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On the Statistical Mechanics of Rigid Particles

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In this paper, generalized functions are used in the configuration partition function for fluids composed of arbitrarily shaped, rigid particles. This leads to new expressions for the basic statistical thermodynamic functions and some equations that may be useful in developing approximate theories, such as the scaled particle theory, for such fluids. The results are applicable to a large class of arbitrarily shaped, rigid particles and reduce exactly to the usual hard-sphere expressions.

KEY WORDS: Statistical mechanics of arbitrary, rigid-particle systems; equations of state for arbitrary, rigid-particle fluids; use of generalized functions in statistical mechanics of rigid-particle systems; scaled particle theory equations for arbitrary, rigid-particle systems.

1. INTRODUCTION

Rigid-particle fluids have proven to be very useful in developing the statistical theory of real fluids. In particular, hard-sphere fluids have been studied extensively.[(1–4)] Because of this, it is advantageous to develop a statistical theory that is specific to a rigid-particle fluid. Section 2 shows how this type of theory may be obtained by exploiting the discontinuous nature of the rigid-particle potential via the theory of generalized functions. The usefulness of this technique for rigid particles is illustrated by deriving new expressions

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for the pressure and chemical potential for fluids composed of arbitrarily shaped, rigid particles. The generalized function representation of the partition function used in Section 2 also facilitates the exact evaluation of the partition function for some coupled systems. This derivation and its possible applications are discussed in Sections 3 and 4.

2. CANONICAL ENSEMBLE DISTRIBUTION FUNCTIONS AND THE PARTITION FUNCTION

The system for consideration is one composed of N identical, arbitrarily shaped, rigid particles. These particles have been referred to as arbitons in previous research.[5] The particles, not necessarily convex, are assumed to have the following property: there must exist at least one point in the interior of a particle such that any line drawn outward from that point intersects the surface only once (see Fig. 1). If more than one such point exists, then the most convenient one is chosen as the center of the particle.

It is further assumed that the particles are large enough so that the translational and rotational degrees of freedom may be treated classically. The total partition function for this system is

$$Q_N = (1/\sigma_r{}^N N!\, h^{6N}) \int d\mathbf{r}^N\, d\mathbf{p}^N\, d\mathbf{e}^N\, d\mathbf{p}'^N\, e^{-\beta H} \tag{1}$$

where σ_r denotes the rotational symmetry number of a particle, h is Planck's constant, H is the classical Hamiltonian for the system, and $\beta = 1/kT$. The integration in (1) is over the phase variables which describe the system; i.e., the N position coordinates $\mathbf{r}^N$, the N translational momentum coordinates $\mathbf{p}^N$, the N angular momentum coordinates $\mathbf{p}'^N$, and the N internal coordinates $\mathbf{e}^N$, which are taken to be the Eulerian angles (ϕ, θ, ψ) of the individual particles. For this system, the Hamiltonian is separable as

$$H = \sum_{i=1}^{N} (p_i^2/2m) + H(\{p_i'\}) + U_N \tag{2}$$

where $H(\{p_i'\})$ is the rotational contribution to the kinetic energy and U_N is the total potential energy of interaction. It may be written as the pair-additive sum

$$U_N = \sum_{i>j\geqslant 1}^{N} u_{ij}$$

for rigid-particle systems. As is well known,[6] $H(\{\mathbf{p}_i'\})$ may be written as a sum over particles, with each term depending on $\mathbf{p}_i'$ and $\mathbf{e}_i$ of a single particle.

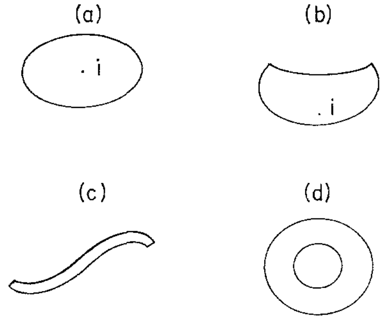

Fig. 1. Two-dimensional projections of typical arbitons: (a) (an ellipsoid) and (b) are admissible arbiton particles with their centers marked i; (c, d) (a toroid) are examples of inadmissible arbitons.

The integrals over the translational and rotational momenta in Eq. (1) may be evaluated, and Q_N is

$$Q_N = (1/N\Lambda^3)^N \, q_r{}^N Z_N \tag{3}$$

where Λ is the thermal de Broglie wavelength, $h/(2\pi mkT)^{1/2}$, q_r is the rotational partition function for a single particle, $(8\pi^2/\sigma_r)(kT/h^2)^{3/2}(8I_A I_B I_C)^{1/2}$, with I_i the moment of inertia about the ith principal axis of a particle, and Z_N is the configuration partition function. It is defined as

$$Z_N = \int d\mathbf{r}^N \, d\mathbf{e}'^N \, e^{-\beta U_N} \tag{4}$$

where $d\mathbf{e}_i'$ denotes $\sin\theta_i \, d\theta_i \, d\phi_i \, d\psi_i$.

The Boltzmann factor, $e^{-\beta U_N}$, in Z_N may be simplified considerably by utilizing the rigid nature of the interparticle potential. The relative configuration of any two particles (i, j) is fixed by $\mathbf{e}_i$, $\mathbf{e}_j$, and $\hat{r}_{ij}$, and, depending on the shape of the particles, there exists a single-valued function $\sigma_{ij} = \sigma_{ij}(\mathbf{e}_i, \mathbf{e}_j, \hat{r}_{ij})$ which gives the center–center contact distance σ_{ij} for a given configuration. The interparticle potential is then

$$\begin{aligned} u_{ij} &= \infty \qquad \text{for} \quad r_{ij} < \sigma_{ij} \\ &= 0 \qquad \text{for} \quad r_{ij} > \sigma_{ij} \end{aligned}$$

The Boltzmann factor for this pair is expressible in terms of the Heaviside function

$$e^{-\beta u_{ij}} = \eta(r_{ij} - \sigma_{ij})$$

where

$$\eta(x) = 0, \qquad x < 0$$
$$= 1 \qquad x > 0$$

Thus, the Boltzmann factor for the entire system is

$$e^{-\beta U_N} = \prod_{i>j\geqslant 1}^{N} \eta(r_{ij} - \sigma_{ij})$$

and Z_N is

$$Z_N = \int d\mathbf{r}^N \, d\mathbf{e}'^N \prod_{i>j\geqslant 1}^{N} \eta(r_{ij} - \sigma_{ij}) \tag{5}$$

The configuration partition for a system in which a coupling parameter λ is associated with particle 1 may be written as

$$Z_N(\lambda) = \int d\mathbf{r}^N \, d\mathbf{e}'^N \prod_{j\geqslant 2} \eta(r_{1j} - \lambda\sigma_{1j}) \prod_{l>k\geqslant 2}^{N} \eta(r_{lk} - \sigma_{lk}) \tag{6}$$

Clearly, for $\lambda = 0$, particle 1 is completely uncoupled from the system and $Z_N(\lambda = 0) = 8\pi^2 \Omega Z_{N-1}$, where Z_{N-1} is the configuration partition function for a system of $N - 1$ identical solvent particles, and Ω is the system volume. This scaling is discussed in Section 3.

The n-particle density correlation function of a λ-coupled system of N particles is defined as

$$g_N^{(n)}(\mathbf{r}^n, \mathbf{e}^n; \lambda) = [(8\pi^2\Omega)^n / Z_N(\lambda)] \int d\mathbf{r}^{N-n} \, d\mathbf{e}'^{N-n} \, e^{-\beta U_N(\lambda)}$$

This correlation function may be rewritten in terms of the generalized functions as

$$g_N^{(n)}(\mathbf{r}^n, \mathbf{e}^n; \lambda) = [(8\pi^2\Omega)^n / Z_N(\lambda)] \int d\mathbf{r}^{N-n} \, d\mathbf{e}'^{N-n}$$
$$\times \prod_{j>1}^{N} \eta(r_{1j} - \lambda\sigma_{1j}) \prod_{l>k\geqslant 2}^{N} \eta(r_{lk} - \sigma_{lk})$$

However, in treating arbiton systems, it is more convenient to define reduced n-particle correlation functions as

$$\tilde{g}_N^{(n)}(\mathbf{r}^n, \mathbf{e}^n; \lambda) = [(8\pi^2\Omega)^n / Z_N(\lambda)] \int d\mathbf{r}^{N-n} \, d\mathbf{e}'^{N-n} \, e^{-\beta[U_N(\lambda) - U_n(\lambda)]}$$

where $U_n(\lambda)$ refers to the total potential energy of interaction of the subset of particles $\{1, 2,..., n\}$ in a λ-coupled system. In terms of the generalized functions, $\tilde{g}_N^{(n)}$ is

$$\tilde{g}_N^{(n)}(\mathbf{r}^n, \mathbf{e}^n; \lambda) = [(8\pi^2\Omega)^n/Z_N(\lambda)] \int d\mathbf{r}^n \, d\mathbf{e}'^n \prod_{j>n}^{N} \eta(r_{1j} - \lambda\sigma_{1j})$$

$$\times \prod_{k>l\geqslant n}^{N} \eta(r_{lk} - \sigma_{lk}) \prod_{m>1}^{n} \prod_{p>n}^{N} \eta(r_{mp} - \sigma_{mp}) \qquad (7)$$

and it is related to $g_N^{(n)}$ by

$$g_N^{(n)}(\mathbf{r}^n, \mathbf{e}^n; \lambda) = \prod_{j=2}^{n} \eta(r_{1j} - \lambda\sigma_{1j}) \prod_{k>l>1}^{n} \eta(r_{lk} - \sigma_{lk}) \, \tilde{g}_N^{(n)}(\mathbf{r}^n, \mathbf{e}^n; \lambda) \qquad (8)$$

It should be noted that, for arbiton systems, the reduced correlation functions defined above are continuous in all arguments, whereas the usual correlation functions are not. The discontinuities in $g_N^{(n)}(\mathbf{r}^n, \mathbf{e}^n; \lambda)$ arise from the hard-particle interactions among the subset of particles $\{1, 2,..., n\}$. As shown in Eq. (7), these interactions are specifically excluded from the definition of $\tilde{g}_N^{(n)}(\mathbf{r}^n, \mathbf{e}^n; \lambda)$. For example, $g_N^{(2)}(\mathbf{r}_{12}, \mathbf{e}_{12}; \lambda = 1)$ is known to be zero for $r_{12} < \sigma_{12}$ because of the interaction between 1 and 2, whereas

$$\tilde{g}_N^{(2)}(\mathbf{r}_{12}, \mathbf{e}_{12}; \lambda = 1)$$

is nonzero for $r_{12} < \sigma_{12}$. Furthermore, from Eq. (8), it is apparent that

$$\tilde{g}_N^{(2)}(\sigma_{12}, \hat{r}_{12}, \mathbf{e}_{12}; \lambda=1) = g_N^{(2)}(r_{12} = \sigma_{12}^{+}, \hat{r}_{12}, \mathbf{e}_{12}; \lambda=1) \qquad (9)$$

The pressure of a system is related to Q_N by the expression

$$\begin{aligned} p &= kT[\partial(ln Q_N)/\partial\Omega]_{T,N} \\ &= kT[\partial(ln Z_N)/\partial\Omega]_{T,N} \end{aligned}$$

For arbitons, the pressure is

$$p = \rho kT + [\rho^2 kT/6\Omega(8\pi^2)^2] \int d\mathbf{r}^2 \, d\mathbf{e}'^2 \, \sigma_{12}\delta(r_{12} - \sigma_{12}) \, \tilde{g}_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2; \lambda=1)$$

Because $\tilde{g}_N^{(2)}$ depends only on $\mathbf{r}_{12}$ and $\mathbf{e}_{12}$, the integrations over $\mathbf{r}_1$ and $\mathbf{e}_1$ may be carried out to obtain the result

$$p = \rho kT + \tfrac{1}{2}\rho^2 kT \, \overline{\sigma_{12}^3 G_N(\sigma_{12})} \qquad (10)$$

where

$$\overline{\sigma_{12}^3 G_N(\sigma_{12})} = [1/3(8\pi^2)] \int d\hat{r}_{12} \, d\mathbf{e}'_{12} \, \sigma_{12}^3 \, \tilde{g}_N^{(2)}(r_{12} = \sigma_{12}, \hat{r}_{12}, \mathbf{e}_{12}; \lambda = 1) \quad (11)$$

Equation (10) is similar to the usual virial equation of state for hard spheres[1] in that it involves only $r_{12}^3 \tilde{g}_N^{(2)}(\mathbf{r}_{12}, \mathbf{e}_{12}; \lambda = 1)$, evaluated at contact, $r_{12} = \sigma_{12}$, although in this case, it is angled-averaged as shown in Eq. (11).

A simple expression for the chemical potential may also be derived from Eq. (6). By definition,

$$\mu = -[kT\, \partial(lnQ_N)/\partial N]_{T,\Omega} = -kTln(Q_N/Q_{N-1})$$

for large N. For the arbiton system, μ is

$$\mu/kT = +\, ln(\rho\Lambda^3) - lnq_r - ln(Z_N/8\pi^2\Omega Z_{N-1}) \tag{12}$$

The final term above, denoted μ^ϕ/kT, is exactly

$$\begin{aligned}\mu^\phi/kT &= -\int_0^1 d\lambda\, (\partial/\partial\lambda)[\ln Z_N(\lambda)] \\ &= [(N-1)/(8\pi^2\Omega)^2] \int_0^1 d\lambda \int d\mathbf{r}^2\, d\mathbf{e}'^2\, \sigma_{12}\delta(r_{12} - \lambda\sigma_{12})\, \tilde{g}_N^{(2)}(\mathbf{r}_{12}, \mathbf{e}_{12}; \lambda) \\ &= 3\rho \int_0^1 d\lambda\, \lambda^2\, \overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} \end{aligned} \tag{13}$$

with

$$\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} = [1/3(8\pi^2)] \int d\hat{r}_{12}\, d\mathbf{e}_{12}'\, \sigma_{12}^3\, \tilde{g}_N^{(2)}(r_{12}{=}\lambda\sigma_{12}, \hat{r}_{12}, \mathbf{e}_{12}; \lambda) \tag{14}$$

As in the equation of state, only the angle-averaged quantity, $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$, is involved in Eq. (13). This is the angle-averaged contact value of $r_{12}^3 \tilde{g}_N^{(2)}(\mathbf{r}_{12}, \mathbf{e}_{12}; \lambda)$ for a λ-coupled system.

Thus, the determination of the equation of state and chemical potential for arbiton systems is reduced to one of determining the angle-averaged contact function $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$. This is quite similar to the hard-sphere problem, except here the problem is complicated somewhat by the lack of spherical symmetry in the system. Presumably, the scaled particle theory, which has been quite successful in the case of hard spheres, could be applied to this problem. This will be discussed in Section 4.

Before closing this section, it is useful to develop an equation which might be the basis for a scaled particle theory for arbitons. The Gibbs–Duhem relation for an isothermal, single-component system is $(dp)_T = \rho(d\mu)_T$, so that the pressure for the system is given by

$$p = \int_0^\rho d\rho'\, \rho'(\partial\mu/\partial\rho')_T$$

Using Eqs. (10) and (13), this is

$$\tfrac{1}{6}\rho^2\, \overline{\sigma_{12}^3 G_N(\sigma_{12})} = \rho^2 \int_0^1 d\lambda\, \lambda^2\, \overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} - \int_0^\rho d\rho'\, \rho' \int_0^1 d\lambda\, \lambda^2\, \overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} \tag{15}$$

This is an integral equation for $\overline{\sigma_{12}^3 G_N(\sigma_{12})}$ and, if solved, it would provide a virial equation of state for the system. One approximate solution of this is discussed in Section 4. Equation (15) is the arbiton version of a similar hard-sphere equation derived by Reiss *et al.*[7]

3. AN EXACT EVALUATION OF $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$ FOR SOME VALUES OF λ

In this section, $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$ is evaluated exactly for a restricted range of λ by explicitly using the generalized function representation of $Z_N(\lambda)$. In this case of a hard-sphere system, our result reduces exactly to the well-known expression derived and used by Reiss *et al.*[7] in their scaled particle theory.

The maximum and minimum values of $\sigma(\hat{r}_{ij}, \mathbf{e}_{ij})$ will be denoted by $\sigma_{\max}$ and $\sigma_{\min}$, respectively. λ in the range $\lambda \leqslant \lambda^* = \sigma_{\min}/2\sigma_{\max}$ will be considered. By direct differentiation of Eq. (6), $\partial Z_N(\lambda)/\partial\lambda$ is

$$\partial Z_N(\lambda)/\partial\lambda = -(N-1)\int dr^N\, de'^N\, \sigma_{12}\delta(r_{12} - \lambda\sigma_{12}) \times \prod_{j=3}^{N} \eta(r_{1j} - \lambda\sigma_{1j}) \prod_{l>k\geqslant 2}^{N} \eta(r_{lk} - \sigma_{lk}) \tag{16}$$

so that $r_{12} = \lambda\sigma_{12}$ in the integrand. A typical term in the integrand is $\eta(r_{ij} - \lambda\sigma_{ij})\,\eta(r_{2j} - \sigma_{2j})$. A necessary condition that this term [and $\eta(r_{2j} - \sigma_{2j})$ itself] be nonzero is that $r_{2j} > \sigma_{\min}$. The triangle inequality for particles $(1, 2, j)$ with $\lambda \leqslant \lambda^*$, $r_{12} = \lambda\sigma_{12}$, and $r_{2j} > \sigma_{\min}$ is

$$r_{12} + r_{1j} \geqslant r_{2j} > \sigma_{\min}$$

or

$$r_{1j} > \sigma_{\min} - r_{12} = \sigma_{\min} - \lambda\sigma_{12} \geqslant \sigma_{\min} - \lambda^*\sigma_{\max} = \sigma_{\min}/2$$

so that $r_{1j} = \frac{1}{2}\sigma_{\min} + \gamma$, where $\gamma > 0$. One property of the Heaviside function is $\eta(x) \geqslant \eta(y)$ for $x \geqslant y$. Therefore,

$$\eta(r_{1j} - \lambda\sigma_{1j}) \geqslant \eta(\tfrac{1}{2}\sigma_{\min} + \gamma - \lambda^*\sigma_{\max}) = \eta(\gamma) \equiv 1$$

Thus, for $\lambda \leqslant \lambda^*$, the quantity $\eta(r_{1j} - \lambda\sigma_{1j})\,\eta(r_{2j} - \sigma_{2j})$ is equal to

$\eta(r_{2j} - \sigma_{2j})$. Moreover, this holds for all j, so the $\prod_{j=3}^{N} \eta(r_{1j} - \lambda\sigma_{1j})$ term may be removed from the integrand in Eq. (16) and $\partial Z_N/\partial\lambda$ is

$$\begin{aligned}\partial Z_N(\lambda)/\partial\lambda &= -(N-1)\int d\mathbf{r}_{12}\, d\mathbf{e}'_{12}\, \sigma_{12}\delta(r_{12} - \lambda\sigma_{12}) \\ &\quad\times \int d\mathbf{r}^{N-1}\, d\mathbf{e}'^{N-1} \prod_{l>k\geqslant 2}^{N} \eta(r_{lk} - \sigma_{lk}) \\ &= -(N-1)\int d\mathbf{r}_{12}\, d\mathbf{e}'_{12}\, \sigma_{12}\delta(r_{12} - \lambda\sigma_{12})\, Z_{N-1} \\ &= -\lambda^2(N-1)\, Z_{N-1} 3(8\pi^2)\, \overline{\sigma_{12}^3} \end{aligned} \tag{17}$$

where

$$\overline{\sigma_{12}^3} = [1/3(8\pi^2)] \int d\hat{r}_{12}\, d\mathbf{e}'_{12}\, \sigma_{12}^3 \tag{18}$$

Equation (17) may be integrated over λ to give

$$Z_N(\lambda) - Z_N(0) = -\lambda^3(N-1)\, Z_{N-1} 8\pi^2\, \overline{\sigma_{12}^3}$$

and since $Z_N(0) = 8\pi^2\Omega Z_{N-1}$,

$$Z_N(\lambda) = 8\pi^2\Omega Z_{N-1}(1 - \rho\lambda^3\, \overline{\sigma_{12}^3}) \tag{19}$$

for $0 \leqslant \lambda \leqslant \lambda^*$.

Similarly, $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$ may be evaluated for these λ. By definition,

$$\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} = [1/3(8\pi^2\Omega)^2] \int d\mathbf{r}^2\, d\mathbf{e}'^2\, \sigma_{12}\delta(r_{12} - \lambda\sigma_{12})\, \tilde{g}_N^{(2)}(\mathbf{r}_{12}, \mathbf{e}_{12}; \lambda)$$

and this may be written as

$$\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} = -(1/3\rho\lambda^2)(\partial/\partial\lambda)[\ln Z_N(\lambda)] = -[\partial Z_N(\lambda)/\partial\lambda]/3\rho\lambda^2 Z_N(\lambda)$$

Using Eqs. (17) and (19), we see that this is

$$\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} = \overline{\sigma_{12}^3}/(1 - \rho\lambda^3\, \overline{\sigma_{12}^3}) \tag{20}$$

Since this is exact for $\lambda \leqslant \lambda^*$, all of the derivatives of $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$ with respect to λ may be obtained from Eq. (20) for $\lambda < \lambda^*$. At $\lambda = \lambda^*$, however, the second derivative of $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$ has a discontinuity. This is shown in the appendix.

The quantity $\overline{\sigma_{12}^3}$ defined in Eq. (18) has an interesting physical meaning. Clearly,

$$V(\mathbf{e}_{12}) = \tfrac{1}{3} \int d\hat{r}_{12}\, \sigma_{12}^3$$

is the volume contained in the surface determined by the locus of the set of points which the center of 2 takes as it moves around 1 for a fixed relative orientation $\mathbf{e}_{12}$. Then, $V(\mathbf{e}_{12})$ is averaged over all relative orientation coordinates $\mathbf{e}_{12}$ as

$$\overline{\sigma_{12}^3} = (1/8\pi^2) \int d\mathbf{e}_{12}'\, V(\mathbf{e}_{12})$$

This is called the average excluded volume for particles 1 and 2.

The quantity $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$ is related in a simple way to the reversible work $W(\lambda)$ of λ-coupling a solute particle in the system. For arbitrary λ, $W(\lambda)$ is, by definition,

$$W(\lambda) = -kT \ln[Z_N(\lambda)/Z_N(0)] = +3\rho kT \int_0^\lambda d\lambda'\, \overline{\sigma_{12}^3 G_N(\lambda'\sigma_{12})}\, \lambda'^2 \qquad (21)$$

Differentiating this, we obtain

$$\partial W(\lambda)/\partial\lambda = +3\rho kT\lambda^2\, \overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} \qquad (22)$$

and this gives the connection between $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$ and $W(\lambda)$. Furthermore, using Eq. (20), $W(\lambda)$ may be evaluated exactly for $0 \leqslant \lambda \leqslant \lambda^*$. By direct integration,

$$W(\lambda) = -kT \ln(1 - \rho\lambda^3\, \overline{\sigma_{12}^3}) \qquad (23)$$

a result implying that for $\lambda \leqslant \lambda^*$, the work of λ-coupling is equivalent to the reversible work of forming a cavity of volume $\lambda^3\, \overline{\sigma_{12}^3}$ in an arbiton fluid.

Because λ appears as a scalar multiplier of σ_{1j} in the Boltzmann factors involving particles $(1, j)$, it represents a coupling by scaling in size of the particles in the system. For $\lambda < 1$, the interaction between particle 1 and any other solvent particle is one between the two particles scaled down in size by a factor of λ. The interactions between solvent particles are unaffected by this scaling, so they remain full-sized. The scaling is shown in Fig. 2. It should be noted that this coupling procedure is not unique. Others may be devised that produce the above results, although they are not as convenient as the one used here.

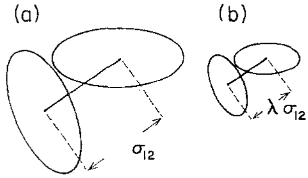

Fig. 2. The scaling procedure is actually the size scaling scheme shown here. Here, for ellipsoids, (a) is the fully coupled system and (b) is the ($\lambda = \frac{1}{2}$)-coupled system. The dimensions and center–center contact distance of (b) are one-half of those in (a).

4. CONCLUDING REMARKS

In this paper, we have shown that it is both convenient and advantageous to develop a statistical theory of fluids that is specific to substances which interact via the rigid-particle potential. Systems of this sort are usually treated by passing to the rigid-particle limit in a statistical theory formulated for substances with a continuous interparticle potential. This technique, however, can lead to mathematical difficulties unless care is exercised in passing to the limit. As shown above, these difficulties can be avoided by using the singular nature of the hard-particle potential to express the Boltzmann factors in terms of generalized functions. Furthermore, the reduced correlation functions arise naturally from this formulation of the theory and, therefore, are the best ones to use for hard-particle systems. Although the use of generalized functions is not intended to add any new physics to the analysis, it is intended to simplify the mathematics and, hopefully, to yield formulas suggestive of approximate solutions to the statistical problem.

As mentioned in Section 2, the arbiton equations for p and μ involve only the angle-averaged contact value of the pair correlation function for a λ-coupled system. Therefore, it should be possible to develop a scaled particle theory for arbiton fluids. Gibbons[8,9] has proposed one such theory and has derived a compressibility equation of state for rigid, convex particle systems. His solution utilizes the results of Isihara and Hayashida[10] and Kihara[11] in expressing $\overline{\sigma_{12}^3}$ in Eq. (20) in terms of the volume, surface area, and mean radius of curvature of the solvent particles. Our result for $Z_N(\lambda)$ at $\lambda = \lambda^*$, Eq. (19), can be shown to agree exactly with his result. However, the extension of our result to his general form $Z_N(\lambda)$ is not immediate. This suggests that it should be possible to derive an alternative form of the scaled particle theory for arbiton systems.

As mentioned previously, hard spheres are admissible arbiton particles. Indeed, the above derivations may be reduced to the hard-sphere case by choosing the geometric center of a sphere as the center of an arbiton. For this case, then, $\lambda^* = \frac{1}{2}$ and σ_{ij} is singled-valued, $\sigma_{ij} = a$. Thus, the derivation of Eqs. (10), (13), (15), and (20) constitutes an alternative method of deriving both the thermodynamic functions and the basic scaled particle theory equations for hard-sphere systems. Furthermore, since Eq. (15) holds for all arbiton systems, the technique used to obtain an approximate solution for the hard-sphere problem may be directly applicable to general arbiton systems.

APPENDIX: EVALUATION OF $\partial^2\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}/\partial\lambda^2$ FOR $\lambda = \lambda^{*+}$

In this appendix, the second derivative of $\overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$ is shown to have a discontinuity at $\lambda = \lambda^{*+}$. The first derivative for $\lambda \leqslant \lambda^{*+}$ is

$$(\partial/\partial\lambda)\, \overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})} = 3\rho\lambda^2[\overline{\sigma_{12}^3}/(1 - \rho\lambda^3\, \overline{\sigma_{12}^3})]^2 - [(N-1)/3\rho\lambda^2 Z_N(\lambda)] \int d\mathbf{r}^N\, d\mathbf{e}'^N\, \sigma_{12}\delta(r_{12} - \lambda\sigma_{12}) \times [\sigma_{12}(\partial/\partial r_{12}) + (\partial/\partial\lambda)] \times \prod_{j=3}^{N} \eta(r_{1j} - \lambda\sigma_{1j}) \prod_{l>k\geqslant 2}^{N} \eta(r_{lk} - \sigma_{lk}) \tag{A.1}$$

Since

$$(\partial/\partial r_{12})(\cdots)_{\hat{r}_{12},\mathbf{r}_j, j\neq 1} = \hat{r}_{12} \cdot (\partial/\partial \mathbf{r}_1)(\cdots)_{\hat{r}_{12},\mathbf{r}_j, j\neq 1}$$

the differentiations above may be carried out and the second term above is

$$[(N-1)(N-2)/3\rho\lambda^2 Z_N(\lambda)] \int d\mathbf{r}^N\, d\mathbf{e}'^N\, \sigma_{12}\delta(r_{12} - \lambda\sigma_{12})[-\sigma_{12}\hat{r}_{12}\cdot\hat{r}_{13} + \sigma_{13}] \times \prod_{j=4}^{N} \eta(r_{1j} - \lambda\sigma_{1j}) \prod_{l>k\geqslant 2}^{N} \eta(r_{lk} - \sigma_{lk})\, \delta(r_{13} - \lambda\sigma_{13})$$

$$= [(N-1)(N-2)/3\rho\lambda^2(8\pi^2\Omega)^3] \int d\mathbf{r}^3\, d\mathbf{e}'^3\, \sigma_{12}\delta(r_{12} - \lambda\sigma_{12})\, \delta(r_{13} - \lambda\sigma_{13}) \times (-\sigma_{12}\hat{r}_{12}\cdot\hat{r}_{13} + \sigma_{13})\, \eta(r_{23} - \sigma_{23})\, \tilde{g}_N^{(3)}(\mathbf{r}^3, \mathbf{e}^3; \lambda) \tag{A.2}$$

The definition of $\tilde{g}_N^{(3)}$ has been used in obtaining Eq. (A.2). $\tilde{g}_N^{(3)}$ is a scalar field that depends upon $\hat{r}_{12}$, $\hat{r}_{13}$, $\hat{r}_{23}$, $\mathbf{e}_{12}$, $\mathbf{e}_{13}$, and $\mathbf{e}_{23}$. Actually, this set of six vectors overspecifies the system. The entire set may be replaced by the set (r_{12}, r_{13}, r_{23}, $\hat{r}_{12}$, χ, $\mathbf{e}_{12}$, $\mathbf{e}_{13}$, $\mathbf{e}_{23}$), where χ is the angle of rotation of the plane containing 1, 2, and 3 from some fixed vector $\hat{p}$ that is normal to $\hat{r}_{12}$. This bipolar coordinate system is shown in Fig. 3. This coordinate system provides the bipolar coordinate system (r_{13}, r_{23}, χ) for doing the $\mathbf{r}_3$ integration. We have

$$d\mathbf{r}_3 = (r_{13}r_{23}/r_{12})\, dr_{13}\, dr_{23}\, d\chi$$

$$0 \leqslant r_{13} < \infty, \qquad |r_{12} - r_{13}| \leqslant r_{23} \leqslant r_{12} + r_{13}$$

and $0 \leqslant \chi \leqslant 2\pi$. Also, since $\hat{r}_{12} \cdot \hat{r}_{13} = (r_{12}^2 + r_{13}^2 - r_{23}^2)/2r_{12}r_{13}$, the term given by (A.2) is

$$[-\rho/6\lambda^2(8\pi^2)^3] \int d\hat{r}_{12}\, d\chi\, d\mathbf{e}'^3 \int_{\lambda|\sigma_{12}-\sigma_{13}|}^{\lambda(\sigma_{12}+\sigma_{13})} dr_{23}\, \sigma_{12}\sigma_{12}\lambda^2(\sigma_{12}^2 + \sigma_{13}^2)$$
$$- \sigma_{12}r_{23}^2\eta(r_{23} - \sigma_{23})\, \tilde{g}_N^{(3)}(r_{12} = \lambda\sigma_{12}, r_{13} = \lambda\sigma_{13}, r_{23}, \chi, \mathbf{e}^3; \lambda) \quad \text{(A.3)}$$

A necessary condition that this be nonzero is that $r_{23} > \sigma_{\min}$, but for $\lambda \leqslant \lambda^*$, this can never happen, so (A.3) is zero and the first derivative is given by the first term in Eq. (A.1) alone.

The second derivative is

$$(\partial^2/\partial\lambda^2)\, \overline{\sigma_{12}^3 G_N(\lambda\sigma_{12})}$$
$$= 6\rho\lambda[\overline{\sigma_{12}^3}/(1 - \rho\lambda^3\overline{\sigma_{12}})]^2 + 18(\rho\lambda^2)^2\, [\overline{\sigma_{12}^3}/(1 - \rho\lambda^3\, \overline{\sigma_{12}^3})]^3 + A(\lambda) \quad \text{(A.4)}$$

where $A(\lambda)$ is the derivative of (A.3). For $\lambda < \lambda^*$, the only nonzero term in $A(\lambda)$, is the boundary term, i.e.,

$$-[\rho/6(8\pi^2)^3] \int d\hat{r}_{12}\, d\chi\, d\mathbf{e}'^3\, (\sigma_{12} + \sigma_{13})\, \sigma_{12}(\sigma_{12}^3 - \sigma_{12}^2\sigma_{13} - \sigma_{12}\sigma_{13}^2 - \sigma_{13}^3)$$
$$\times\, \eta(\lambda(\sigma_{12} + \sigma_{13}) - \sigma_{23})$$
$$\times\, \tilde{g}_N^{(3)}\, (r_{12} = \lambda\sigma_{12}, r_{13} = \lambda\sigma_{13}, r_{23} = \lambda(\sigma_{12} + \sigma_{13}), \hat{r}_{12}, \chi, \mathbf{e}^3; \lambda) \quad \text{(A.5)}$$

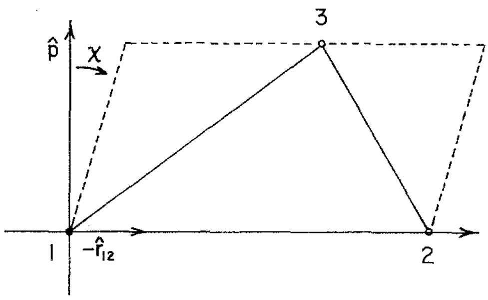

Fig. 3. A nonplanar, bipolar coordinate system. Particles 1, 2, and 3 are in a plane that is rotated around $\hat{r}_{12}$ by an angle χ with respect to the reference $\hat{p}\hat{r}_{12}$ plane.

For $\lambda < \lambda^*$, this is zero because of the $\eta(\lambda(\sigma_{12} + \sigma_{13}) - \sigma_{23})$. Depending on the geometry of the particles, i.e., the form of σ_{12}, this may be nonzero for $\lambda = \lambda^{*+}$. Thus, for $\lambda < \lambda^*$, the second derivative is given by the first two terms in (A.4) and the discontinuity at λ^{*+} is given by (A.5).

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