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Hard-Particle Fluids. II. General *y*-Expansion-Like Descriptions

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We present a critical discussion of the "y-expansion" approach to the thermodynamics of hard-particle fluids. First we discuss briefly our original formulation for many-component mixtures of anisotropic species, using the usual virial series as a point of departure. Difficulties arising in the case of attractive tails and nonadditive hard-core interactions are exposed. To resolve these problems we suggest a straightforward generalization of the expansion quantity y. Instead of $y_\alpha \equiv \rho_\alpha/(1 - \sum_{\gamma=1}^{\nu} v_{0\gamma}\rho_\gamma)$, where $v_{0\gamma}$ and ρ_γ are the particle volume and number density of the γth species in the ν-component mixture, we define $y_\alpha \equiv \rho_\alpha/(1 - \sum_{\gamma=1}^{\nu} \psi_\gamma{}^\alpha \rho_\gamma)$, where the $\psi_\gamma{}^\alpha$ are determined by optimizing the convergence of the series expressing thermodynamic functions in powers of the y_α. This procedure provides in particular a good description of nonadditive binary mixtures of hard spheres with $\sigma_{22} = 0$ and $\sigma_{12} = (1/2)\sigma_{11}(1 + \Delta)$ ($\Delta \neq 0, \geqslant -1$ is the usual nonadditivity parameter.) We present a generalization of the analysis of Widom and Rowlinson whereby such systems are shown to be equivalent to *pure* fluids of *attracting* hard spheres. Critical point properties of the pure fluid are determined via this equivalence, using our y-expansion description of the nonadditive *mixture*. Finally, we present the results of y-expansion studies of some anisotropic (i.e., orientationally ordered) states of fluids composed of asymmetric hard particles. For the case of rectangular parallelepipeds whose allowed orientations are restricted, we can compare our description of the isotropic–nematic liquid crystal phase transition with those obtained earlier by virial expansions and Padé approximants. Finally, generalization to continuously allowed orientations is discussed.

KEY WORDS: y-Expansion; hard-core particles; nonadditive pair potential; Widom–Rowlinson correspondence; isotropic–nematic liquid crystal phase transition.

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1. INTRODUCTION

As in the preceding paper (hereafter referred to as I), we consider the statistical thermodynamics of a collection of anisotropic particles of different types confined to a volume V at pressure P and temperature T. The system is assumed to be in either an isotropic phase or an anisotropic state without periodic structure.

2. MAYER–ONSAGER CLUSTER THEORY

Let $\rho_\alpha^{(1)}(\mathbf{X})$ be the singlet distribution function associated with molecules of the αth species; $\rho_\alpha = N_\alpha/V$ is the concentration (number density) of this species and $\mathbf{X}$ describes its position and orientation. Then

$$f_\alpha(\mathbf{X}) = \rho_\alpha^{(1)}(\mathbf{X})/\rho_\alpha \tag{1}$$

is a dimensionless measure of the distribution of α-type particles in different spatial orientations. (Since we confine ourselves to nonperiodic phases, f depends only on two or three angles $\mathbf{\Omega}$ characterizing the orientation of a particle-fixed coordinate system in a space-fixed frame. We shall be dealing with three-dimensional systems here, but most of our results are applicable to any number of dimensions.) Assuming pairwise-additive intermolecular forces characterized by the potential $u_{\alpha\beta}$ and introducing Mayer functions

$$f_{\alpha\beta}(\mathbf{X}) = \exp[-u_{\alpha\beta}(\mathbf{X})/kT] - 1 \tag{2}$$

we can express the Helmholtz free energy F in the form of an infinite expansion in powers of the densities ρ_α,(1,2)

$$\begin{aligned}\beta F = {} & \sum_{\gamma=1}^{\nu} \int \rho_\gamma^{(1)}(\ln \rho_\gamma^{(1)} - 1 + \beta\mu_\gamma{}^0)\, d\mathbf{X}_\gamma \\ & - \sum_{n=2}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \frac{1}{n!} \int \cdots \int S_{\gamma_1\cdots\gamma_n} \prod_{i=1}^{n} \rho_{\gamma_i}^{(1)}\, d\mathbf{X}_{\gamma_i} \\ = {} & \sum_{\alpha=1}^{\nu} N_\alpha \Big\{ \beta\mu_\alpha{}^0 - 1 + \frac{1}{V} \int f_\alpha \ln f_\alpha\, d\mathbf{X} + \ln \rho_\alpha \\ & + \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \frac{1}{n} \bar{B}_{\alpha\gamma_1\cdots\gamma_n} \prod_{i=1}^{n} \rho_{\gamma_i} \Big\}\end{aligned} \tag{3}$$

Here $\beta = 1/kT$ is the reciprocal temperature times the Boltzmann constant, $\mu_\gamma{}^0$ is the standard chemical potential, $S_{\gamma_1\ldots\gamma_n}$ is the irreducible cluster sum of different products of $f_{\gamma_i\gamma_j}$ $(i, j = 1,\ldots, n)$ associated with a doubly connected diagram:

$$S_{\gamma_1\cdots\gamma_n} = \sum \prod_{i>j}^{n} f_{\gamma_i\gamma_j} \tag{4}$$

and

$$\bar{B}_{\gamma_1\cdots\gamma_n} = \frac{1-n}{Vn!}\int\cdots\int S_{\gamma_1\cdots\gamma_n}\prod_{i=1}^{n} f_{\gamma_i}\,d\mathbf{X}_{\gamma_i} \qquad (n>1) \tag{5}$$

is the nth-order virial coefficient. $d\mathbf{X}$ and f_γ are normalized in (3) and (5) so that

$$\int d\mathbf{X} = V \tag{6}$$

and

$$\int f_\gamma(\mathbf{X})\,d\mathbf{X} = V \tag{7}$$

Since for a given distribution f_γ, $\gamma = 1,\ldots,\nu$, the coefficients $\bar{B}_{\gamma_1\cdots\gamma_n}$ are V and N_γ independent, the differentiation of (3) with respect to these variables yields the following expressions for the pressure and chemical potential:

$$\beta P \equiv -\left.\frac{\partial\beta F}{\partial V}\right|_{\{N_\gamma,f_\gamma\},T} = \sum_{n=1}^{\infty}\sum_{\gamma_1=1}^{\nu}\cdots\sum_{\gamma_n=1}^{\nu}\bar{B}_{\gamma_1\cdots\gamma_n}\prod_{i=1}^{n}\rho_{\gamma_i} \tag{8}$$

with

$$\bar{B}_\gamma = 1 \tag{5a}$$

and

$$\beta\mu_\alpha \equiv \left.\frac{\partial\beta F}{\partial N_\alpha}\right|_{V,\{N_{\gamma\neq\alpha},f_\gamma\},T} = \beta\mu_\alpha{}^0 + \ln\rho_\alpha + \frac{1}{V}\int f_\alpha\ln f_\alpha\,d\mathbf{X} + \sum_{n=1}^{\infty}\sum_{\gamma_1=1}^{\nu}\cdots\sum_{\gamma_n=1}^{\nu}\frac{n+1}{n}\bar{B}_{\alpha\gamma_1\cdots\gamma_n}\prod_{i=1}^{n}\rho_{\gamma_i} \tag{9}$$

On the other hand, keeping fixed V and N_γ, $\gamma = 1,\ldots,\nu$, and minimizing the free energy with respect to f_γ will give the equilibrium distribution of molecular orientations:

$$\begin{aligned}\left.\frac{\delta\beta F}{\delta\rho_\alpha^{(1)}(\mathbf{X}_\alpha)}\right|_{V,\{\rho^{(1)}_{\gamma\neq\alpha}\},T} &= \beta\mu_\alpha = \beta\mu_\alpha{}^0 + \ln\rho_\alpha^{(1)}(\mathbf{X}_\alpha)\\ &\quad - \sum_{n=1}^{\infty}\sum_{\gamma_1=1}^{\nu}\cdots\sum_{\gamma_n=1}^{\nu}\frac{1}{n!}\int\cdots\int S_{\alpha\gamma_1\cdots\gamma_n}(\mathbf{X}_\alpha,\mathbf{X}_{\gamma_1},\cdots,\mathbf{X}_{\gamma_n})\\ &\quad\times\prod_{i=1}^{n}\rho_{\gamma_i}^{(1)}(\mathbf{X}_{\gamma_i})\,d\mathbf{X}_{\gamma_i}\end{aligned} \tag{10}$$

The chemical potential

$$\mu_\alpha = \frac{1}{V}\int\frac{\delta F}{\delta\rho_\alpha^{(1)}(\mathbf{X}_\alpha)}f_\alpha(\mathbf{X}_\alpha)\,d\mathbf{X}_\alpha \tag{10a}$$

is now the Lagrange undetermined multiplier. Introducing orientationally *un*averaged virial coefficients (the integration is carried out over $\mathbf{r}$ instead of $\mathbf{X} \equiv \mathbf{r}, \mathbf{\Omega}$)

$$B_{\gamma_1 \cdots \gamma_n} = \frac{1-n}{Vn!} \int \cdots \int S_{\gamma_1 \cdots \gamma_n} \prod_{i=1}^{n} d\mathbf{r}_{\gamma_i} \qquad (n > 1) \tag{5b}$$

Eq. (10) takes the form

$$\begin{aligned} \ln f_\alpha(\mathbf{\Omega}_\alpha) = {} & \beta(\mu_\alpha - \mu_\alpha{}^0) - \ln \rho_\alpha \\ & - V \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \frac{n+1}{n} \int \cdots \int B_{\alpha\gamma_1 \cdots \gamma_n}(\mathbf{\Omega}_\alpha, \mathbf{\Omega}_{\gamma_1}, \dots, \mathbf{\Omega}_{\gamma_n}) \\ & \times \prod_{i=1}^{n} \rho_{\gamma_i} f_{\gamma_i}(\mathbf{\Omega}_{\gamma_i}) \, d\mathbf{\Omega}_{\gamma_i} \end{aligned} \tag{10b}$$

Onsager,[2] Zwanzig,[3] Helfand and Stillinger,[4] Runnels and Colvin,[5] Ree and Hoover,[6] Barker and Henderson,[7] and many others[8] have used these series to investigate the thermodynamics of pure fluids and fluid mixtures composed of spherically symmetric or anisotropic molecules. It is now well known that the virial expansion converges slowly and is a poor means for investigating dense fluids exhibiting phase transitions.

3. y-EXPANSION

Recently we have shown[9] that this situation can be significantly improved by rearranging series (3) in such a way that the thermodynamic properties are expressed as an expansion in powers of functions $y_\alpha = y_\alpha(\{\rho_\gamma\})$ (rather than the densities ρ_α themselves).

Consider first the hard-particle (h.p.) potential

$$u_{\alpha\beta}^{\text{h.p.}}(\mathbf{X}) = \begin{cases} +\infty, & r = |\mathbf{X}| < \sigma_{\alpha\beta}(\mathbf{\Omega}, \mathbf{\Omega}_{\mathbf{r}}) \\ 0, & \text{otherwise} \end{cases} \tag{11}$$

where r is the distance between molecules α and β, and $\sigma_{\alpha\beta}$ is an orientationally dependent collision diameter

$$\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2 \tag{11a}$$

Writing[3]

$$v_{0\alpha} = \int_{r < \sigma_{\alpha\alpha}/2} d\mathbf{r} \tag{12}$$

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[3] Equation (11a) is strictly satisfied for convex bodies. Otherwise $\sigma_{\alpha\beta}$ is bigger than the arithmetic mean; in this case relation (11a) is symbolic and simply emphasizes that the collision diameter can be calculated by geometric considerations. A similar qualification applies to the limit of integration in (12). In the next section we consider the example of nonadditive hard-particle mixtures.

for the molecular volume, and introducing the simple function

$$y_\alpha = \rho_\alpha/(1 - \textstyle\sum_{\gamma=1}^{\nu} v_{0\gamma}\rho_\gamma) \tag{13}$$

we can express the free energy in the following form [in analogy with Eq. (3)]:

$$\beta F = \sum_{\alpha=1}^{\nu} N_\alpha \Big\{ \beta\mu_\alpha{}^0 - 1 + \frac{1}{V}\int f_\alpha \ln f_\alpha \, d\mathbf{X} + \ln y_\alpha$$
$$+ \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \frac{1}{n} \bar{C}_{\alpha\gamma_1\cdots\gamma_n} \prod_{i=1}^{n} y_{\gamma_i} \Big\} \tag{14}$$

Relations between the coefficients $\bar{B}$ and $\bar{C}$ in (3) and (14) may be obtained by expanding (13) in powers of the $\{\rho_\alpha\}$, inserting it into (14), and comparing the resulting expression term by term with (3). More explicitly, we have

$$y_\alpha = \rho_\alpha \Big(1 + \sum_{m=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_m=1}^{\nu} \prod_{i=1}^{m} v_{0\gamma_i}\rho_{\gamma_i} \Big) \tag{15a}$$

$$\ln y_\alpha = \ln \rho_\alpha + \sum_{m=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_m=1}^{\nu} \frac{1}{m} \prod_{i=1}^{m} v_{0\gamma_i}\rho_{\gamma_i} \tag{15b}$$

and thus ($n \geqslant 1$)

$$\bar{B}_{\gamma_1\cdots\gamma_{n+1}} = \frac{1}{n+1} \sum_{j=1}^{n+1} \prod_{\substack{i=1\\(i\neq j)}}^{n+1} v_{0\gamma_i}$$
$$+ \sum_{m=1}^{n-1} \sum_{\{i_1\cdots i_{n+1}\}} \frac{1}{m!\,(n-m)!} \bar{C}_{\gamma_{i_1}\cdots\gamma_{i_{m+1}}} \prod_{j=m+2}^{n+1} v_{0\gamma_{i_j}} + \bar{C}_{\gamma_1\cdots\gamma_{n+1}} \tag{16}$$

The second summation in the second term of Eq. (16) is carried out over all $(n + 1)!$ permutations of the numbers $i_1,\ldots\, i_{n+1}$.

The expansions for the pressure and the chemical potential follow from (14) and are

$$\beta P = \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \bar{C}_{\gamma_1\cdots\gamma_n} \prod_{i=1}^{n} y_{\gamma_i} \qquad (\bar{C}_\gamma = 1) \tag{17}$$

and

$$\beta\mu_\alpha = \beta\mu_\alpha{}^0 + \ln y_\alpha + \frac{1}{V}\int f_\alpha \ln f_\alpha \, d\mathbf{X}$$
$$+ \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \frac{n+1}{n} C_{\alpha\gamma_1\cdots\gamma_n} \prod_{i=1}^{n} y_{\gamma_i} + v_{0\alpha}\beta P \tag{18}$$

We have shown(9) for a wide variety of molecular shapes that the above defined y-expansion converges quite rapidly: keeping as few as three terms (i.e., all those through $\bar{C}_{\alpha\beta\gamma}$) provides a simple and accurate thermodynamic description of isotropic pure fluids even at liquid-like densities. In the case of a hard-sphere (h.s.) potential $u_{\alpha\beta}^{\text{h.s.}}(r)$, for example, the three-term truncated y-expansion coincides with the pressure obtained from the Percus–Yevick (PY)$^{(10)}$ and scaled particle (SP)$^{(11)}$ theories (see I) which is known to agree well with machine experiments.$^{(12a)}$

Instead of (13) we can also consider a slightly different function

$$y_\alpha = \rho_\alpha \Big/ \left(1 - \kappa \sum_{\gamma=1}^{\nu} v_{0\gamma}\rho_\gamma\right) \tag{13a}$$

with the parameter κ chosen to provide still faster convergence of the y-expansion. Expressions (16)–(18) still hold if $v_{0\gamma}$ is replaced everywhere by $\kappa v_{0\gamma}$. For a single-component system κ can be determined, for example, by requiring that the fourth C coefficient vanish identically:

$$\bar{C}_4(\kappa) = \bar{B}_4 - 3\kappa v_0 \bar{B}_3 + 3\kappa^2 v_0 \bar{B}_2 - \kappa^3 v_0{}^3 = 0 \tag{19}$$

From the known virial coefficients of a hard-sphere fluid,$^{(6,13)}$ Eq. (19) gives

$$\kappa^{\text{h.s.}} = 0.9338 \tag{20}$$

This same value of κ is appropriate to hard-sphere mixtures. Figure 1 compares the machine computation data$^{(12)}$ for several hard-sphere systems against the three-term truncated y-expansion (referred to as Y_3) with y_α and κ given by Eqs. (13a) and (20). The Y_3 is seen to provide an excellent pressure equation of state for a pure hard-sphere fluid as well as for hard-sphere mixtures. Note that the value of κ determined from Eq. (19) is quite close to unity, consistent with the PY–SP equation (Y_3 with $\kappa = 1$) being so good.

The question of convergence for the y-expansion is as difficult as that for the virial series; rather than attempt to resolve it in general, we show instead how close to each other successive truncations of the y-expansions are. This procedure requires that a sufficient number of virial coefficients be known. In the case of hard spheres, the first ten $\bar{B}_i$ are available.$^{(13)}$ But the uncertainties in the $\bar{B}_{i\geqslant 6}$ do not permit a meaningful determination of the corresponding $\bar{C}_i$ and Y_i.$^{(9)}$ Nevertheless, rapid convergence of (14) is suggested by the following. Requiring that the nth-order term in the y-expansion vanish identically,

$$\bar{C}_n(\kappa) = \sum_{i=0}^{n-1} (-\kappa v_0)^i \binom{n-1}{i} \bar{B}_{n-i} = 0 \tag{19a}$$

we obtain

$$\kappa^{\text{h.s.}}(n = 5) = 1.064 \tag{20a}$$

which is very close to unity and the earlier obtained value of $\kappa^{\text{h.s.}}(n = 4) = 0.9338$: Y_3, Y_4, and Y_5 for both $\kappa^{\text{h.s.}}$ and $\kappa^{\text{h.s.}} = 1$ are very close to each other, and to machine calculation data.

The case of parallel hard cubes also provides us with a large number of virial coefficients; at present, exact values of the first seven $\bar{B}_i$ are known.$^{(14)}$

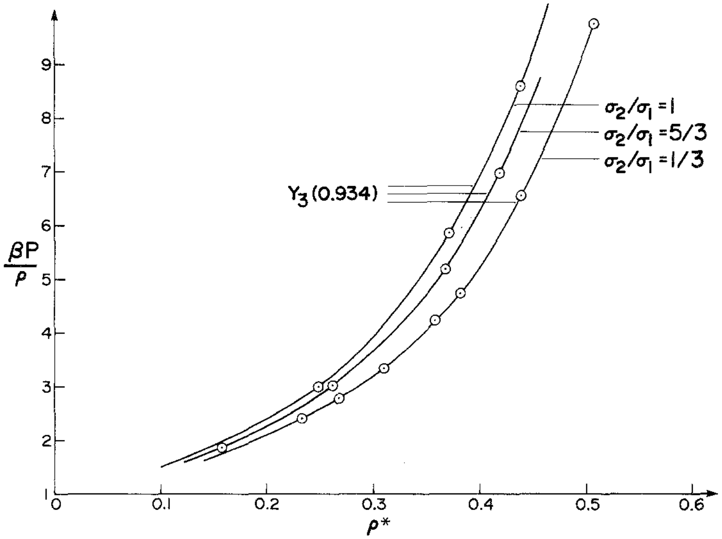

Fig. 1. Pressure equation of state for three hard-sphere mixtures with additive diameters. $\rho^* \equiv v_{01}\rho_1 + v_{02}\rho_2$, and σ_2/σ_1 denotes the ratio of diameters. The solid curves show our calculated Y_3 results (with $\kappa = 0.934$ nullifying C_4) and the circled points denote the machine computation data.(12)

The $\kappa^{\text{h.c.}}$ and the corresponding $\bar{C}_i(\kappa^{\text{h.c.}})$ for $n = 4, 5, 6, 7$ are displayed in Table I. Even though κ (and hence $\bar{C}_i$) oscillates widely as a function of n (probably the consequence of the artificial restriction of particle orientations), it tends nevertheless to a value near unity. There are, unfortunately, no machine simulations for this system against which we can compare our Y_i truncations.

Table I. Coefficients $\bar{B}_i$ and $\bar{C}_i$, for Different Values of the Parameter κ, for Parallel Hard Cubes

		$\bar{C}_i/v_0^{i-1}$			
i	$\bar{B}_i/v_0^{i-1}$	$\kappa(n = 4) =$ 0.5464	$\kappa(n = 5) =$ 1.1567	$\kappa(n = 6) =$ 0.7176	$\kappa(n = 7) =$ 1.0520
1	1	1	1	1	1
2	4	3.4536	2.8433	3.2824	2.9480
3	9	4.9273	1.0845	3.7741	1.6910
4	34/3	0	−5.3896	−2.2320	−4.9542
5	455/144	−8.0095	0	−7.2145	−2.1731
6	−2039/108	−6.6235	8.9277	0	8.3508
7	−169,149,119 ÷ 3,888,000	6.4547	5.4878	9.7975	0

Table II. Coefficients $\overline{B}_i$ and $\overline{C}_i$, for Different Values of the Parameter κ, for Hard Rods $(L \gg B)$

		$\overline{C}_i/(L^2B)^{i-1}$				
i	$\overline{B}_i/(L^2B)^{i-1}$	$\kappa(n = 4) = 0.1908$	$\kappa(n = 5) = 0.06524$	$\kappa(n = 6) = 0.1700$	$\kappa(n = 7) = 0.08867$	$\kappa(n = 8) = 0.1601$
1	1	1	1	1	1	1
2	2/3	0.4759	0.6014	0.4967	0.5780	0.5066
3	0	−0.2180	−0.08273	−0.1978	−0.1104	−0.1878
4	−16/243	0	−0.05761	−0.01295	−0.05082	−0.01871
5	−4/243	0.01659	0	0.01605	0.005094	0.01542
6	$2926/5025 \times 3^5$	−0.001703	0.005023	0	0.004718	0.0007845
7	$3424/3^{10} \times 25$	−0.001229	0.0006914	−0.001335	0	−0.001311
8	$7,497,527 \div 2 \cdot 3^{13} \cdot 5^3 \cdot 7^2$	0.0002813	−0.0003426	0.00009251	−0.0003987	0

Another example along the above lines is provided by the system of hard, very long and very thin rectangular parallelepipeds ($L \times B \times B$, with $L \gg B$), where the first eight virial coefficients are available$^{(3,5)}$; only those orientations are allowed in which the (long axis of the) rod lies along one of the space-fixed coordinate axes. Table II shows that $\kappa^{\text{h.r.}}$ oscillates with n and tends to a value near 0.1. The y-expansion (as well as the virial series) converges quite fast as long as the dimensionless density $L^2B\rho$ is less than about 1.3 (the limit of stability of an isotropic phase—see below).

4. GENERALIZED y-EXPANSION

While the y-expansion provides an excellent description of the thermodynamics of hard-particle fluids, some problems arise when we try to use it for *smooth* potentials or for potentials with attracting tails on top of the hard cores. In these cases it is not clear how to define in a unique way the particle volume v_0 and thereby the basic function y. Difficulties are, in fact, not exhausted by arbitrariness in the choice of v_0; unphysical behavior is predicted by the y-expansion for *non*additive mixtures when interaction between unlike particles tends to zero.

4.1. Attractive Forces: y-Expansion Difficulties

Consider, for example, a square-well potential

$$u^{\text{sw}}(r) = \begin{cases} +\infty, & r < \sigma \\ -\epsilon, & \sigma < r < \lambda\sigma \\ 0, & \lambda\sigma < r \end{cases} \tag{21}$$

We set

$$v_0 = \tfrac{1}{6}\pi\sigma^3[1 + \lambda^3(e^{-\beta\epsilon} - 1)] \tag{22}$$

so that in the limit of high temperatures ($\beta \to 0$), v_0 tends to a hard-core volume, while in the opposite case ($T \to 0$), v_0 becomes a difference between the hard core volume $\frac{1}{6}\pi\sigma^3$ and the "whole" volume $\frac{1}{6}\pi\lambda^3\sigma^3$ of the potential (including both repulsive and attractive forces). With κ given by (20),[4] the choice (22) yields the following critical parameters ($\lambda = 1.5$):

$$\tilde{T}_c = 1.459, \quad \tilde{\rho}_c = 0.244, \quad \tilde{P}_c = 0.103, \quad \beta_c\tilde{P}_c/\tilde{\rho}_c = 0.289 \tag{23}$$

in good agreement with experimental data for simple fluids.$^{(15)}$ (Here the tilde on a quantity denotes its having been reduced in the usual way to dimensionless form: $\tilde{T} = kT/\epsilon$, $\tilde{\rho} = \frac{1}{6}\rho\pi\sigma^3$, $\tilde{P} = \frac{1}{6}P\pi\sigma^3/\epsilon$). But it turns out

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[4] If we instead chose κv_0 to satisfy Eq. (19) for all T we would find $|v_0\kappa| \sim \exp(2\beta\epsilon) \gg 1$ at low temperature, and thus $y \sim \exp(-2\beta\epsilon)$. Then $|B_n| \sim \exp[n(n-1)\beta\epsilon/2]$, with the same holding for $|C_n|$, and the y-expansion diverges. The choice (20) and (22) does not prevent this catastrophe, but at least leads to reasonable critical parameters, while (19) does not.

that the Maxwell construction in the two-phase region is possible only for a narrow range of temperature ($\tilde{T}_c > \tilde{T} > \tilde{T}_0 = 1.19$); below $\tilde{T}_0$, Y_3 exhibits unphysical behavior [$\bar{C}_3(\tilde{T} < \tilde{T}_0) < 0$]. In addition, the y-expansion converges very slowly (if at all) in the neighborhood of the critical point.

4.2. Nonadditivity: Further Problems

Difficulties also appear when the y-expansion is applied to systems whose molecules interact through the potential (11) but with condition (11a) violated. Consider, for example, a hard-sphere binary mixture with *non*additive diameters:

$$\sigma_{12} \equiv \tfrac{1}{2}(\sigma_{11} + \sigma_{22})(1 + \Delta), \qquad \Delta \geqslant -1, \Delta \neq 0 \tag{11b}$$

In the case of positive nonadditivity—in particular, $\Delta = 0.2$—Y_3 represents machine calculation well, although not so well as for $\Delta = 0$.$^{(9)}$ For *negative* Δ the description of the mixture thermodynamics is worse; use of Y_3 even leads to the conclusion that a system with $\Delta < -0.2$ (see Fig. 7 of Ref. 9) undergoes a phase separation at high densities (hardly a probable result). In the extreme case $\Delta = -1$ (for which unlike particles do not interact between themselves) no truncation of the y-expansion can represent the true ("ideal gas") behavior of such a system:

$$F_{\text{mixture}}(\Delta = -1) = \sum_{\gamma=1}^{\nu} F_\gamma \tag{24}$$

4.3. Generalized y-Expansion

4.3.1. Definition. These examples point up the need for generalization of the y-expansion. Probably the simplest one comes from replacing the basic function (13a) by

$$y_\alpha = \rho_\alpha \bigg/ \left(1 - \sum_{\gamma=1}^{\nu} \psi_\gamma{}^\alpha \rho_\gamma\right) \tag{13b}$$

Expression (14) still holds, if the coefficients $\bar{C}_{\gamma_1 \ldots \gamma_n}$ satisfy the following relation:

$$\begin{aligned} \bar{B}_{\gamma_1 \cdots \gamma_{n+1}} = {} & \frac{1}{n+1} \sum_{j=1}^{n+1} \prod_{\substack{i=1 \\ i \neq j}}^{n+1} \psi_{\gamma_i}^{\gamma_j} + \bar{C}_{\gamma_1 \cdots \gamma_{n+1}} \\ & + \sum_{m=1}^{n-1} \sum_{\{i_1 \ldots i_{n+1}\}} \sum_{\substack{n-m \geqslant l_1, \cdots, l_m \geqslant 0 \\ (\sum_{j=1}^{m} l_j = n-m)}} \frac{n}{m(n+1)!} \\ & \times \bar{C}_{\gamma_{i_1} \cdots \gamma_{i_{m+1}}} \prod_{\substack{j=1 \\ (p = m+1+l_1+\cdots+l_{j-1}+k_j)}}^{m} \prod_{k_j=1}^{l_j} \psi_{\gamma_{i_p}}^{\gamma_{i_j}} \end{aligned} \tag{16a}$$

Equations (17) and (18) are also replaced by somewhat more complicated ones:

$$\beta P = \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \bar{C}_{\gamma_1 \cdots \gamma_n} \varphi^{\gamma_1 \cdots \gamma_n} \prod_{i=1}^{n} y_{\gamma_i} \qquad (\bar{C}_\gamma = \varphi_\gamma = 1) \tag{17a}$$

and

$$\beta\mu_\alpha = \beta{\mu_\alpha}^0 + \ln y_\alpha + \frac{1}{V} \int f_\alpha \ln f_\alpha \, d\mathbf{X}$$

$$+ \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \left(\frac{1 + \sum_{i=1}^{n} \varphi_\alpha^{\gamma_i}}{n} \bar{C}_{\alpha\gamma_1 \cdots \gamma_n} + \bar{C}_{\gamma_1 \cdots \gamma_n} \psi_\alpha^{\gamma_1 \cdots \gamma_n} \right) \prod_{i=1}^{n} y_{\gamma_i} \tag{18a}$$

Here

$${\varphi_\beta}^\alpha = \frac{1 - \sum_{\gamma=1}^{\nu} {\psi_\gamma}^\alpha \rho_\gamma}{1 - \sum_{\gamma=1}^{\nu} {\psi_\gamma}^\beta \rho_\gamma} = \frac{\rho_\alpha}{\rho_\beta} \frac{y_\beta}{y_\alpha} \tag{25}$$

$$\psi_\alpha^{\gamma_1 \cdots \gamma_n} = \frac{1}{n(n-1)} \sum_{j=1}^{n} \sum_{\substack{i=1 \\ j \neq i}}^{n} \varphi_{\gamma_i}^{\gamma_j} \psi_\alpha^{\gamma_i} \tag{26}$$

and

$$\varphi^{\gamma_1 \cdots \gamma_n} = \frac{1}{n(n-1)} \sum_{j=1}^{n} \sum_{\substack{i=1 \\ j \neq i}}^{n} \varphi_{\gamma_i}^{\gamma_j} \tag{27}$$

Equations (16a)–(18a) reduce to (16)–(18) when ${\psi_\alpha}^\gamma \to \kappa v_{0\alpha}$ and thus ${\varphi_\gamma}^\alpha \to 1$, $\varphi^{\gamma_1 \cdots \gamma_n} \to 1$, and $\psi_\alpha^{\gamma_1 \cdots \gamma_n} \to \kappa v_{0\alpha}$.

Comparing Eq. (18a) with Eq. (47) of I shows that the scaled particle theory can be derived by applying the following procedure: (i) represent μ_α by a Y_3 truncation of expansion (18a); (ii) calculate ${\psi_\beta}^\alpha$ with the help of the second virial coefficient [see Eq. (36a) of I]; (iii) write $\bar{C}_{\alpha\beta} = \bar{B}_{\alpha\beta} - \frac{1}{2}({\psi_\beta}^\alpha + {\psi_\alpha}^\beta)$, consistent with (16a); (iv) represent the third-order coefficient $\bar{C}_{\alpha\beta\gamma}$ as the asymmetric product $\bar{C}_{\alpha\beta}\bar{C}_{\alpha\gamma}$; (v) take ${\varphi_\beta}^\alpha$ to be identically unity; and (vi) replace the last term on the right-hand side of (18a)—which reduces to $\beta v_{0\alpha}P$ when ${\psi_\alpha}^\gamma \to v_{0\alpha}$—by expression (42) of I. As discussed in I, steps (iv)–(vi) are incorrect in general and lead under several important circumstances to fundamental inconsistencies.

The limit mentioned just above suggests that we should set

$${\psi_\alpha}^\alpha = \kappa v_{0\alpha} \tag{28}$$

which assures

$$\bar{C}_{\underbrace{\alpha \cdots \alpha}_{n}} = \sum_{i=1}^{n-1} (-{\psi_\alpha}^\alpha)^i \binom{n-i}{i} B_{\underbrace{\alpha \cdots \alpha}_{n-i}} = 0 \tag{19a}$$

But, in general, the remaining $\binom{n+\nu-1}{n} - \nu$ coefficients of the nth-order terms in (14) cannot be nullified by means of $\nu(\nu - 1)$ parameters $\psi_\beta{}^\alpha$ $(\alpha, \beta = 1,\ldots, \nu;\ \alpha \neq \beta)$. We can, however, *minimize* their contribution, using, for example, the following procedure. First, define a general set of "mole fractions" by

$$x_\alpha = y_\alpha \Big/ \sum_{\gamma=1}^{\nu} y_\gamma \tag{29a}$$

Then consider the quantity

$$I_\alpha^{(n)} = \left| \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \bar{C}_{\alpha\gamma_1\cdots\gamma_n} \prod_{i=1}^{n} x_{\gamma_i} \right| \tag{29b}$$

as a function of the $\{x_\gamma\}$ and $\{\psi_\beta{}^\alpha\}$. [Note that $I_\alpha^{(n)}$ times $\sum_{\gamma=1}^{\nu} y_\gamma/n$ is the nth-order term in expansion (14).] For each set of $\{\psi_\beta{}^\alpha\}$ we maximize $I_\alpha^{(n)}$ with respect to $\{x_\gamma\}$ $(\sum_{\gamma=1}^{\nu} x_\gamma = 1)$ and define

$$f_\alpha^{(n)}(\{\psi_\gamma{}^\beta\}) = \underset{\{x_\gamma\}}{\text{maximum}}\ I_\alpha^{(n)}(\{\psi_\gamma{}^\beta;\ x_\gamma\}) \tag{29c}$$

Finally, we choose the $\{\psi_\alpha{}^\beta\}$ so as to minimize the sum of the $f_\alpha^{(n)}$:

$$F_n = \underset{\{\psi_\gamma{}^\beta\}}{\text{minimum}} \sum_{\alpha=1}^{\nu} f_\alpha^{(n)}(\{\psi_\gamma{}^\beta\}) \tag{29d}$$

4.3.2. Additive Binary Hard-Sphere Mixtures. In the case of a binary fluid, for example, the above procedure yields the following simultaneous equations $(n = 4, \nu = 2)$:

$$f_\alpha^{(4)} = \underset{0 \leqslant x_\alpha \leqslant 1}{\text{maximum}} \left| \bar{C}_{\alpha\beta\beta\beta}(1 - x_\alpha)^3 + 3\bar{C}_{\alpha\alpha\beta\beta}x_\alpha(1 - x_\alpha)^2 + 3\bar{C}_{\alpha\alpha\alpha\beta}x_\alpha{}^2(1 - x_\alpha) \right|$$

$$(\alpha, \beta = 1 \text{ or } 2;\ \beta \neq \alpha) \tag{29e}$$

and

$$F_4 = \underset{\{\psi_2^1, \psi_1^2\}}{\text{minimum}} (f_1^{(4)} + f_2^{(4)}) \tag{29f}$$

Thus the $\{\psi_\beta{}^\alpha\}$ can be determined as soon as all of the fourth virial coefficients are known. Table III presents the parameters $\bar{C}_{\alpha\beta\gamma\delta}$, $\psi_\beta{}^\alpha$, and F_4 for two binary mixtures whose $\bar{B}_{\alpha\beta\gamma\delta}$ are available from the literature.(16) It is seen that $\psi_\alpha{}^\beta \approx \psi_\alpha{}^\alpha = \kappa v_{0\alpha}$ [the small difference between $\psi_\alpha{}^\beta$ and $\psi_\alpha{}^\alpha$ derives most probably from $\sim 1\%$ uncertainty in the computed $\bar{B}_{\alpha\beta\gamma\delta}$ and from arbitrariness in the criterion (29)]. Accordingly, the y-expansion based on (13a) should provide a good equation of state for hard-sphere mixtures with additive diameters (consistent with our previous discussions—the isotherms with $\psi_\alpha{}^\beta$ listed in Table III are practically indistinguishable from those depicted in Fig. 1).

Table III. Parameters of the y-Expansion for Two Hard-Sphere Mixtures with Additive Diameters[a]

	$\frac{\pi}{6}\sigma_{11}^3 = 1.5^3;\ \frac{\pi}{6}\sigma_{12}^3 = 1;\ \frac{\pi}{6}\sigma_{22}^3 = 0.5^3$	$\frac{\pi}{6}\sigma_{11}^3 = 1.25^3;\ \frac{\pi}{6}\sigma_{22}^3 = 0.75^3;\ \frac{\pi}{6}\sigma_{12}^3 = 1$
$\psi_1{}^1$	3.1517	1.8239
$\psi_2{}^1$	0.1012	0.3700
$\psi_1{}^2$	3.3287	2.0184
$\psi_2{}^2$	0.1167	0.3940
$\bar{B}_{1111}$	706.0034	136.8282
$\bar{B}_{1112}$	85.510	47.341
$\bar{B}_{1122}$	7.2915	14.564
$\bar{B}_{1222}$	0.5530	4.6235
$\bar{B}_{2222}$	0.03587	1.3789
$\bar{C}_{1112}$	0.08012	0.2549
$\bar{C}_{1122}$	-0.2259	-0.6699
$\bar{C}_{1222}$	0.00071	-0.0672
F_4	0.1646	0.5301

[a] We have optimized convergence of the y-expansion at the $n = 4$ level (see text).

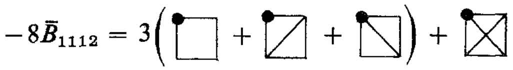
4.3.3. Nonadditive Binary Hard-Sphere Mixtures.

In the case of *extreme* nonadditivity—for which unlike particles do not interact at all with each other [$\Delta = -1$ in Eq. (11b)]—we can determine the $\psi_\beta{}^\alpha$ parameters simply by taking

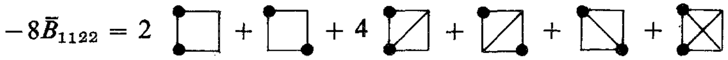
$$\psi_\beta{}^\alpha = \tfrac{1}{6}\kappa\pi\sigma_{\alpha\beta}^3 \quad (= 0 \quad \text{if} \quad \alpha \neq \beta) \tag{30}$$

It follows further from (30) and from the "diagonality" of the virial coefficients (and hence $\bar{C}$) that Eq. (24) is satisfied exactly, removing the difficulty mentioned earlier (see Section 4.2) of the y-expansion.

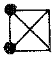
But when $\sigma_{12} \neq 0$ (and $\Delta \neq 0$) numerical calculations show that the simple rule (30) no longer leads to an adequate equation of state. For example, Y_3 with $\psi_2{}^1 = \psi_1{}^2 = 0.3v_{12}$ provides an excellent equation of state for the binary h.s. mixture $\sigma_{11} = \sigma_{22}$ and $\sigma_{12} = 1.2\sigma_{11}$ ($\Delta = 0.2$); this system has been the subject of a recent molecular dynamics simulation.(17) Thus we turn instead to relations (29), which require knowledge of all the fourth virial coefficients (in the case $n = 4$). As is clear from the usual diagrammatic representations



(31a)



(31b)

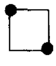
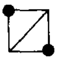
the $\bar{B}_{\alpha\beta\gamma\delta}$ incorporate a fully connected diagram (, ) which requires for its evaluation the use of Monte Carlo techniques.[5] For these reasons the $\bar{B}_{\alpha\beta\gamma\delta}$ have been computed only for the cases listed in Table III, i.e., for hard spheres with additive diameters.

Fortunately, for a special nonadditive mixture where molecules of one component (say 2) do not interact among themselves ($\sigma_{22} = 0$), the fourth virial coefficients can be determined in a relatively straightforward way. In fact it follows from (31) that the only nonvanishing $\bar{B}^{\text{nonadd}}_{\alpha\beta\gamma\delta}$ are

$$\bar{B}^{\text{nonadd}}_{1112}\left(\sigma_{11};\, \sigma_{12} = \sigma_{11}\frac{1+\Delta}{2};\, \sigma_{22} = 0\right)$$

$$= \bar{B}^{\text{add}}_{1112}\left(\sigma_{11};\, \sigma_{22} = \sigma_{11}\frac{1+\Delta}{2};\, \sigma_{22} = \Delta\sigma_{11}\right)$$

and

$$\bar{B}^{\text{nonadd}}_{1122} = -\frac{1}{8}\Bigg($$  $$+$$  $$\Bigg) \equiv -\tfrac{1}{8}(J_4 + J_5) \tag{32}$$

Here

$$J_k = 4\pi(-1)^k \int_0^{a_k} r^2\, dr\, [g(r)]^2 \tag{33}$$

$$g(r) = \int d\mathbf{s}\, H(\sigma_{12} - s)H(\sigma_{12} - |\mathbf{s} - \mathbf{r}|) \tag{34}$$

and

$$a_4 = 2\sigma_{12}, \qquad a_5 = \text{minimum}(\sigma_{11}, 2\sigma_{12}) \tag{35}$$

[$H(x)$ is the unit step function.] Inserting$^{(18)}$

$$g(r) = \tfrac{4}{3}\pi(\sigma_{12}^3 - \tfrac{3}{4}r\sigma_{12}^2 + \tfrac{1}{16}r^3)H(2\sigma_{12} - r) \tag{34a}$$

into (33) and performing the r integration, we get

$$\begin{aligned} &B^{\text{nonadd}}_{1122}\left(\sigma_{11};\, \sigma_{12} = \sigma_{11}\frac{1+\Delta}{2};\, \sigma_{22} = 0\right) \\ &\quad = 0, \qquad \Delta \leqslant 0 \\ &\quad = \frac{128}{105}\left(\frac{\pi}{6}\sigma_{12}^3\right)^2 \left[\frac{420}{(1+\Delta)^3} - \frac{945}{(1+\Delta)^4} + \frac{567}{(1+\Delta)^5} \right. \\ &\qquad \left. + \frac{210}{(1+\Delta)^6} - \frac{270}{(1+\Delta)^7} + \frac{35}{(1+\Delta)^9} - 17\right], \qquad \Delta \geqslant 0 \end{aligned} \tag{32a}$$

---

[5] See the Monte Carlo calculations described in Ref. 16, and earlier work cited there.

Table IV presents the fourth virial coefficients of several hard-sphere binary mixtures with nonadditive diameters. Unfortunately, (29e) and (29f) do not always lead to a reasonable set of $\{\psi_\beta{}^\alpha\}$.

Consider, for example, the extreme case $\Delta = \infty$; this is the familiar "penetrable hard sphere" model ($\sigma_{11} = 0 = \sigma_{22}$, $\sigma_{12} \neq 0$). We have

$$\begin{aligned} \bar{C}_{1112} &= \tfrac{1}{8}(\psi_1{}^2)^2(\psi_2{}^1 + \psi_1{}^2 - 8) \\ \bar{C}_{1122} &= B_{1122} + \tfrac{1}{3}\psi_2{}^1\psi_1{}^2(16 - \psi_2{}^1 - \psi_1{}^2) \\ \bar{C}_{1222} &= \tfrac{1}{8}(\psi_2{}^1)^2(\psi_2{}^1 + \psi_1{}^2 - 8) \end{aligned} \tag{36}$$

All of these $\bar{C}_4$'s can be nullified (hence guaranteeing $F_4 = 0$) by setting

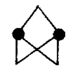
$$\psi_2{}^1 = 4 \pm (16 + 0.375\bar{B}_{1122})^{1/2}, \qquad \psi_1{}^2 = 4 \mp (16 + 0.375\bar{B}_{1122})^{1/2} \tag{37}$$

But these results violate the condition

$$\psi_2{}^1 = \psi_1{}^2 \tag{38}$$

which follows from the fact that both components enter symmetrically into the y-expansion and the symmetry of the system under consideration. Thus we need to apply (29c) and (29d) at the $n = 5$ level. Fortunately the simplicity of the $\Delta = \infty$ case allows us to calculate the necessary fifth virial coefficients ($\alpha, \beta = 1$ or 2):

$$\bar{B}_{\alpha\alpha\alpha\alpha\alpha} = 0 = \bar{B}_{\alpha\alpha\alpha\alpha\beta} \tag{39}$$

$$\bar{B}_{\alpha\alpha\alpha\beta\beta} = -\frac{1}{30}$$  $$= -\frac{\pi}{15}\int_0^{2\sigma_{12}} r^2\, dr\, [g(r)]^3 = -\frac{2^8(41)}{525}\left(\frac{\pi}{6}\sigma_{12}^3\right)^4$$

and accordingly

$$\begin{aligned} \bar{C}_{\alpha\alpha\alpha\alpha\beta} &= \tfrac{1}{30}(\psi_\alpha{}^\beta)^3(\psi_\beta{}^\alpha + 3\psi_\alpha{}^\beta - 8) \\ \bar{C}_{\alpha\alpha\alpha\beta\beta} &= \bar{B}_{\alpha\alpha\alpha\beta\beta} - \tfrac{6}{5}\bar{B}_{\alpha\alpha\beta\beta}\psi_\alpha{}^\beta + \tfrac{1}{60}\psi_\beta{}^\alpha(\psi_\alpha{}^\beta)^2(7\psi_\beta{}^\alpha - 5\psi_\alpha{}^\beta - 88) \end{aligned} \tag{40}$$

The parameters $\{\psi_\alpha{}^\beta\}$ can then be determined via the F_n criterion with $n = 5$. Table V displays the results, along with the corresponding values of the $\bar{B}$'s and $\bar{C}$'s. Note that the condition (38) is satisfied and that F_5 is indeed quite small.

For finite Δ the necessary information about the fifth virial coefficients is not available and the values of $\psi_2{}^1$ and $\psi_1{}^2$ cannot be determined via the above-described route. We can, however, proceed instead by simply *interpolating* between the known limits involving $\Delta = \infty$ and $\Delta = 0$. [For the $\Delta = 0$ case the $\psi_2{}^1$, $\psi_1{}^2$ parameters can be evaluated exactly—see Eq. (68) below.] In this way we find

$$\begin{aligned} \psi_2{}^1 &= 0.82815(v_{12} - \tfrac{1}{8}v_{11}) \\ \psi_1{}^2 &= 0.82815(v_{12} - \tfrac{1}{8}v_{11}) + v_{11} \end{aligned} \tag{41}$$

Table IV. The Fourth Virial Coefficient of Hard-Sphere Mixtures with $\sigma_{11} = 2\sigma_{12}/(1 + \Delta)$, $\sigma_{22} = 0$ $(\frac{1}{6}\pi\sigma_{12}^3 = 1)$

Δ	∞	3	5/3	1	3/5	1/3	0
$\bar{B}_{1111}$	0	0.035869	1.37891	18.36477	136.82819	706.0034	9702.7619
$\bar{B}_{1112}$	0	0.55296	4.62336	18.36477	47.3408	85.5104	128
$\bar{B}_{1122}$	−20.7238	−16.50624	−11.00435	5.61190	−1.96895	−0.36796	0

Table V. The $\psi_\alpha{}^\beta$ Parameters of the y-Expansion for a Mixture of "Penetrable Hard Spheres" ($\sigma_{11} = \sigma_{22} = 0$, $\frac{1}{6}\pi\sigma_{12}^3 = 1$)[a]

$\psi_2{}^1 = \psi_1{}^2$	0.8282	$\bar{C}_{112}$	-1.9797
$\bar{B}_{12}$	4	$\bar{C}_{1112}$	-0.5438
$\bar{B}_{1122}$	-20.7238	$\bar{C}_{1122}$	-17.445
$\bar{B}_{11122}$	-19.9924	$\bar{C}_{11112}$	-0.08874
$\bar{C}_{12}$	3.1719	C_{11122}	-0.2150
		F_5	0.1775

[a] We have optimized convergence at the $n = 5$ level.

where

$$v_{11} = \tfrac{1}{6}\pi\sigma_{11}^3 \qquad \text{and} \qquad v_{12} = \tfrac{1}{6}\pi\sigma_{12}^3 \tag{41a}$$

Although there are no machine calculation data available to check the results discussed above, our previous experience with the y-expansion suggests that we might expect it to provide a respectable equation of state for nonadditive mixtures with $\sigma_{22} = 0$. This is especially useful since such fluids are equivalent (see Ref. 19 and Section 4.3.4) to a system whose particles interact via a potential with an attractive tail.

4.3.4. Widom–Rowlinson Correspondence.

Consider a ν-component mixture whose total intermolecular potential is given by $U_N(\mathbf{X}^{(n)})$. Let us add to this system a $(\nu + 1)$th component—call it species 0—whose particles do not interact among themselves, but exert instead a potential $U_N{}^0$ upon the remaining species. The grand canonical partition function for this $(\nu + 1)$-component system can be written exactly as

$$\Xi_{\nu+1} = \sum_{N_0=0}^{\infty} \sum_{N_1=0}^{\infty} \cdots \sum_{N_\nu=0}^{\infty} \left(\prod_{\alpha=0}^{\nu} \frac{z_\alpha^{N_\alpha}}{N_\alpha!} \right) \int \cdots \int d\mathbf{X}^{(N+N_0)} \exp(-\beta U_{N+N_0}) \tag{42}$$

where ($N = \sum_{\alpha=1}^{\nu} N_\alpha$)

$$U_{N+N_0} \equiv U_N + \sum_{i_0=1}^{N_0} U_N{}^0(\mathbf{X}_{i_0}; \mathbf{X}^{(N)}) \tag{43}$$

and

$$z_\alpha = \exp[\beta(\mu_\alpha - \mu_\alpha{}^0)] \tag{44}$$

Let $-\ln W_N(\mathbf{X}^{(n)})$ be a potential of mean force[6] acting on a molecule of species 0:

$$W_N(\mathbf{X}^{(N)}) = \int d\mathbf{X}_0 \exp[-\beta U_N{}^0(\mathbf{X}_0; \mathbf{X}^{(N)})] \tag{45}$$

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[6] Our definition of $-\ln W$ differs from Hill's (see Ref. 18, pp. 193–195) by an additive constant.

Then we can write

$$\sum_{N_0=0}^{\infty} \frac{z_0^{N_0}}{N_0!} \int \cdots \int d\mathbf{X}^{N_0} \exp\left[-\beta \sum_{i_0=1}^{N_0} U_N{}^0(\mathbf{X}_{i_0})\right] = \sum_{N_0=0}^{\infty} \frac{z_0^{N_0}}{N_0!} W_N^{N_0} = \exp(Z_0 W_N) \tag{46}$$

Inserting this into (42) yields

$$\begin{aligned} &\exp[V(\beta P_{\nu+1} - z_0)] \\ &\quad = \Xi_{\nu+1} \exp(-V z_0) \\ &\quad = \sum_{N_1=0}^{\infty} \cdots \sum_{N_\nu=0}^{\infty} \left(\prod_{\alpha=1}^{\nu} \frac{\hat{z}_\alpha^{N_\alpha}}{N_\alpha!}\right) \int \cdots \int d\mathbf{X}^{(N)} \exp(-\beta \hat{U}_N) \\ &\quad = \hat{\Xi}_\nu = \exp(V\beta \hat{P}_\nu) \end{aligned} \tag{47}$$

where

$$\hat{U}_N = U_N + \frac{z_0}{\beta}\left(V - W_n - 2\sum_{\alpha=1}^{\nu} N_\alpha \bar{B}_{0\alpha}\right) \tag{48}$$

$$\hat{z}_\alpha = z_\alpha \exp(-2\bar{B}_{0\alpha} z_0) \tag{49}$$

and

$$\bar{B}_{0\alpha} = \frac{1}{2}\int d\mathbf{X}_{0\alpha} \{1 - \exp[-\beta U_1{}^0(\mathbf{X}_0; \mathbf{X}_\alpha)]\} \tag{50}$$

is the second virial coefficient.

Since the activity z_0 (i.e., the concentration ρ_0) is arbitrary, we can set it proportional to the reciprocal temperature

$$z_0 = \epsilon\beta/\bar{v}_0 \tag{51}$$

where

$$\bar{v}_0 = \frac{2}{N}\sum_{\alpha=1}^{\nu} N_\alpha \bar{B}_{0\alpha} \tag{52}$$

ϵ is a constant with dimensions of energy; $\bar{v}_0$, defined by the particular choice shown in (52), is a volume. It follows from (47) that $P_{\nu+1} - \epsilon/\bar{v}_0$ is the pressure $\hat{P}$ of a ν-component mixture whose molecules interact via potential $\hat{U}_N$ which incorporates, in addition to the total potential U_N, a nonpairwise-additive interaction

$$U_N^{\text{tail}}(\mathbf{X}^{(N)}) = \epsilon\left[\frac{V - W_N(\mathbf{X}^{(N)})}{\bar{v}_0} - N\right] \tag{53}$$

(Obviously, in the special case where $U_N{}^0$ is a cutoff potential and U_N repulsions prohibit more than two molecules from interacting simultaneously with a 0 particle, U_N^{tail} will be pairwise additive even if $U_N{}^0$ itself is not.)

Equations (49) and (51) determine the activity (chemical potential) of the αth component. Thus the $(\nu + 1)$-component mixture with total potential U_{N+N_0} [Eq. (43)] is thermodynamically equivalent to a ν-component mixture with potential $\hat{U}_N$ [Eq. (48)]. This equivalence is established explicitly by the following equalities:

$$P_{\nu+1} = \hat{P}_\nu + \frac{\epsilon}{\bar{v}_0} \tag{54}$$

$$\frac{1}{z_0}\frac{\epsilon}{k\bar{v}_0} = T \tag{55}$$

$$\rho_\alpha = z_\alpha \frac{\partial \beta P_{\nu+1}}{\partial z_\alpha} = z_\alpha \left(\sum_{\gamma=1}^{\nu} \frac{\partial \beta \hat{P}_\nu}{\partial \hat{z}_\gamma} \frac{\partial \hat{z}_\gamma}{\partial z_\alpha} + \frac{\partial \beta \hat{P}_\nu}{\partial \beta} \frac{\partial \beta}{\partial z_\alpha} \right) = \hat{\rho}_\alpha, \qquad \alpha = 1,\ldots,\nu \tag{56}$$

$$\rho_{\nu+1} \equiv \rho_0 = \frac{\beta\epsilon}{\bar{v}_0}\left(1 - 2\sum_{\gamma=1}^{\nu} \hat{\rho}_\gamma \bar{B}_{0\gamma}\right) - \frac{\beta\hat{E}}{V} \tag{57}$$

and

$$\beta\mu_\alpha = \beta\hat{\mu}_\alpha + 2\frac{\bar{B}_{0\alpha}}{\bar{v}_0}\beta\epsilon \tag{58}$$

Here $\hat{E}$ is the internal energy and, as before, the caret on properties refers to their values for a ν-component system with interaction U_N^{tail} added to the original U_N.

In addition to these thermodynamic quantities, it is possible to show further that the *microscopic* structure of the ν-component system also follows from the $(\nu + 1)$-component system. Introducing the n-particle distribution function

$$\rho_{\nu+1}^{(n)}(\mathbf{X}^{(n)}) = \frac{1}{\Xi_{\nu+1}} \sum_{N_0=0}^{\infty} \sum_{N_1=n_1}^{\infty} \cdots \sum_{N_\nu=n_\eta}^{\infty} \left[\prod_{\alpha=0}^{\nu} \frac{z_\alpha^{N_\alpha}}{(N_\alpha - n_\alpha)!} \right] \times \int \cdots \int d\mathbf{X}^{(N+N_0-n)} \exp(-\beta U_{N+N_0}) \tag{59}$$

and inserting (46) into its integrand leads to

$$\rho_{\nu+1}^{(n)}(\mathbf{X}^{(n)}) = \frac{1}{\hat{\Xi}_\nu} \sum_{N_1=n_1}^{\infty} \cdots \sum_{N_\nu=n_\nu}^{\infty} \left[\prod_{\alpha=1}^{\nu} \frac{\hat{z}_\alpha^{N_\alpha}}{(N_\alpha - n_\alpha)!} \right] \times \int \cdots \int d\mathbf{X}^{(N-n)} \exp(-\beta \hat{U}_N) = \hat{\rho}_\nu^{(n)}(\mathbf{X}^{(n)}) \tag{60}$$

[Here the $n \equiv \sum_{\alpha=1}^{\nu} n_\alpha$ molecules do not include any of the 0 species ($n_0 = 0$).]

For our present purposes we take $\nu = 1$, and U_N and $U_N{}^0$ to be a sum of hard-sphere potentials with diameters σ_{11} and $\sigma_{12} = \frac{1}{2}\sigma_{11}(1 + \Delta)$: recall that $\sigma_{22} = 0$. (Now it is convenient to write 2 instead of 0 for the added species.) It follows from the definition (45) of W_N that the difference $V - W_N$ is here the total volume forbidden to a molecule of species 2, and

$$V - W_N \leqslant 2N\bar{B}_{12} = N\bar{v}_0 \tag{61}$$

thereby guaranteeing that the right-hand side of (53) is nonpositive ($U_N^{\text{tail}} \leqslant 0$).

This same quantity vanishes identically when $\Delta \leqslant 0$, and thus

$$\hat{E} = \langle U_N^{\text{tail}} \rangle = 0 \tag{62}$$

Then from (54)–(58) we can write

$$z_2 = \frac{\beta\epsilon}{\bar{v}_0} = \frac{\rho_2}{1 - 2\rho_1\bar{B}_{12}} \tag{63}$$

$$\beta\mu_1(\rho_1, \rho_2) = \beta\mu_{\text{h.s.}}(\rho_1) + \frac{2\bar{B}_{12}\rho_2}{1 - 2\rho_1\bar{B}_{12}} \tag{64}$$

$$\beta\mu_2(\rho_1, \rho_2) = \ln z_2 + \beta\mu_2{}^0 = \beta\mu_2{}^0 + \ln\frac{\rho_2}{1 - 2\rho_1\bar{B}_{12}} \tag{65}$$

$$\beta P_{\text{mixture}}(\rho_1, \rho_2) = \beta P_{\text{h.s.}}(\rho_1) + \frac{\rho_2}{1 - 2\rho_1\bar{B}_{12}} \tag{66}$$

and thus

$$\beta F_{\text{mixture}}(\rho_1, \rho_2) = \beta F_{\text{h.s.}}(\rho_1) + N_2\left[\beta\mu_2{}^0 - 1 + \ln\frac{\rho_2}{1 - 2\rho_1\bar{B}_{12}}\right] \tag{67}$$

Here F_{mixture} and $F_{\text{h.s}}$ are the Helmholtz free energies of the hard-sphere mixture (σ_{11}; $\sigma_{12} = \frac{1}{2}\sigma_{11}(1 + \Delta)$; $\sigma_{22} = 0$) and of the pure hard-sphere fluid (σ_{11})—recall that $U_N^{\text{tail}} = 0$. Comparing this last result with Eq. (14) shows that in this case we can put

$$\psi_1{}^1 = \tfrac{1}{6}\kappa\pi\sigma_{11}^3, \qquad \psi_2{}^1 = 0, \qquad \psi_1{}^2 = \tfrac{4}{3}\pi\sigma_{12}^3 = 2\bar{B}_{12}, \qquad \psi_2{}^2 = 0 \tag{68}$$

and

$$\bar{C}_{2\gamma_1\cdots\gamma_n} = 0, \qquad \gamma_i = 1 \text{ or } 2; \quad n \geqslant 1 \tag{69}$$

Finally, it follows from (16a) that the corresponding virial coefficients are

$$\bar{B}_{2\gamma_1\cdots\gamma_n} = \frac{1}{n+1}\prod_{i=1}^{n}\psi_{\gamma_i}^2 = \frac{1}{n+1}\left(\tfrac{4}{3}\pi\sigma_{12}^3\right)^n\prod_{i=1}^{n}\delta_{1\gamma_i} \tag{70}$$

($\delta_{1\gamma}$ is the usual Kronecker delta function).

For *positive* nonadditivity ($\Delta > 0$), the situation is more interesting. Here the two-component hard-sphere mixture with nonadditive diameters is equivalent (in the above-described sense) to a one-component system whose molecules are "attracting hard spheres." More explicitly, their pair potential is

$$u(r) = \begin{cases} +\infty, & r < \sigma_{11} = 2\sigma_{12}/(1+\Delta) \\ -\dfrac{\epsilon}{2}\left(1 - \dfrac{r}{2\sigma_{12}}\right)^2\left(2 + \dfrac{r}{2\sigma_{12}}\right) & \\ \quad = -\epsilon_m\left(\dfrac{1 - r/2\sigma_{12}}{1 - 1/(1+\Delta)}\right)^2\left(\dfrac{2 + r/2\sigma_{12}}{2 + 1/(1+\Delta)}\right), & \sigma_{11} < r < 2\sigma_{12} \\ 0, & r > 2\sigma_{12} \end{cases} \tag{71}$$

where $\epsilon_m = u(\sigma_{11}+)$ is the depth of the attraction well. For small enough nonadditivity ($\Delta < 2/\sqrt{3} - 1 \approx 0.155$) the U_N^{tail} defined by (53) becomes a sum of the $u(r_{ij})$ in (71); as mentioned earlier, however, it is in general non-pairwise-additive.

The thermodynamics of the fluid with "triangle"-well potential (53) is described completely by the correspondences (54)–(58) and the y-expansion (14). The relevant $\psi_\beta{}^\alpha$ parameters for the y-expansion are given by (28) and (41); Table VI presents the critical parameters of a fluid of these attracting hard spheres as calculated from Y_3 for different values of the tail length $[(2\sigma_{12}/\sigma_{11}) - 1 \equiv \Delta]$. To determine a "physically reasonable" choice of Δ, we can compare the second virial coefficient for the potential (71),

$$B_2^{(71)} = \tfrac{2}{3}\pi\sigma_{11}^3\left(1 - 3(1+\Delta)^3\int_{1/(1+\Delta)}^{1} t^2\,dt\,\{\exp[\beta\epsilon^{(71)}(1-t)^2(2+t)] - 1\}\right) \tag{72a}$$

with that for the square-well (sw) potential (21),

$$B_2^{\text{sw}} = \tfrac{2}{3}\pi\sigma_{11}^3\{1 - (\lambda^3 - 1)[\exp(\beta\epsilon^{\text{sw}}) - 1]\} \tag{72b}$$

For $\epsilon^{(71)} \approx \epsilon^{\text{sw}}$ we find that $B_2^{(71)}$ recovers the temperature dependence of B_2^{sw} for $1/\beta\epsilon \equiv kT/\epsilon > 1$ if $\Delta \approx \lambda$: $\Delta \approx 1.42$ for $\lambda = 1.5$ and $\Delta \approx 1.82$ for $\lambda = 1.75$. The data listed in Table VI indicate that the systems with these

Table VI. The Y_3 Critical Parameters of a Fluid Attracting Hard Spheres[a]

Δ	$\beta P/\rho$	$v_{12}P/\epsilon$	$v_{12}\rho$	kT/ϵ_m	$(\mu - \mu_0)/\epsilon$	$v_{12}E/\epsilon V$
∞	0.256	0.0117	0.1294	0.353	−1.367	−0.0501
5	0.270	0.0112	0.126	0.521	−1.258	−0.046
5/3	0.291	0.0096	0.115	0.620	−1.030	−0.034
1	0.348	0.0069	0.098	0.631	−0.705	−0.200

[a] See text for determination of $\psi_\beta{}^\alpha$ and discussion of the nonadditivity parameter Δ.

Table VII. The Y_3 Critical Parameters of the Gaussian Model Fluid[a]

$\beta P/\rho$	$(\sqrt{\pi}\sigma)^3 P/\epsilon$	$(\sqrt{\pi}\sigma)^3\rho$	kT/ϵ	$(\mu-\mu^0)/\epsilon$	$(\sqrt{\pi}\sigma)^3 E/\epsilon V$
0.277	0.1018	0.12	2.925	−10.140	−0.3730

[a] $\psi_1{}^1 = \psi_2{}^2 = 0$ and $\psi_2{}^1 = \psi_1{}' = 0.34615(\sqrt{\pi}\sigma)^3$.

values of Δ (i.e., $\Delta \approx 5/3$) are the best in describing real examples of simple fluids.(15) Our Y_3 results for the penetrable hard-sphere model ($\Delta \to \infty$) can be compared with those found in the mean field approximation,(19) $\beta P/\rho = 0.282$, $v_{12}\rho = 0.125$, $kT/\epsilon = 0.368$, and $v_{12}P/\epsilon = 0.0130$; and in the Percus–Yevick approximation,(20) $v_{12}\rho = 0.140$, $kT/\epsilon = 0.330$, $v_{12}E/\epsilon V = -0.0605$, and $(\mu-\mu_0)/\epsilon = -0.634$.

Helfand and Stillinger(4) and Melnyk *et al.*(20) have considered the "Gaussian" model according to which $U_N \equiv 0$ and

$$U_N{}^0 = -kT \sum_{i=1}^{N} \ln[1 - \exp(-r_{0i}^2/\sigma^2)] \tag{73}$$

where r_{0i} is the distance between the test particle of the 2 species and the ith molecule of species 1. The critical parameters for this system (with virial coefficients from Ref. 4 and $n = 5$ optimization[7]) are displayed in Table VII.

Note that either of the above mixtures can be used as a reference system for perturbation calculations on fluids of molecules interacting via potentials including both repulsions and attractions. The required radial distribution function $\hat{g}$ of the reference system is given by Eq. (60) and the corresponding y-expansion of g_{11} in the binary mixture. In general we have

$$g_{\alpha\beta}(\mathbf{X}) \equiv \frac{\rho_{\alpha\beta}^{(2)}(\mathbf{X})}{\rho_\alpha\rho_\beta} = \exp[-\beta u_{\alpha\beta}(\mathbf{X})]\left(1 + \sum_{n=1}^{\infty}\sum_{\gamma_1=1}^{\nu}\cdots\sum_{\gamma_n=1}^{\nu} D_{\gamma_1\cdots\gamma_n}^{\alpha\beta}(\mathbf{X})\prod_{i=1}^{n} y_{\gamma_i}\right) \tag{74a}$$

where the coefficients $D_{\gamma_1\cdots\gamma_n}^{\alpha\beta}$ are related to the coefficients $G_{\gamma_1\cdots\gamma_n}^{\alpha\beta}$ in the virial expansion

$$g_{\alpha\beta}(\mathbf{X}) = \exp[-\beta u_{\alpha\beta}(\mathbf{X})]\left\{1 + \sum_{n=1}^{\infty}\sum_{\gamma_1=1}^{\nu}\cdots\sum_{\gamma_n=1}^{\nu} G_{\gamma_1\cdots\gamma_n}^{\alpha\beta}(\mathbf{X})\prod_{i=1}^{n} \rho_{\gamma_i}\right\} \tag{74b}$$

via an equation similar to (16a):

$$G_{\gamma_1\cdots\gamma_n}^{\alpha\beta} = D_{\gamma_1\cdots\gamma_n}^{\alpha\beta} + \sum_{m=1}^{n-1}\sum_{\{i_1,\cdots,i_n\}}\sum_{\substack{n-m \leqslant l_1,\cdots,l_m \geqslant 0 \\ (\sum_{j=1}^{m} l_j = n-m)}} \times \frac{n-1}{mn!} D_{\gamma_{i_1}\cdots\gamma_{i_m}}^{\alpha\beta} \prod_{\substack{j=1 \\ (p=m+l_1+\cdots+l_{j-1}+k_j)}}^{m} \prod_{k_j=1}^{l_j} \psi_{\gamma_{i_p}}^{\gamma_{i_j}} \tag{74c}$$

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[7] Equations (36) and (37) hold here as well and thus n must be equal to or greater than 5.

4.3.5. Anisotropic Fluids. In the previous sections we have concentrated on systems of spherically symmetric particles. More important (and problematic) is the application of the y-expansion to fluids of asymmetric molecules. In this section we consider anisotropic phases of liquid-crystal-forming systems composed of asymmetric particles. Unfortunately, no computer simulation to date has succeeded in seeing the isotropic → nematic transition in a three-dimensional system of hard particles whose positions and orientations are unrestricted.[21] We are therefore not able to compare our y-expansion results with "experiment."

(a) General Formulation. For our present purposes Eq. (14) for the free energy can be written in the following, more convenient form:

$$\beta F = \sum_{\alpha=1}^{\nu} N_\alpha \Big\{ \beta\mu_\alpha{}^0 - 1 + \int f_\alpha \ln f_\alpha \, d\boldsymbol{\Omega} + \ln y_\alpha$$
$$+ \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \frac{1}{n} \int \cdots \int C_{\alpha\gamma_1\cdots\gamma_n} f_\alpha \, d\boldsymbol{\Omega}_\alpha \prod_{i=1}^{n} y_{\gamma_i} f_{\gamma_i} \, d\boldsymbol{\Omega}_{\gamma_i} \Big\} \tag{14a}$$

Here the coefficients $C_{\gamma_1\cdots\gamma_n}$ (dependent on orientational coordinates) are given by Eq. (16a) but with the averaged quantities $\bar{B}_{\gamma_1\cdots\gamma_n}$ and $\bar{C}_{\gamma_1\cdots\gamma_n}$ replaced by the *un*averaged $B_{\gamma_1\cdots\gamma_n}$ [defined by Eq. (5b)] and $C_{\gamma_1\cdots\gamma_n}$. Recall that f_α is a function of particle orientation $\boldsymbol{\Omega}_\alpha$, but not of position $\mathbf{r}_\alpha$. Minimizing F with respect to $f_\gamma(\boldsymbol{\Omega}_\gamma)$ at given volume, temperature, and densities yields

$$\beta\mu_\alpha = \beta\mu_\alpha{}^0 + \ln y_\alpha + \ln f_\alpha(\boldsymbol{\Omega}_\alpha)$$
$$+ \sum_{n=1}^{\infty} \sum_{\gamma_1=1}^{\nu} \cdots \sum_{\gamma_n=1}^{\nu} \Big(\prod_{i=1}^{n} y_{\gamma_i} \Big) \Big\{ \psi^{\alpha}_{\gamma_1\cdots\gamma_n} \int \cdots \int C_{\gamma_1\cdots\gamma_n}(\boldsymbol{\Omega}_{\gamma_1},\ldots,\boldsymbol{\Omega}_{\gamma_n})$$
$$\times \prod_{i=1}^{n} f_{\gamma_i}(\boldsymbol{\Omega}_{\gamma_1}) \, d\boldsymbol{\Omega}_{\gamma_i}$$
$$+ \frac{1 + \sum_{i=1}^{n} \varphi_\alpha^{\gamma_i}}{n} \int \cdots \int C_{\alpha\gamma_1\cdots\gamma_n}(\boldsymbol{\Omega}_\alpha, \boldsymbol{\Omega}_{\gamma_1},\ldots,\boldsymbol{\Omega}_{\gamma_n}) \prod_{i=1}^{n} f_{\gamma_i}(\boldsymbol{\Omega}_{\gamma_i}) \, d\boldsymbol{\Omega}_{\gamma_i} \Big\} \tag{75}$$

For simplicity we have assumed in (75) that the coefficients $\psi_\beta{}^\alpha$ are independent of the distributions f_γ ($\gamma = 1,\ldots, \nu$). Note further that all but the third and last terms in (75) are independent of $\boldsymbol{\Omega}_\alpha$—this variable enters the equation only through the functional dependence of f_α and $C_{\alpha\gamma_1\cdots\gamma_n}$. Therefore, to calculate the equilibrium distribution of orientations $[f_\alpha(\boldsymbol{\Omega}_\alpha)]$, we need to know "only" the angle dependence of the $C_{\gamma_1\cdots\gamma_n}$ (i.e., of the virial coefficients $B_{\gamma_1\cdots\gamma_n}$).

Although formal expressions for $B_{\alpha\beta}(\boldsymbol{\Omega})$ [and thereby $C_{\alpha\beta}(\boldsymbol{\Omega})$] are known for arbitrary shaped convex bodies,[22] explicit, analytical results are available at present only for hard right-circular cylinders and spherocylinders[2] and hard ellipsoids of revolution.[23] Equations (30)–(31) in the preceding paper provide $B_{\alpha\beta}(\mathbf{\Omega})$ for a *smooth* potential having these shapes. For $B_{\alpha\beta\gamma}$ and all higher order virial coefficients (or even for $B_{\alpha\beta}$ in the case of other potentials) no analytical or formal expressions have been derived; see, however, Straley(24) for an *approximate* estimation of the angle-dependent B_3 for hard cylinders.

(b) Restricted Molecular Orientations. To simplify things, Zwanzig(3) considered systems whose molecules are artificially restricted to a few orientations. If, for example, we investigate a fluid of rectangular parallelepipeds ($L \times B \times W$), we allow only the six orientations for which the principal axes of the particles are coincident with those of a space-fixed coordinate system. In Table VIII we have collected the results (see Appendix) for the second and third virial coefficients of this system. Equation (16), with $\bar{B}_n$ and $\bar{C}_n$ replaced by the corresponding *un*averaged quantities, allows us to obtain $C_2(\mathbf{\Omega}_{12})$ and $C_3(\mathbf{\Omega}_{12}, \mathbf{\Omega}_{13})$. Inserting these values into (75), we find six coupled, nonlinear equations for the distribution function $f(\mathbf{\Omega})$. The chemical potential (or density, via y) can be eliminated by use of Eq. (18), or, equivalently, by the normalization (7) and the fact that μ_α is $\mathbf{\Omega}$-independent. This gives the orientational distribution as a function of y (density ρ) or μ. Note that the temperature is not involved since we are dealing with interparticle repulsions which are either infinite or zero. Furthermore, (75) is nonlinear *integral* equation for $f(\mathbf{\Omega})$ only in the case of *continuous* orientation. For our present restriction to *six* orientations, (75) turns into a nonlinear *algebraic* equation where integrations have been replaced by summations. The six possible Euler-angle triplets (α, β, γ) lead then to six coupled equations whose solution determines the equilibrium distribution of parallelepipeds among the six allowed orientations.

Numerical calculations based on Y_2 and Y_3 show that there exists a special density ρ^*, depending on the ratios L/W and B/W, such that for $\rho < \rho^*$ the only real solution of (75) describes a uniform orientational distribution. For higher densities ($\rho > \rho^*$) more solutions appear; we choose the nonuniform one which minimizes the free energy. This means that an anisotropic state of the fluid is stable at high enough densities. (For $L \neq B \neq W$ there are in fact *two* special densities, ρ^* and ρ^{**}, corresponding to the thresholds for uniaxial and biaxial distributions—we shall be concerned here only with the *uniaxial* solutions for f.) Using the thermodynamic relations $P_{\text{iso}} = P_{\text{aniso}}$ and $\mu_{\text{iso}} = \mu_{\text{aniso}}$, we have located the first-order phase transition and calculated the differences in ρ (and f) between the coexisting isotropic and anisotropic phases. Some of these results have already been published.(25) We have shown, in particular, that deviations ($L \neq B \neq W$) from axial symmetry can be crucial in explaining the dramatic weakness (very small $\Delta\rho$, Δf, etc.) observed for the isotropic–nematic transition.

Two basic questions must now be confronted: (1) How quickly does the

Table VIII. The Second and Third Virial Coefficients for Rectangular Parallelepipeds ($L \times B \times W$) with Restricted Orientations

Euler angles of							
Particle 2			Particle 3				
α	β	γ	α	β	γ	$B_2(\alpha_2, \beta_2, \gamma_2)$	$B_3(\alpha_2, \beta_2, \gamma_2, \alpha_3, \beta_3, \gamma_3)$
0	0	0	0	0	0	$4LBW$	$9L^2B^2W^2$
0	0	$\frac{1}{2}\pi$	0	0	0	$L(B + W)^2$	$L^2BW(B + 2W)(W + 2B)$
0	$\frac{1}{2}\pi$	0	0	0	0	$W(L + B)^2$	$W^2LB(L + 2B)(B + 2L)$
0	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	0	0	$\frac{1}{2}(L + B)(B + W)(W + L)$	$\frac{1}{3}LBW(L + 2W)(W + 2B)(B + 2L)$
$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	0	0	0	$\frac{1}{2}(L + B)(B + W)(W + L)$	$\frac{1}{3}LBW(L + 2B)(B + 2W)(W + 2L)$
$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	0	0	$B(L + W)^2$	$B^2LW(L + 2W)(W + 2L)$
$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	0	$\frac{1}{2}\pi$	$B(L + W)^2$	$\frac{1}{3}LB(L + 2W)(B + 2W)(LB + BW + WL)$
$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	0	0	$\frac{1}{2}\pi$	$\frac{1}{2}(L + B)(B + W)(W + L)$	$\frac{1}{3}LW(L + 2B)(W + 2B)(LB + BW + WL)$
$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	0	$\frac{1}{2}\pi$	0	$\frac{1}{2}(L + B)(B + W)(W + L)$	$\frac{1}{3}BW(B + 2L)(W + 2L)(LB + BW + WL)$
$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	0	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	$\frac{1}{2}(L + B)(B + W)(W + L)$	$\frac{1}{3}(LB + BW + WL)^3$

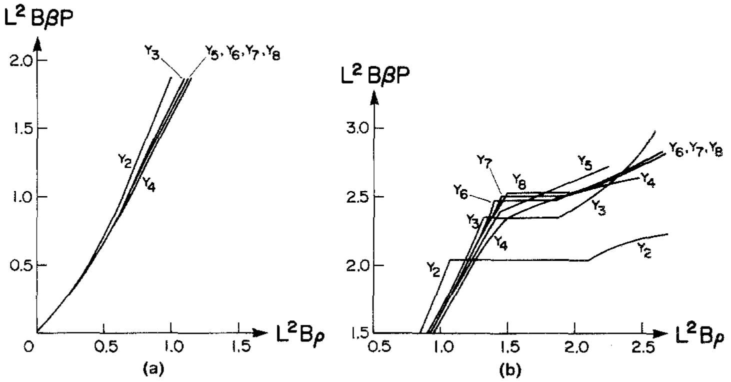

Fig. 2. Pressure vs density curves for Y_2–Y_8 levels of description of a fluid of very long and very thin rods ($L \gg B$) whose long axes can point only along the spaced-fixed X, Y, or Z directions. (a) The isotropic phase; (b) the isotropic–nematic phase transition tie lines and the anisotropic phase.

y-expansion converge in the anisotropic phase? (2) What is the effect of restricting molecular orientations on the thermodynamics predicted by the truncated y-expansions?

In addressing the first problem we can consider two limiting cases: hard cubes ($L = B = W$) and hard, very long and very thin rods ($L \gg B = W$). Although both cases are problematic (see later discussion), a large number of virial coefficients are available—seven for the cubes(14) and eight for the rods.(5,26),[8] Whereas the fluid of cubes can only exhibit isotropic phases, the fluid of rods is expected to show nonuniform (e.g., nematic) states at sufficiently high density.

In Tables I, II, and IX the virial coefficients $B_{m,n,k}$ and y-expansion coefficients $C_{m,n,k}$ are listed for these two systems. Since we have assumed that the parameter ψ in (13b) [or κ in (13a)] is independent of the orientational distribution, we have calculated its value from consideration of the isotropic phase. The subscripts m, n, and k denote the number of particles pointed along the space-fixed X, Y, and Z axes. The *averaged* virial coefficients are calculated for an isotropic phase:

$$\bar{B}_i = (1/3^i)\sum_{n=0}^{i}\sum_{k=0}^{i} B_{n,k,i-n-k} = (1/3^i)\sum_{i \geqslant n \geqslant k \geqslant i-n-k \geqslant 0} a_{n,k,i-n-k}B_{n,k,i-n-k}$$

From Fig. 2a we see that the y-expansion converges quickly throughout the density range of the isotropic phase: in this region the pressure should be well represented by Y_3. A simple interpolation between the cube ($L = B = W$)

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[8] Runnels and Colvin(5) have supplemented the calculations of Zwanzig(3) by computing the *eighth* virial coefficient for very long, very thin rods.

Table IX. Coefficients $B_{m,n,k}$ and $C_{m,n,k}$ for a Long, Thin, Hard-Rod Fluid

i	m	n	k	$B_{m,n,k}$	$C_{m,n,k}(\kappa = 1/9)$	$a_{m,n,k}$
1	1	0	0	1	1	3
2	1	1	0	1	0.88889	6
	2	0	0	0	-0.11111	3
3	1	1	1	0	-0.20988	6
	2	1	0	0	-0.13580	18
	3	0	0	0	0.12346×10^{-1}	3
4	2	1	1	0	0.29492×10^{-1}	36
	2	2	0	-0.29630	-0.27298	18
	3	1	0	0	0.17147×10^{-1}	24
	4	0	0	0	-0.13717×10^{-2}	3
5	2	2	1	0	0.22100×10^{-1}	90
	3	1	1	0	-0.36885×10^{-2}	60
	3	2	0	-0.66667×10^{-1}	0.92059×10^{-2}	60
	4	1	0	0	-0.20424×10^{-2}	30
	5	0	0	0	0.15242×10^{-3}	3
6	2	2	2	0	-0.67232×10^{-2}	90
	3	2	1	0	-0.60119×10^{-3}	360
	3	3	0	0.50074×10^{-1}	0.65603×10^{-1}	60
	4	1	1	0	0.44031×10^{-3}	90
	4	2	0	-0.14222×10^{-1}	-0.37733×10^{-2}	90
	5	1	0	0	0.23709×10^{-3}	36
	6	0	0	0	-0.16935×10^{-4}	3
7	3	2	2	0	0.37445×10^{-3}	630
	3	3	1	0	-0.62767×10^{-2}	420
	4	2	1	0	0.33060×10^{-3}	630
	4	3	0	0.25848×10^{-1}	0.43783×10^{-2}	210
	5	1	1	0	-0.51343×10^{-4}	126
	5	2	0	-0.28219×10^{-2}	0.34774×10^{-3}	126
	6	1	0	0	-0.27150×10^{-4}	42
	7	0	0	0	0.18817×10^{-5}	3
8	3	3	2	0	0.59186×10^{-3}	1680
	4	4	0	-0.21717×10^{-2}	-0.90469×10^{-4}	210
	4	3	1	0	-0.42241×10^{-3}	1680
	4	2	2	0	-0.14500×10^{-1}	1260
	5	3	0	0.88858×10^{-2}	-0.30541×10^{-4}	336
	5	2	1	0	0.14206×10^{-2}	1008
	6	2	0	-0.51830×10^{-3}	0.59064×10^{-5}	168
	6	1	1	0	-0.37661×10^{-4}	168
	7	1	0	0	0.30839×10^{-5}	48
	8	0	0	0	-0.20908×10^{-6}	3

Table X. Parameters of the Isotropic–Nematic Phase Transition Obtained from Different Levels of Approximate Description

Approximation[a]	βPL^2B	Isotropic density $\rho_i L^2 B$	Mesophase density $\rho_a L^2 B$	η
B_2	2.314	1.258	1.916	0.915
B_4	2.494	1.419	2.138	0.934
B_5	2.563	1.513	2.139	0.909
B_7	2.494	1.443	1.783	0.701
B_8	2.500	1.443	1.899	0.798
[2, 3] Padé	2.514	1.45	1.92	0.81
[3, 3] Padé	2.512	1.45	1.95	0.84
[3, 4] Padé	2.510	1.45	1.93	0.82
Y_2	2.016	1.064	2.038	0.983
Y_3	2.351	1.311	1.883	0.870
Y_4	2.370	1.508	1.513	0.057
Y_5	2.387	1.414	1.419	0.072
Y_6	2.479	1.417	1.848	0.774
Y_7	2.502	1.438	1.972	0.849
Y_8	2.515	1.459	1.985	0.850

[a] See text.

and long-rod ($L \gg B = W$) limits, in fact, gives $\psi \approx LB^2 = v_0$ for $L = 3B$, i.e., $\kappa \approx 1$, in agreement with the value of unity used in our earlier work.

The data listed in Table X show the parameters characterizing the isotropic–nematic phase transition in the long-rod limit, obtained from different truncations of the virial$^{(3,5)}$ and Y- (present results) expansions and from various Padé approximants.$^{(5)}$ Note that both Y_4 and Y_5 fail to give a proper account of the orientational ordering (see Table X and Fig. 2b); similarly, Zwanzig$^{(3)}$ has shown that B_6 fails to show a phase transition (Table X). (These anomalies are most probably an artifact of having restricted the particle orientations.) Figure 2b displays the pressure vs density curves, and the phase transition tie lines, for Y_2 through Y_8 levels of description. The Y_3 appears to err at very high densities in the ordered state, but provides a qualitatively good accounting of the phase transition (i.e., of the pressure and coexisting densities); Y_6, Y_7, and Y_8 are virtually identical throughout the entire range of density.

4.4. Continuous Orientations

To resolve (at least partly) the second problem of the Zwanzig model we can compare results of Lasher's$^{(27)}$ scaled-particle treatment of hard spherocylinders (of diameter d and total length $l + d$)—which can in fact be

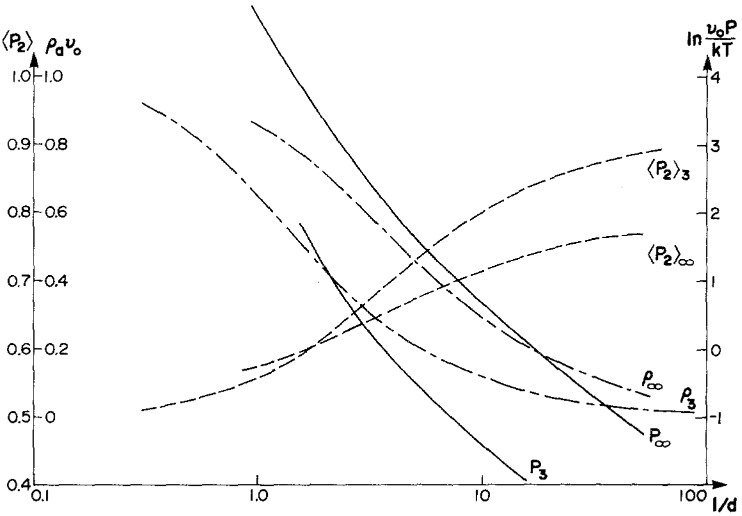

Fig. 3. Results for order parameter $\langle P_2\rangle$, nematic density ρ_a, and pressure P at the isotropic–nematic phase transition in a fluid of spherocylindrical rods with different length-to-width ratios. The subscript 3 refers to our Y_2 calculations in which only three orientations are allowed; the subscript ∞ refers to Y_2 with continuously allowed orientations.(27)

shown(9) to be identical to Y_2 with continuous $\mathbf{\Omega}$—against our Y_2 calculations for restricted orientations. Figure 3 displays Lasher's and our phase-transition properties for different length-to-width ratios L/B ($B = W$),[9]

$$\frac{12(l/d)^2}{\pi(2 + 3l/d)} = \frac{B}{L}\left(\frac{L}{B} - 1\right)^2$$

It is seen that our Y_2 results for $\eta = \langle P_2\rangle$ (P_2 is the second Legendre polynomial) agree closely with Lasher's in the range $1 < l/d < 3$, corresponding to the shapes of real liquid-crystal-forming molecules.(25) But comparison of P or ρ values in this region shows large discrepancies. Furthermore, it can easily be shown that $\langle P_4\rangle$ always exceeds $\langle P_2\rangle$ in the restricted orientation case, whereas measured values of $\langle P_4\rangle$ are often small and even negative.(28) Quantitative and detailed description of the phase transition clearly requires treating $\mathbf{\Omega}$ as a continuous variable. But then we are confronted with the impossibility of obtaining analytical expressions for $B_2(\mathbf{\Omega})$ and $B_3(\mathbf{\Omega}, \mathbf{\Omega}')$. One solution would be to pursue the suggestion of Straley's,(29) according to which the constituent particles (axially symmetric, say), instead of being constrained to point along X, Y, or Z, are allowed to point into the faces of a dodecahedron (six orientations), or an icosahedron (ten orientations), etc. An alternative approach involves allowing for continuous quantities from the

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[9] The expression follows from the equality $B_2^{\text{sp.cyl}}(l, d) = B_2^{\text{rec.par.}}(L, B)$.

outset, and then truncating various series expansions for the relevant angle-dependent quantities.

More explicitly, suppose we expand $B_2(\mathbf{\Omega})$ and $B_3(\mathbf{\Omega}, \mathbf{\Omega}')$ in their Fourier series:

$$B_2 = B_2(\alpha\beta\gamma) = \sum_{m,n,k} b_{mnk} \exp[i(m\alpha + n\beta + k\gamma)] \tag{76}$$

and

$$B_3 = \sum_{m,n,k} \sum_{\mu,\nu,\kappa} b_{mnk'\mu\nu\kappa} \exp[i(m\alpha + n\beta + k\gamma + \mu\alpha' + \nu\beta' + \kappa\gamma')] \tag{77}$$

Inserting (76) and (77) into (75) yields the Fourier expansion of the distribution function $f(\mathbf{\Omega})$. Since we are interested in low-symmetry shapes characterized by, say, ellipsoids or rectangular parallelepipeds all of whose axes are different, it is appropriate to consider the general case of d_{2h} molecular symmetry. In this case the coefficients $B_2(\alpha\beta\gamma)$ and $C_2(\alpha\beta\gamma)$ must be invariant with respect to the following angle transformations:

$$\begin{aligned}
&\alpha \rightarrow \alpha + p\pi \\
&\beta \rightarrow \beta(2\delta_{p0} - 1) + l\pi \\
&\gamma \rightarrow \gamma(2\delta_{p0}\delta_{l0} - 2\delta_{p0} + 1) + j\pi
\end{aligned} \tag{78}$$

where $p, l, j = 0, \pm 1$. An additional symmetry relation follows from the fact that the coordinate frame can be tied to either of the two particles; thus

$$\mathbf{\Omega}_{12} \rightarrow \mathbf{\Omega}_{21} \qquad \text{or} \qquad \{\alpha \rightarrow -\gamma, \beta \rightarrow -\beta, \gamma \rightarrow -\alpha\} \tag{79}$$

Requiring that (76) be invariant under the transformations (78) and (79) leads to stringent conditions on the b_{mnk} and hence to the following for B_2:

$$B_2 = \sum_{m,n,k} b'_{mnk} \cos 2m\alpha \cos 2n\beta \cos 2k\gamma, \qquad b'_{mnk} = b'_{knm} \tag{76a}$$

Determination of the coefficients b'_{mnk} for an arbitrary molecular (hard core) shape constitutes the original problem of obtaining an explicit analytical expression for B_2. Thus we choose instead to approximate B_2 by dropping in (76a) all terms with m, n, or k greater than 1. Following Straley,(30) we can then calculate the coefficients of the remaining terms by requiring that the truncated ($m \leqslant 1, n \leqslant 1, k \leqslant 1$) expansion recover the exact values of B_2 listed in Table VIII for the special orientations. In this way we find (see Appendix) that B_2 must have the form

$$B_2(\alpha\beta\gamma) = \sum_{i=0}^{3} V_i F_i \tag{80}$$

where

$$\begin{aligned} 3V_0 &= (L + B)(B + W)(W + L) + 4LBW \\ 3V_1 &= 3LBW + \tfrac{1}{2}L(B^2 + W^2) - B(L^2 + W^2) - W(L^2 + B^2) \\ 4V_2 &= (B - W)(BW - L^2) \\ 2V_3 &= -L(B - W)^2 \end{aligned} \tag{81}$$

and

$$\begin{aligned} F_0 &= 1 \\ F_1 &= P_2(\cos\beta) \\ F_2 &= (\sin^2\beta)(\cos 2\alpha + \cos 2\gamma) \\ F_3 &= (1 + \cos^2\beta)\cos 2\alpha \cos 2\gamma \end{aligned} \tag{82}$$

[A similar equation for B_2 has been suggested by Straley,(30) who starts with an expansion in Wigner rotation functions instead of a Fourier series. He finds $4LBW$ instead of $3LBW$ in the second of Eqs. (81) and $-V_2$ instead of $+V_2$; also, his F_3 includes an extra term which is not invariant under the transformations (78).]

For the *third* virial coefficient, $B_3(\mathbf{\Omega}_{12}\mathbf{\Omega}_{13})$, transformation (79) must be replaced by a more complicated set of angle relations involving the full group of $1 \leftrightarrow 2 \leftrightarrow 3$ permutations. With conditions (78) these symmetry constraints reduce the Fourier expansion (77) to a fairly straightforward series whose $(m \leqslant 1, n \leqslant 1,\ldots)$ truncation can be forced to yield the B_3 values listed in Table VIII. We then construct $C_2(\mathbf{\Omega}_{12})$ and $C_3(\mathbf{\Omega}_{12}\mathbf{\Omega}_{13})$ and use them in Eq. (75) to provide a Y_3-level theory for the continuous orientation case. The corresponding integral equations must be solved by truncated Fourier series representations of the solution, or by related methods.

APPENDIX

A.1. Second Virial Coefficient of Rectangular Parallelepipeds

Let us place the origin of our space-fixed Cartesian coordinate system at a vertex of the first parallelepiped, and take the three edges meeting at that vertex to be the coordinate axes. Suppose now that at least one principal axis of the second parallelepiped is parallel to one of the coordinate axes, so that the cross section—cut by a plane perpendicular to this axis—of the two parallelepipeds in contact is comprised of two rectangles touching each other (see Fig. 4a). As rectangle 2 moves around rectangle 1 (the two parallelepipeds remain in contact with one another and keep fixed their relative orientation), the center of particle 2 circumscribes the figure shown in Fig. 4b. Its area is

$$A_{12} = b_1 l_1 + b_2 l_2 + (b_1 l_2 + b_2 l_1)|\cos\varphi| + (l_1 l_2 + b_1 b_2)|\sin\varphi| \tag{A1}$$

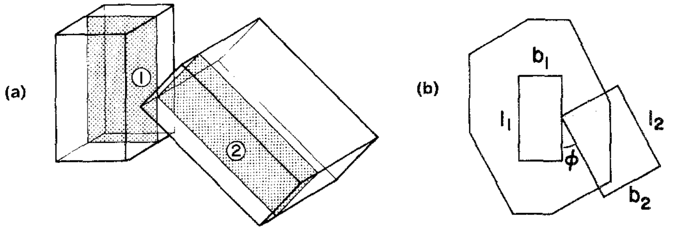

Fig. 4. (a) Configuration of two parallelepipeds which have only a single pair of principal axes parallel to one another. The shaded rectangles show the cross-sectional area formed by a plane cutting the bodies perpendicular to their line of tangency. (b) Locus of the second particle's center as it moves around the first particle, maintaining tangency and fixed relative orientation.

A_{12} is twice the second virial coefficient of a two-dimensional hard-rectangle fluid.

The volume v_{12} excluded by parallelepiped 1 to parallelepiped 2 is

$$v_{12} = A_{12}(w_1 + w_2) \tag{A2}$$

where w_i is the width (the third dimension) of particle i. Since $v_{12} = 2B_{12}(\varphi)$, Eqs. (A1) and (A2) lead directly to the second virial coefficient of the system whose orientations are restricted to those shown in Fig. 4a.

A.2. Third Virial Coefficient of Rectangular Parallelepipeds

When *all* principal axes of both parallelepipeds are coincident in pairs ($\varphi = 0$), the integration along each axis is independent of those along the others and the third virial coefficient may be expressed as

$$B_{123} = \tfrac{1}{3}J_{123}(x)J_{123}(y)J_{123}(z) \tag{A3}$$

Here

$$J_{123} = I^{(1231)} + I^{(1321)} + I^{(2132)} + I^{(2312)} + I^{(3123)} + I^{(3213)} \tag{A4}$$

$$\begin{aligned} I^{(kmnk)} &= \int dt \int du\, H(a_{km} - t)H(a_{mn} - u)H(a_{nk} - t - u) \\ &= \int_0^{c_1} dt \int_0^{c_2} du \end{aligned} \tag{A5}$$

$$H(a) = \begin{cases} 0, & a < 0 \\ \frac{1}{2}, & a = 0 \\ 1, & a > 0 \end{cases} \tag{A6}$$

$$a_{km} = \tfrac{1}{2}(a_{kk} + a_{mm}) \tag{A7}$$

$$c_1 = \min(a_{km}, a_{kn}), \qquad c_2 = \min(a_{nm}, a_{nk} - t) \tag{A8}$$

and a_{kk} ($k = 1, 2$, or 3) is the length (l_k), breadth (b_k) ,or width (w_k) of the kth particle. The integrations in (A5) are trivial to perform; after simple but tedious algebraic transformations one gets

$$I^{(kmnk)} = a_{km}a_{mn} - \tfrac{1}{2}[a_{mm}^2 - S_{mk}^2 H(S_{mk}) - S_{mn}^2 H(S_{mn})] \tag{A9}$$

with

$$S_{km} = \tfrac{1}{2}(a_{kk} - a_{mm}) \tag{A10}$$

Substituting (A9) into (A4) yields

$$J_{123} = a_{11}a_{22} + a_{22}a_{33} + a_{33}a_{11} \tag{A11}$$

and therefore

$$B_{123} = \tfrac{1}{3}(l_1l_2 + l_2l_3 + l_3l_1)(b_1b_2 + b_2b_3 + b_3b_1)(w_1w_2 + w_2w_3 + w_3w_1) \tag{A12}$$

Consider now a single-component fluid of parallelepipeds with dimensions L, B, and W ($L \geqslant B \geqslant W$) and let each quantity l_i, b_i, and w_i in Eqs. (A1), (A2), and (A12) be equal to L, B, or W. There will then be six mutual orientations of the two particles and ten of three particles. Characterizing these orientations by the three Euler angles α, β, and γ (α and γ specify rotation about the long axis L, and β about the short axis W) we represent the possible configurations and corresponding expressions for B_{12} and B_{123} shown in Table XIII.

APPENDIX C. REPRESENTATION OF B_{12} FOR CONTINUOUS ORIENTATIONS

By requiring the $m \leqslant 1$, $n \leqslant 1$, $k \leqslant 1$ truncation of Eq. (76a) to recover exactly the six values of B_2 listed in Table VIII, we obtain six coupled equations for the b'_{mnk} which can be solved to give

$$\begin{aligned} b'_{000} &= \tfrac{1}{2}V_0 + \tfrac{1}{6}V_2 - \tfrac{1}{3}(b'_{001} + b'_{100}) \\ b'_{010} &= \tfrac{3}{8}V_1 + \tfrac{1}{4}V_2 - \tfrac{1}{2}(b'_{001} + b'_{100}) \\ b'_{101} &= \tfrac{3}{4}V_3 + \tfrac{1}{4}V_2 - \tfrac{1}{2}(b'_{001} + b'_{100}) \\ b'_{110} + b'_{011} &= (b'_{001} + b'_{100}) - V_2 \\ b'_{111} &= \tfrac{1}{4}(V_3 + V_2) - \tfrac{1}{2}(b'_{001} + b'_{100}) \end{aligned} \tag{A13}$$

where the V_i are given by Eqs. (81); $b'_{001} + b'_{100}$ is arbitrary. If one puts $b'_{001} + b'_{100} = \tfrac{1}{2}V_2$, then the truncated equation (76a), with b'_{mnk} given by (A13), coincides with Eq. (A2) for $2B_{12}$, with absolute values of the trigonometric functions replaced by their squared values. That is, for this choice of $b'_{001} + b'_{100}$, Eq. (76a) becomes (80)–(82).

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