures, both the median and Barker-Henderson reference systems were found to give somewhat poorer, though still commendable results. More importantly, both these reference potentials were found to be additive in mixtures.

The Rowlinson-Barker-Henderson<sup>7,15</sup> soft reference potential (for soft systems) developed in ref 3 and the median reference potential (which is already soft for soft potentials) should both be tested on soft systems of the types considered here. Further study is also warranted in other, more complex systems, both hard and soft.

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