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Quantum-mechanical third virial coefficient of a hard-sphere gas at high temperature

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The third virial coefficient B_3 of a gas of hard spheres, of diameter a and mass m, has been expanded in powers of λ/a, where λ is the thermal wavelength $(2\pi/kT)^{1/2}$ ($\hbar = m = 1$). B_3 can be expressed in terms of integrals on all configurations of the quantum-statistical-mechanical probability density of the configurations of a three-sphere system. This probability density is proportional to a Green's function which must satisfy zero boundary conditions on the manifolds of the six-space which correspond to contact between two spheres. In the high-temperature limit, where λ/a is small, the effects of the sphere curvature can be treated as corrections. To a first approximation, we need only the three-dimensional Green's function h which vanishes on the faces of a trihedral, and the two-dimensional Green's function g which vanishes on the edges of a plane wedge. The curvature effects can in turn be expressed as series of integrals involving h and g. Using suitable approximate expressions of h and g, we find $B_3 = (5\pi^2 a^6/18)[1 + (3\sqrt{2}/2)\lambda/a + 1.708(\lambda/a)^2 + 0.63(\lambda/a)^3 + \cdots]$. (The first three terms were already known).

I. INTRODUCTION

In a previous paper,[1] the quantum-mechanical third virial coefficient of a hard-sphere gas at high temperature was expanded as a series in powers of the thermal wavelength $\lambda = (2\pi\beta)^{1/2}$ (here, we take $m = 1$ for the molecular mass and $\hbar = 1$ for Planck's constant; $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T the absolute temperature); since there are only two lengths in the problem, λ and the sphere diameter a, the series is actually in powers of λ/a. The series was obtained up to the order λ^2. In the present paper, we give a systematic method of construction for this (presumably asymptotic) series, and we explicitly compute the next term, of order λ^3.

The third virial coefficient B_3 can be obtained from the second virial coefficient B_2 and the third cluster integral b_3 by[2]

$$B_3 = 4B_2^2 - 2b_3. \qquad (1.1)$$

A λ expansion of B_2 is known.[3] Our task here will be to compute b_3, which will be expressed as an integral involving Green's functions of the three-body problem, the relative coordinate configuration space of which is six dimensional.

In Sec. II, we define these Green's functions, and relate b_3 to them. Section III is devoted to some geometrical studies of the boundary hypersurfaces and of their tangent hyperplanes, in the six-dimensional configuration space. In Sec. IV, we expand the Green's functions as series in powers of a^{-1}, the coefficients of which can be expressed in terms of a two-dimensional Green's function obeying zero-boundary conditions on the edges of a plane wedge, and of a three-dimensional Green's function obeying zero-boundary conditions on the faces of a trihedral. In Sec. V, we use the a^{-1} expansion of the Green's functions to build a λ/a expansion of the third cluster integral b_3. The explicit calculation of the coefficients is done in Sec. VI, through the use of suitable approximations for the wedge and trihedral Green's functions. The final result for the third virial coefficient is given in Sec. VII.

II. GREEN'S FUNCTIONS AND THIRD CLUSTER INTEGRAL

Let us consider a system of three spheres of diameter a and mass $m = 1$. We take as independent relative coordinates the pair of variables $(\vec{x}_1, \vec{y}_1)$ defined by

$$\vec{x}_1 = \vec{r}_2 - \vec{r}_3, \quad \vec{y}_1 = \tfrac{2}{3}\sqrt{3}\,[\vec{r}_1 - \tfrac{1}{2}(\vec{r}_2 + \vec{r}_3)], \qquad (2.1)$$

where the $\vec{r}_i$ $(i = 1, 2, 3)$ are the particle coordinates. We shall also use the other pairs of independent variables $(\vec{x}_i, \vec{y}_i)$ $(i = 2, 3)$, the expressions of which in terms of the particle coordinates $\vec{r}_i$ are obtained from (2.1) by cyclic permutation of the subscripts.

We shall combine a pair $(\vec{x}_i, \vec{y}_i)$ $(i = 1, 2, 3)$ of coordinates into a six-vector $\vec{X} = (\vec{x}_i, \vec{y}_i)$; each coordinate pair $(\vec{x}_i, \vec{y}_i)$ corresponds to some choice of the basis in the Euclidean six-dimensional space R^6. The coordinate pairs $(\vec{x}_i, \vec{y}_i)$ are related to one another by

$$\vec{x}_2 = -\tfrac{1}{2}\vec{x}_1 - \tfrac{1}{2}\sqrt{3}\,\vec{y}_1, \quad \vec{y}_2 = \tfrac{1}{2}\sqrt{3}\,\vec{x}_1 - \tfrac{1}{2}\vec{y}_1, \qquad (2.2)$$

and cyclically permuted equations. We shall denote by C_i a Cartesian coordinate system in R^6 associated with the pair $(\vec{x}_i, \vec{y}_i)$.

The kinetic-energy operator H_0 is

$$H_0 = -\Delta \equiv -\Delta_{\vec{x}_i} - \Delta_{\vec{y}_i},$$

where Δ is the six-dimensional Laplacian and $\Delta_{\vec{x}_i}$ ($\Delta_{\vec{y}_i}$) are the three-dimensional Laplacians acting on the variables $\vec{x}_i$ ($\vec{y}_i$) only.

The wave function Ψ of the hard-sphere system obeys the Schrödinger equation

$$-\Delta\Psi = E\Psi,$$

with the boundary conditions that the wave function vanishes on an hypersurface S which is defined by one of the relations

$$x_1 = a, \quad x_2 = a, \quad x_3 = a.$$

The corresponding Hamiltonian will be called H. We shall denote by V the physical configuration space which is the exterior ($x_i > a$, $i = 1, 2, 3$) of the volume bounded by the hypersurface S.

We shall also consider the problem when two spheres only interact. The wave function Ψ_i, in the six-dimensional space, then obeys the equation

$$-\Delta\Psi_i = E\Psi_i,$$

with the boundary condition that Ψ_i vanishes on the six-dimensional cylinder σ_i which is defined by the equation

$$x_i = a.$$

The corresponding Hamiltonian will be called H_i. The part of the cylinder σ_i that belongs to the boundary S will be called S_i, $S_i = S \cap \sigma_i$. Note that the surfaces S_i intersect pairwise through the manifolds S_{ij}, $S_{ij} = S_i \cap S_j$. The boundary S_0 of these manifolds consists of the points where all three surfaces intersect,

$$S_0 = \bigcap_i S_i.$$

To illustrate these notions, let us consider a motion of the three spheres on a straight line. The configuration subspace is a two-dimensional plane in this case (Fig. 1). The surface S is the boundary of the region V and the manifold S_{ij} is the set of the wedge vertices formed by the straight lines S_i and S_j. There is no part of S_0 within the drawn subspace.

We shall use the thermal Green's functions $G(\vec{X}, \vec{X}^0;\ \beta)$ and $G_i(\vec{X}, \vec{X}^0;\ \beta)$ of the boundary-value problems corresponding to the Hamiltonians H and H_i. The Green's function G obeys the equation

$$\left(\frac{\partial}{\partial\beta} - \Delta_{\vec{X}}\right) G(\vec{X}, \vec{X}^0;\ \beta) = \delta(\beta)\delta(\vec{X} - \vec{X}^0) \qquad (2.3)$$

and the boundary conditions

$$G(\vec{X}, \vec{X}^0;\ 0^-) = 0, \quad G(\vec{X}, \vec{X}^0;\ \beta)|_{\vec{X}\in S} = 0. \qquad (2.4)$$

The Green's function G_i obeys the same equation (2.3) and the boundary conditions

$$G_i(\vec{X}, \vec{X}^0;\ 0^-) = 0, \quad G_i(\vec{X}, \vec{X}^0;\ \beta)|_{\vec{X}\in \sigma_i} = 0. \qquad (2.5)$$

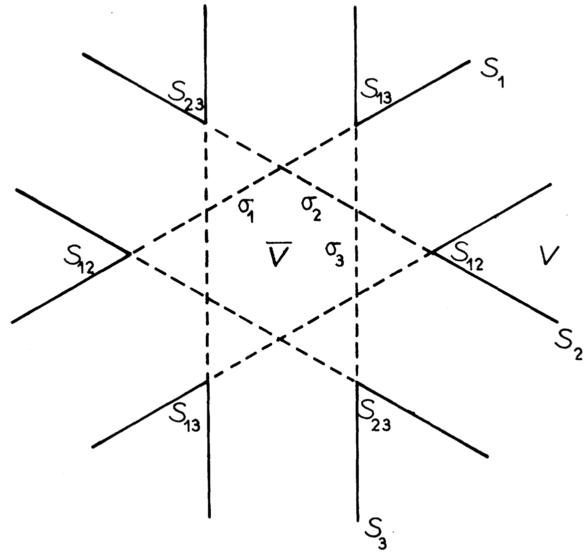

FIG. 1. Configuration subspace for the motion of the three spheres on a straight line.

We shall denote by $G_0(\vec{X}, \vec{X}^0;\ \beta)$ the free three-particle Green's function, which also obeys (2.3):

$$G_0(\vec{X}, \vec{X}^0;\ \beta) = (4\pi\beta)^{-3} e^{-(\vec{X} - \vec{X}^0)^2/4\beta}. \qquad (2.6)$$

$\vec{X}^0$ will be called the source point.

$(4\pi\beta)^3 G(\vec{X}^0, \vec{X}^0;\ \beta)$ is the probability density[4] for the configuration $\vec{X}^0$ (normalized to unity when all particles are far apart from one another). The cluster integral b_3 therefore is[2]

$$b_3 = \frac{1}{6}\int d\vec{r}_2^{\,0}\, d\vec{r}_3^{\,0} (4\pi\beta)^3 G_c(\vec{X}^0, \vec{X}^0;\ \beta)$$
$$= 4\sqrt{3}\pi^3\beta^3 \int d\vec{X}^0\, G_c(\vec{X}^0, \vec{X}^0;\ \beta), \qquad (2.7)$$

where G_c is the connected part of the Green's function

$$G_c = G - G_0 - \sum_{i=1}^{3} (G_i - G_0); \qquad (2.8)$$

$\vec{r}_2^{\,0}$ and $\vec{r}_3^{\,0}$ are the particle coordinates corresponding to the configuration $\vec{X}^0$.

The integral in (2.7) is on the whole configuration space, including the interior $\bar{V}$ of S; G however is defined as being zero in $\bar{V}$, and similarly G_i is defined as being zero in the interior of σ_i. The contribution $b_{\bar{V}}$ of $\bar{V}$ to b_3 therefore involves only G_0 and the G_i, and is easy to compute. $\bar{V}$ is defined by the condition that one at least of the distances x_i^0 is smaller than a. Omitting for brevity the superscripts 0, we find

$$b_{\overline{V}} = \frac{1}{3}\int_{x_1, x_2, x_3 < a} d\vec{r}_2\, d\vec{r}_3 - \frac{1}{2}\int_{x_3 > a} d\vec{x}_3 [(4\pi\beta)^3 G_3 - 1]\int_D d\vec{r}_3\,, \tag{2.9}$$

where D is the union of the domains defined by $x_1 < a$ and $x_2 < a$, respectively. Since $1-(4\pi\beta)^3 G_3$ decreases exponentially[5] like $\exp[-(x_3-a)^2/\beta]$, we can use for $\int_D d\vec{r}_3$ its value in the range $a \leq x_3 \leq 2a$. Thus

$$b_{\overline{V}} = \frac{3\pi^2 a^6}{4} - \frac{8\pi^2 a^3}{3}\int_a^\infty dx_3\, x_3^2\left(1 + \frac{3x_3}{4a} - \frac{x_3^2}{16a^3}\right) \times [(4\pi\beta)^3 G_3 - 1]. \tag{2.10}$$

The integral in (2.10) can be expressed as a sum of integrals on the variable $x_3 - a$; these integrals have been computed as series in powers of λ/a when the second virial coefficient was studied.[5] Using these calculations, we find

$$b_{\overline{V}} = \frac{3\pi^2 a^6}{4}\left[1 + \frac{3}{\sqrt{2}}\frac{\lambda}{a} + \frac{5}{2\pi}\left(\frac{\lambda}{a}\right)^2 + \frac{17}{48\pi\sqrt{2}}\left(\frac{\lambda}{a}\right)^3 + \cdots\right]. \tag{2.11}$$

The full third cluster integral is

$$b_3 = b_{\overline{V}} + b_V\,. \tag{2.12}$$

The main content of the present paper will now be the computation of the contribution b_V to (2.7) of the exterior V of S. Actually, the regions of V which are not in the neighborhood of the intersection manifolds S_{ij} give to b_V only negligible contributions in the high-temperature limit. This can be shown as follows: $G_0 - G$ obeys an inequality

$$(4\pi\beta)^3[G_0(\vec{X}^0, \vec{X}^0;\ \beta) - G(\vec{X}^0, \vec{X}^0;\ \beta)] < Ae^{-Cd^2/\beta}, \tag{2.13}$$

where A and C are positive constants and where d is the shortest distance between $\vec{X}^0$ and the surface S. The inequality (2.13) is easily obtained by noticing that G decreases when the forbidden region $\overline{V}$ is extended, because G can be written as a Wiener integral[6] on trajectories which do not enter $\overline{V}$; an extension of $\overline{V}$ suppresses trajectories and makes G smaller. In order to obtain an upper bound to $G_0 - G$, we can replace S in (2.4) by the surface of an hypercube, with its center at $\vec{X}^0$, and small enough for lying entirely within V. With zero-boundary conditions on the surface of an hypercube, G can be explicitly computed by the method of images, and the bound (2.13) can be proved. A similar reasoning proves that

$$(4\pi\beta)^3[G_i(\vec{X}^0, \vec{X}^0;\ \beta) - G(\vec{X}^0, \vec{X}^0;\ \beta)] < Ae^{-Cd^2/\beta}, \tag{2.14}$$

where d is now the shortest distance between $\vec{X}^0$ and the surface $\overline{S}_i$, the complement of S_i in S. Using (2.13) and (2.14), we can show that the points $\vec{X}^0$ lying in V at a distance from all the manifolds S_{ij} larger than $(a^2/\beta)^\nu \beta^{1/2}$, $\nu > 0$, give to (2.7) only exponentially small contributions behaving like $\exp[-C(a^2/\beta)^{2\nu}]$, and thus smaller than any power of β in the high-temperature limit.

In what follows, we shall define the neighborhood of a manifold as the set of the points $\vec{X}$, $\vec{X} \in V$, the shortest distance of which to this manifold is smaller than $(a^2/\beta)^\nu \beta^{1/2}$. Thus, since we are looking here only for the contributions in powers of $\beta^{1/2}$ to (2.7), we shall obtain b_V by integrating only on the union $V(\beta)$ of the neighborhoods of the manifolds S_{ij}. In this situation, we expect that the curvature effects will be small, and that it will be possible to approximate the Green's functions G and G_i by simpler Green's functions that satisfy zero-boundary conditions on hyperplanes tangent to S. Curvature effects will be then treated as corrections.

Therefore, we shall need a description of S and its tangent manifolds in the neighborhood of S_{ij} and S_0. This description will be given in Sec. III.

III. BOUNDARY SURFACES AND THEIR TANGENT MANIFOLDS IN SIX-DIMENSIONAL SPACE

Let $V_{ij}(\beta)$, $V_{ij}(\beta) \subset V$, be that part of the neighborhood of S_{ij} which is not in the neighborhood of the triple intersection manifold S_0. It is by now clear that, if the source point $\vec{X}^0$ lies in $V_{ij}(\beta)$, only the boundary conditions on the surfaces S_i and S_j must be taken into account. We shall therefore describe first the structure of the cylinders σ_1 and σ_2 near a source point $\vec{X}^0$, $\vec{X}^0 \in V_{12}(\beta)$. Cyclically permuted formulae hold of course in $V_{23}(\beta)$ and $V_{31}(\beta)$.

Consider a straight line through the point $\vec{X}^0$ and orthogonal to the cylinder σ_1 (σ_2). Let $\vec{X}_1$ ($\vec{X}_2$) be the nearest point of intersection of this line with the surface σ_1 (σ_2) and let $\tilde{\mathcal{S}}_1$ ($\tilde{\mathcal{S}}_2$) be the hyperplane tangent to the surface σ_1 (σ_2) at the point $\vec{X}_1$ ($\vec{X}_2$) (Fig. 2). These five-dimensional tangent planes intersect through the four-dimensional hyperplane M_{12}. Thus the six-dimensional space R^6 is the orthogonal sum

$$R^6 = M_{12} \oplus L_{12}\,, \tag{3.1}$$

where L_{12} is the two-dimensional subspace spanned by the normals $\hat{n}_1$ and $\hat{n}_2$ to the surfaces σ_1 and σ_2 at the points $\vec{X}_1$ and $\vec{X}_2$. We shall denote by $\vec{u}$ the vectors of the subspace L_{12} and by $\vec{v}$ the vectors of the subspace M_{12}; $\vec{X} = \vec{u} \oplus \vec{v}$.

Besides the C_1 and C_2 coordinate systems, we shall use below other coordinate systems C_{12} and

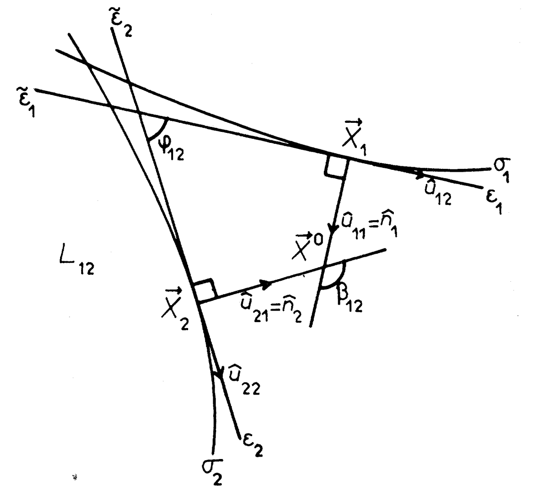

FIG. 2. Boundary surfaces and their tangent manifolds near S_{12}.

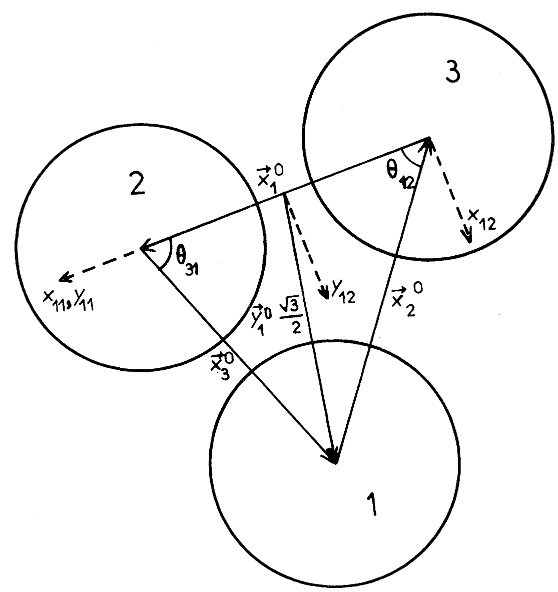

FIG. 3. Source configuration.

C_{21} associated with the decomposition (3.1). C_{12} is a Cartesian coordinate system with its origin at the point $\vec{X}_1$ and its u_{11} axis ($\vec{u} = u_{11}, u_{12}$) parallel to the normal $\hat{n}_1$. In the subspace L_{12} we take the v_{11} axis ($\vec{v} = v_{11}, v_{12}, v_{13}, v_{14}$) in the subspace $\{\vec{x}_1, 0\}$, the v_{12} axis such that the three-dimensional subspace $\{\vec{x}_1, 0\}$ is in the four-dimensional subspace spanned by the axes u_{11}, u_{12}, v_{11}, v_{12}, and the v_{13} axis in the subspace $\{0, \vec{y}_1\}$.

The Cartesian coordinate system C_{21}, the origin of which will be at the point $\vec{X}_2$, is described in terms of the $(\vec{x}_2, \vec{y}_2)$ pair in a similar way. The corresponding coordinates will be denoted by $\vec{u} = (u_{21}, u_{22})$, $\vec{v} = (v_{21}, v_{22}, v_{23}, v_{24})$. If the vectors $\vec{u}, \vec{v}$ bear subscripts, $(\vec{u}_i, \vec{v}_i)$ means $(\vec{u}, \vec{v})$ given in the C_{12} $(i=1)$ or the C_{21} $(i=2)$ coordinate system.

Let us now give the C_{12} basis elements in the C_1 basis. The C_1 basis will be chosen in such a way that the x_{11} and y_{11} axes $[\vec{x}_1 = (x_{11}, x_{12}, x_{13})$, $\vec{y}_1 = (y_{11}, y_{12}, y_{13})]$ are parallel to the vector $\vec{x}_1^0$ associated with the source point $\vec{X}^0 = (\vec{x}_1^0, \vec{y}_1^0)$, and the parallel x_{12} and y_{12} axes are in the plane spanned by the vectors $\vec{x}_1^0$ and $\vec{y}_1^0$ (Fig. 3). It is easy to see that the exterior normal $\hat{n}_1$ is parallel to the vector $(\vec{x}_1^0, 0)$ given in the C_1 coordinate system, and the normal $\hat{n}_2$ is parallel to the vector $(\vec{x}_2^0, 0)$ given in the C_2 coordinate system. Note that the distances $|\vec{X}_1 - \vec{X}^0|$ and $|\vec{X}_2 - \vec{X}^0|$ are, respectively, equal to the surface-to-surface distances of the spheres $x_1^0 - a$ and $x_2^0 - a$. Using the change-of-basis formulas (2.2), we get $\hat{n}_1$ and $\hat{n}_2$ in the C_1 coordinate system:

$$\hat{n}_1 = (1, 0, 0, 0, 0, 0),$$

$$\hat{n}_2 = (\tfrac{1}{2}\cos\theta_{12}, \tfrac{1}{2}\sin\theta_{12}, 0, \tfrac{1}{2}\sqrt{3}\cos\theta_{12}, \tfrac{1}{2}\sqrt{3}\sin\theta_{12}, 0), \tag{3.2}$$

where θ_{12} is the angle between the vectors $\vec{x}_1^0$ and $-\vec{x}_2^0$. Note that the angle between $\hat{n}_1$ and $\hat{n}_2$ is β_{12} such that

$$\cos\beta_{12} = \hat{n}_1 \cdot \hat{n}_2 = \tfrac{1}{2}\cos\theta_{12}. \tag{3.3}$$

We get the following possible expressions for the C_{12} basis elements in the C_1 coordinate system:

$$\begin{aligned}
\hat{u}_{11} &= (1, 0, 0, 0, 0, 0),\\
\hat{u}_{12} &= (4 - \cos^2\theta_{12})^{-1/2}\\
&\quad \times (0, \sin\theta_{12}, 0, \sqrt{3}\cos\theta_{12}, \sqrt{3}\sin\theta_{12}, 0),\\
\hat{v}_{11} &= (0, 0, 1, 0, 0, 0),\\
\hat{v}_{12} &= (4 - \cos^2\theta_{12})^{-1/2}\\
&\quad \times (0, -\sqrt{3}, 0, \sin\theta_{12}\cos\theta_{12}, \sin^2\theta_{12}, 0),\\
\hat{v}_{13} &= (0, 0, 0, 0, 0, 1),\\
\hat{v}_{14} &= (0, 0, 0, \sin\theta_{12}, -\cos\theta_{12}, 0).
\end{aligned} \tag{3.4}$$

The C_{21} basis elements can be expressed in the C_2 coordinate system by similar formulas.

Using (3.3) and (3.4), we find that the equation $x_1 = a$ of the cylinder σ_1 becomes, in the C_{12} basis,

$$u_{11} = [a^2 - (1/4\sin^2\beta_{12})(u_{12}\sin\theta_{12} - \sqrt{3}\,v_{12})^2 - v_{11}^2]^{1/2} - a. \tag{3.5}$$

A similar equation holds for the cylinder σ_2 in the C_{21} basis.

Consider now a source point $\vec{X}^0$ in the neighborhood $V_0(\beta)$, $V_0(\beta) \subset V$, of the triple intersection manifold S_0. It will now be necessary to take into account the boundary conditions on all three surfaces S_i, and we shall need a description of the three cylinders σ_i near $\vec{X}^0$. Let $\tilde{\mathcal{E}}_i$ $(i = 1, 2, 3)$ be the hyperplane tangent to the cylinder σ_i at the point $\vec{X}_i$. (The points $\vec{X}_i$ are constructed in the same way as above; note again that $|\vec{X}_i - \vec{X}^0| = x_i^0 - a$.) The hyperplanes $\mathcal{S}_i$ intersect through a three-dimensional subspace M. Thus R^6 is the orthogonal sum

$$R^6 = L \oplus M, \tag{3.6}$$

where L is the three-dimensional subspace spanned by the normals $\hat{n}_1$, $\hat{n}_2$, and $\hat{n}_3$ to the surfaces σ_1, σ_2, and σ_3 at the points $\vec{X}_1$, $\vec{X}_2$, and $\vec{X}_3$. We shall denote by $\vec{p}$ the vectors of the subspace L and by $\vec{q}$ the vectors of the subspace M; $\vec{X} = \vec{p} \oplus \vec{q}$. The exterior normals $\hat{n}_i$ are given in the C_1 coordinate system by (3.2) and

$$\hat{n}_3 = (\tfrac{1}{2}\cos\theta_{31}, -\tfrac{1}{2}\sin\theta_{31}, 0, -\tfrac{1}{2}\sqrt{3}\cos\theta_{31}, \tfrac{1}{2}\sqrt{3}\sin\theta_{31}, 0). \tag{3.7}$$

We shall now define coordinate systems associated with the decomposition (3.6). In the subspace M, we take a Cartesian coordinate system with its axis q_{11} in the subspace $\{\vec{x}_1, 0\}$ and its axis q_{12} in the subspace $\{0, \vec{y}_1\}$. Thus, the basis elements $\hat{q}_{1i}$ are, in the C_1 coordinate system,

$$\begin{aligned}
\hat{q}_{11} &= (0, 0, 1, 0, 0, 0),\\
\hat{q}_{12} &= (0, 0, 0, 0, 0, 1),\\
\hat{q}_{13} &= (1+\cos\theta_{12}\cos\theta_{23}\cos\theta_{31})^{-1/2}(0, \tfrac{1}{2}\sqrt{3}\sin\theta_{23}, 0, -\sin\theta_{31}\sin\theta_{12}, \tfrac{1}{2}\sin(\theta_{31}-\theta_{12}), 0).
\end{aligned} \tag{3.8}$$

We shall denote by C_{01} the nonorthogonal coordinate system with its origin at $\vec{X}_1$ and having as its basis elements $\hat{n}_1, \hat{n}_2, \hat{n}_3, \hat{q}_{11}, \hat{q}_{12}, \hat{q}_{13}$. A vector $\vec{X}$ will be represented by its contravariant coordinates p_{1i} and q_{1i} defined by

$$\vec{X} = a\hat{n}_1 + \sum_{i=1}^{3} (p_{1i}\hat{n}_i + q_{1i}\hat{q}_{1i}). \tag{3.9}$$

Nonorthogonal coordinate systems C_{02} and C_{03} with their origin at $\vec{X}_2$ and $\vec{X}_3$ are similarly defined. In what follows, $(\vec{p}_i, \vec{q}_i)$ will denote a vector $(\vec{p}, \vec{q})$ given in the coordinate system C_{0i}.

Using (3.2), (3.7), and (3.8), we find that the equation $x_1 = a$ of the cylinder σ_1 becomes, in the C_{01} coordinate system,

$$\begin{aligned}
p_{11} = {}&[a^2 - q_{11}^2 - (\tfrac{1}{2}p_{12}\sin\theta_{12} - \tfrac{1}{2}p_{13}\sin\theta_{31} + q_{13}\sqrt{3}\sin\theta_{23}/2(1+\cos\theta_{12}\cos\theta_{23}\cos\theta_{31})^{1/2})^2]^{1/2}\\
&- a - \tfrac{1}{2}p_{12}\cos\theta_{12} - \tfrac{1}{2}p_{13}\cos\theta_{31}.
\end{aligned} \tag{3.10}$$

Similar equations hold for the cylinders σ_2 and σ_3 in the C_{02} and C_{03} bases.

IV. a^{-1} EXPANSION OF GREEN'S FUNCTIONS

A. Green's function G

In order to obtain an expansion in powers of λ/a for the third cluster integral, we now come to an expansion in powers of a^{-1} of the Green's function G, which depends upon the sphere diameter a (a^{-1} will be explicitly displayed as a variable when necessary):

$$G(\vec{X}, \vec{X}^0;\ \beta;\ a^{-1}) = \sum_{k=0}^{\infty} \frac{a^{-k}}{k!} G^{(k)}(\vec{X}, \vec{X}^0;\ \beta), \tag{4.1}$$

where

$$G^{(k)}(\vec{X}, \vec{X}^0;\ \beta) = \frac{\partial^k}{\partial(a^{-1})^k} G(\vec{X}, \vec{X}^0;\ \beta;\ a^{-1})\big|_{a^{-1}=0}. \tag{4.2}$$

In (4.2), the derivative with respect to a^{-1} must be understood in the following sense, in order to have a meaningful limit $a^{-1} \to 0$: The source configuration $\vec{X}^0$ corresponds to surface-to-surface distances $x_i^0 - a$. The configuration $\vec{X}$ is meant to be specified by one of the sets of coordinates $(\vec{u}_i, \vec{v}_i)$ or $(\vec{p}_i, \vec{q}_i)$ which were defined in Sec. III. Then, the derivative with respect to a^{-1} is taken for fixed values of the distances $x_i^0 - a$ and for fixed values of the coordinates $(\vec{u}_i, \vec{v}_i)$ and $(\vec{p}_i, \vec{q}_i)$.

To find the differential equations obeyed by the functions $G^{(k)}$, we substitute (4.1) in (2.3), differentiate k times with respect to a^{-1}, and then set $a^{-1} = 0$. We find

$$\left(\frac{\partial}{\partial\beta} - \Delta_{\vec{X}}\right) G^{(0)}(\vec{X}, \vec{X}^0;\ \beta) = \delta(\beta)\delta(\vec{X} - \vec{X}^0), \tag{4.3}$$

$$\left(\frac{\partial}{\partial\beta} - \Delta_{\vec{X}}\right) G^{(k)}(\vec{X}, \vec{X}^0;\ \beta) = 0, \quad k \geq 1. \tag{4.4}$$

To proceed further, we must consider two cases apart.

1. X^0 lies in region $V_{ij}(\beta)$

Assume for instance that $\vec{X}^0 \in V_{12}(\beta)$ [similar discussions hold for $V_{23}(\beta)$ and $V_{31}(\beta)$]. The boundary conditions for the functions $G^{(k)}$ can then be obtained as follows: G must vanish when $\vec{X}$ belongs to the surfaces S_1 or S_2, which depend upon a^{-1}:

$$G(\vec{X}, \vec{X}^0;\ \beta;\ a^{-1})|_{\vec{X}\in S_i(a^{-1})} = 0, \quad (i=1,2); \qquad (4.5)$$

S_1 is a portion of the cylinder σ_1 defined by (3.5), and a similar equation holds for S_2. Substituting (4.1) in (4.5), differentiating n times with respect to a^{-1}, and setting $a^{-1}=0$, we find the recurrence relation

$$G^{(n)}(\vec{X}, \vec{X}^0;\ \beta)|_{\vec{X}\in\mathcal{S}_i} = -\lim_{a^{-1}\to 0} \frac{\partial^n}{\partial(a^{-1})^n}\left(\sum_{k=0}^{n-1} \frac{a^{-k}}{k!} G^{(k)}(\vec{X}, \vec{X}^0;\ \beta)|_{\vec{X}\in S_i(a^{-1})}\right), \quad (i=1,2), \qquad (4.6)$$

where $\mathcal{S}_i$ is $S_i(a^{-1}=0)$: $\mathcal{S}_1$ and $\mathcal{S}_2$ are those parts of the hyperplanes $\tilde{\mathcal{S}}_1$ and $\tilde{\mathcal{S}}_2$ that limit the region where u_{11} and u_{21} are positive (Fig. 2). In the case $n=0$,

$$G^{(0)}(\vec{X}, \vec{X}^0;\ \beta)|_{\vec{X}\in\mathcal{S}_i} = 0, \quad i=1,2, \qquad (4.7)$$

i.e., $G^{(0)}$ obeys zero-boundary conditions on the faces of the dihedral formed by $\mathcal{S}_1$ and $\mathcal{S}_2$. The following terms $G^{(n)}$ are recurrently determined by their boundary values (4.6) on the same dihedral. It is convenient to express the boundary condition on $\mathcal{S}_i$ by using for $\vec{X}$ the coordinates $(\vec{u}_i, \vec{v}_i)$. In the case $n=1$, (4.6) becomes on $\mathcal{S}_1$

$$G^{(1)}(\vec{u}_1, \vec{v}_1, \vec{X}^0;\ \beta)|_{u_{11}=0} = -\lim_{a^{-1}\to 0} \frac{\partial}{\partial(a^{-1})} G^{(0)}(u_{11}(u_{12}, \vec{v}_1, a^{-1}), u_{12}, \vec{v}_1, \vec{X}^0;\ \beta), \qquad (4.8)$$

where $u_{11}(u_{12}, \vec{v}_1, a^{-1})$ is the function (3.5). Therefore

$$G^{(1)}(\vec{u}_1, \vec{v}_1, \vec{X}^0;\ \beta)|_{u_{11}=0} = \left(\frac{1}{8\sin^2\beta_{12}}(u_{12}\sin\theta_{12} - \sqrt{3}\,v_{12})^2 + \tfrac{1}{2}v_{11}^2\right)\frac{\partial}{\partial u_{11}} G^{(0)}(\vec{u}_1, \vec{v}_1, \vec{X}^0;\ \beta)|_{u_{11}=0}. \qquad (4.9)$$

A similar condition holds on $\mathcal{S}_2$. Thus, $G^{(1)}$ obeys boundary conditions on the dihedral, which can be expressed in terms of the normal derivatives of $G^{(0)}$. The higher-order terms $G^{(n)}$ obey boundary conditions expressed in terms of higher-order normal derivatives of $G^{(0)}$.

Finding $G^{(n)}$ $(n \geq 1)$, which obeys (4.4) and the boundary conditions (4.6), is a Dirichlet problem, the solution of which is

$$G^{(n)}(\vec{X}, \vec{X}^0;\ \beta) = \sum_{i=1,2} \int_0^\beta d\tau \int_{\mathcal{S}_i} dS'\, G^{(n)}(\vec{X}', \vec{X}^0;\ \tau) \frac{\partial G^{(0)}(\vec{X}, \vec{X}';\ \beta-\tau)}{\partial n_i'}, \qquad (4.10)$$

where $\vec{X}' \in \mathcal{S}_i$, dS' is a surface element on $\mathcal{S}_i$ around $\vec{X}'$, and $\partial/\partial n_i'$ denotes the derivative normal to $\mathcal{S}_i$ at $\vec{X}'$. Therefore, $G^{(n)}$ can be expressed in terms of $G^{(0)}$ only.

$G^{(0)}$ itself essentially reduces to a two-dimensional Green's function, because in the decomposition $R^6 = M_{12} \oplus L_{12}$, there are no boundary conditions in M_{12}. Therefore, $G^{(0)}$ factorizes as a free Green's function in M_{12} and a Green's function in L_{12}:

$$G^{(0)}(\vec{X}, \vec{X}^0;\ \beta) = [1/(4\pi\beta)^2] e^{-\vec{v}^2/4\beta} g_{12}(\vec{u}, \vec{u}^0;\ \beta). \qquad (4.11)$$

$g_{12}(\vec{u}, \vec{u}^0;\ \beta)$ is a two-dimensional Green's function in a plane wedge ω_{12}, the summit angle of which is $\varphi_{12} = \pi - \beta_{12}$ (thus $\cos\varphi_{12} = -\frac{1}{2}\cos\theta_{12}$). In this wedge, g_{12} obeys the two-dimensional equation

$$\left(\frac{\partial}{\partial\beta} - \Delta_{\vec{u}}\right) g_{12}(\vec{u}, \vec{u}^0;\ \beta) = \delta(\beta)\delta(\vec{u} - \vec{u}^0). \qquad (4.12)$$

The distances of the source point $\vec{u}^0$ to the edges of the wedge are $u_{11}^0 = x_1^0 - a$ and $u_{21}^0 = x_2^0 - a$. The function g_{12} obeys zero-boundary conditions when $\vec{u}$ is on an edge of the wedge.

Therefore, in the regions $V_{ij}(\beta)$, the Green's function $G(\vec{X}, \vec{X}^0;\ \beta)$ can be expressed as a series in terms of integrals involving only g_{ij}.

2. X^0 lies in region $V_0(\beta)$

Following the same steps as above, we obtain equations similar to (4.5), (4.6), (4.7), where however now $i=1,2,3$. In the limit $a^{-1}=0$, the union of the surfaces S_i becomes a trihedral, the faces $\mathcal{S}_1, \mathcal{S}_2, \mathcal{S}_3$ of which are parts of the tangent hyperplanes $\tilde{\mathcal{S}}_1, \tilde{\mathcal{S}}_2, \tilde{\mathcal{S}}_3$. $G^{(n)}$ is determined by its boundary values on this trihedral. $G^{(0)}$ has zero-boundary values. It is convenient to express the boundary conditions for $G^{(n)}$ $(n \geq 1)$ by using for $\vec{X}$ the coordinates $(\vec{p}_i, \vec{q}_i)$. In the case $n=1$, the analog of (4.6) becomes on $\mathcal{S}_1$

$$G^{(1)}(\vec{p}_1, \vec{q}_1, \vec{X}^0; \beta)|_{\vec{p}_1 \in \mathcal{E}_1} = -\lim_{a^{-1}\to 0} \frac{\partial}{\partial (a^{-1})} G^{(0)}(p_{11}(p_{12}, p_{13}, \vec{q}_1, a^{-1}), p_{12}, p_{13}, \vec{q}_1, \vec{X}^0; \beta), \tag{4.13}$$

where $p_{11}(p_{12}, p_{13}, \vec{q}_1, a^{-1})$ is the function defined by (3.10) and where $\mathcal{E}_1$ is defined by the limit of (3.10) when $a^{-1} \to 0$. Therefore,

$$G^{(1)}(\vec{p}_1, \vec{q}_1, \vec{X}^0; \beta)|_{p_{11}=-(1/2)p_{12}\cos\theta_{12}-(1/2)p_{13}\cos\theta_{13}} = \left[\frac{q_{11}^2}{2} + \frac{1}{8}\left(p_{12}\sin\theta_{12} + p_{13}\sin\theta_{13} + q_{13}\frac{\sqrt{3}\,\sin\theta_{23}}{(1+\cos\theta_{12}\cos\theta_{23}\cos\theta_{31})^{1/2}}\right)^2\right]$$

$$\times \frac{\partial}{\partial p_{11}} G^{(0)}(\vec{p}_1, \vec{q}_1, \vec{X}^0; \beta)|_{p_{11}=-(1/2)p_{12}\cos\theta_{12}-(1/2)p_{13}\cos\theta_{31}}. \tag{4.14}$$

Similar boundary conditions hold on the other faces of the trihedral. The higher-order terms $G^{(n)}$ obey boundary conditions which involve higher-order normal derivatives of $G^{(0)}$.

Finding $G^{(n)}$ is again a Dirichlet problem which is solved by an equation analogous to (4.10), with however a summation on $i=1, 2, 3$, and therefore $G^{(n)}$ can be expressed in terms of $G^{(0)}$ only.

In the present paper, where the expansion of B_3 will be carried to the order $(\lambda/a)^3$ only, it will turn out that there are no contributions from the curvature corrections $G^{(n)}$ $(n \geq 1)$ in the region $V_0(\beta)$. Equation (4.14) has however been given here for the sake of completeness; it would be necessary to use it for higher-order calculations.

In this region $V_0(\beta)$, $G^{(0)}$ essentially reduces to a three-dimensional Green's function, because in the decomposition $R^6 = M \oplus L$, there are no boundary conditions in M. Therefore, $G^{(0)}$ factorizes as

$$G^{(0)}(\vec{X}, \vec{X}^0; \beta) = [1/(4\pi\beta)^{3/2}] e^{-(\vec{q})^2/4\beta} h(\vec{p}, \vec{p}^0; \beta). \tag{4.15}$$

$h(\vec{p}, \vec{p}^0; \beta)$ is a three-dimensional Green's function in a trihedral Ω (Fig. 4). The angles between the faces of this trihedral are φ_{ij}, and $\cos\varphi_{ij} = -\frac{1}{2} \times \cos\theta_{ij}$. Inside the trihedral, h obeys the three-dimensional equation

$$\left(\frac{\partial}{\partial \beta} - \Delta_{\vec{p}}\right) h(\vec{p}, \vec{p}^0; \beta) = \delta(\beta)\delta(\vec{p} - \vec{p}^0). \tag{4.16}$$

The distances of the source point $\vec{p}^0$ to the faces of the trihedral are $p_i^0 = x_i^0 - a$ [note that $p_i^0 = u_{i1}^0$; note also that p_i^0, a covariant coordinate in the nonorthogonal basis $(\hat{n}_1, \hat{n}_2, \hat{n}_3)$ differs from the contravariant coordinates which were introduced in (3.9)]. h obeys zero-boundary conditions when $\vec{p}$ is on a face of the trihedral.

Therefore, in the region $\vec{X}^0 \in V_0(\beta)$, the Green's function $G(\vec{X}, \vec{X}^0; \beta)$ can be expressed as a series in terms of integrals involving only h.

B. Green's functions G_i

There are similar a^{-1} expansions for the Green's functions G_i, which obey zero-boundary conditions on one cylinder σ_i:

$$G_i(\vec{X}, \vec{X}^0; \beta; a^{-1}) = \sum_{k=0}^{\infty} \frac{a^{-k}}{k!} G_i^{(k)}(\vec{X}, \vec{X}^0; \beta). \tag{4.17}$$

Instead of (4.11), we find

$$G_i^{(0)}(\vec{X}, \vec{X}^0; \beta) = [1/(4\pi\beta)^{5/2}] e^{-[(\vec{v})^2 + u_{i2}^2]/4\beta} k_i(u_{i1}, u_{i1}^0; \beta), \tag{4.18}$$

where k_i is a one-dimensional Green's function which satisfies a zero-boundary condition for $u_{i1} = 0$; it has the explicit expression

$$k_i(u_{i1}, u_{i1}^0; \beta) = [1/(4\pi\beta)^{1/2}] \times (e^{-(u_{i1}-u_{i1}^0)^2/4\beta} - e^{-(u_{i1}+u_{i1}^0)^2/4\beta}). \tag{4.19}$$

k_i can also be written using the coordinates $\vec{p}$ rather than $\vec{u}$; u_{i1}^0 is identical with p_i^0.

The curvature corrections for G_i are obtained in the same way as for G. The terms $G_i^{(n)}$ are recurrently determined by their boundary values on the hyperplane $\tilde{\mathcal{E}}_i$.

To summarize the present section, we have expressed all relevant Green's functions as series

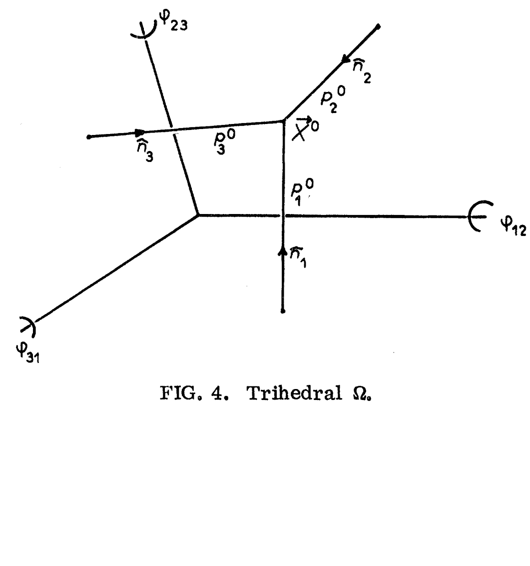

FIG. 4. Trihedral Ω.

in powers of a^{-1}, the coefficients of which involve the two-dimensional Green's functions g_{ij} in plane wedges and the three-dimensional Green's function h in a trihedral. The use of these series in (2.7) will generate an expansion of the third cluster integral b_3 in powers of λ/a.

V. λ/a EXPANSION OF THIRD CLUSTER INTEGRAL

In this section, b_V, the contribution of V to the third cluster integral, will be expanded as a series in powers of λ/a, or equivalently in powers of $\beta^{1/2}/a$, up to the order $(\beta^{1/2}/a)^3$. The coefficients of the series will be expressed as integrals on the Green's functions g_{ij} and h.

Let us denote by $G_c^{(k)}$ the term of order k in the a^{-1} expansion of the connected Green's function:

$$G_c^{(0)} = G^{(0)} - G_0 - \sum_{i=1}^{3} (G_i^{(0)} - G_0),$$
$$G_c^{(k)} = G^{(k)} - \sum_{i=1}^{3} G_i^{(k)}, \quad k \geq 1. \tag{5.1}$$

Since G_c has a range of order $\beta^{1/2}$, the contribution of $V_{ij}(\beta)$ to (2.7) is of order $a^4\beta$; to reach the order $a^3\beta^{3/2}$, it is enough to use in $V_{ij}(\beta)$ the a^{-1} expansion of G_c up to the order a^{-1}, i.e., to keep $G_c^{(0)}$ and $G_c^{(1)}$. The contribution of $V_0(\beta)$ is of order $a^3\beta^{3/2}$; in $V_0(\beta)$ it is enough to keep $G_c^{(0)}$. Thus, to the order $\beta^{3/2}$,

$$b_V = 3b_{12}^{(0)} + b_0^{(0)} + b^{(1)}, \tag{5.2}$$

where

$$b_{12}^{(0)} = \tfrac{1}{6} \int_{V_{12}(\beta)} d\vec{X}_1^0 \, d\vec{X}_2^0 \, (4\pi\beta)^3 \times \Big(G_0(\vec{X}^0, \vec{X}^0; \beta) + G^{(0)}(\vec{X}^0, \vec{X}^0; \beta) - \sum_{i=1}^{2} G_i^{(0)}(\vec{X}^0, \vec{X}^0; \beta) \Big), \tag{5.3}$$

$$b_0^{(0)} = \tfrac{1}{6} \int_{V_0(\beta)} d\vec{X}_1^0 \, d\vec{X}_2^0 (4\pi\beta)^3 G_c^{(0)}(\vec{X}^0, \vec{X}^0; \beta), \tag{5.4}$$

$$b^{(1)} = \tfrac{1}{2} \int_{V_{12}(\beta)} d\vec{X}_1^0 \, d\vec{X}_2^0 \, \frac{(4\pi\beta)^3}{a} \times \Big(G^{(1)}(\vec{X}^0, \vec{X}^0; \beta) - \sum_{i=1}^{2} G_i^{(1)}(\vec{X}^0, \vec{X}^0; \beta) \Big). \tag{5.5}$$

We first study $b_{12}^{(0)}$. Using (2.6), (4.11), and (4.18) (here $\vec{X} = \vec{X}^0$ and $\vec{v} = 0$), we obtain

$$b_{12}^{(0)} = \tfrac{1}{6} \int_{V_{12}(\beta)} d\vec{X}_1^0 \, d\vec{X}_2^0 4\pi\beta g_{12c}(\vec{u}^0, \vec{u}^0; \beta), \tag{5.6}$$

where

$$4\pi\beta g_{12c}(\vec{u}^0, \vec{u}^0; \beta) = 4\pi\beta g_{12}(\vec{u}^0, \vec{u}^0; \beta) - (4\pi\beta)^{1/2} \sum_{i=1}^{2} k_i(u_{i1}^0, u_{i1}^0; \beta) + 1. \tag{5.7}$$

The integrand in (5.6) depends upon the distances $u_{11}^0 = x_1^0 - a$ and $u_{21}^0 = x_2^0 - a$, and the wedge angle φ_{12}. The integration range for $\cos\varphi_{12} = -\frac{1}{2}\cos\theta_{12}$ is $(-\frac{1}{4} + a^{2\nu-1}\beta^{1/2-\nu}, \frac{1}{2})$. We find it convenient to extend this range to $(-\frac{1}{4}, \frac{1}{2})$ and to correct for this by subtracting the contribution δ of the range increment. We obtain, up to the order $\beta^{3/2}$,

$$b_{12}^{(0)} = \tfrac{8}{3}\pi^2 \int_{-1/4}^{1/2} d(\cos\varphi_{12}) [a^4 A_1(\varphi_{12}) + 4a^3 A_2(\varphi_{12})] - \delta, \tag{5.8}$$

where

$$A_1(\varphi_{12}) = \int_0^\infty du_{11}^0 \int_0^\infty du_{21}^0 \, 4\pi\beta g_{12c}(\vec{u}^0, \vec{u}^0; \beta) \tag{5.9}$$

and

$$A_2(\varphi_{12}) = \int_0^\infty du_{11}^0 \int_0^\infty du_{21}^0 \, u_{11}^0 4\pi\beta g_{12c}(\vec{u}^0, \vec{u}^0; \beta). \tag{5.10}$$

In (5.9) and (5.10), the integration ranges for u_{11}^0 and u_{21}^0 have been extended up to ∞, because the corresponding error is exponentially small.

The corrections δ will be combined with $b_0^{(0)}$. It is convenient to use as integration variables $u_{i1}^0 = x_i^0 - a$ ($i = 1, 2, 3$) instead of $u_{11}^0, u_{21}^0, \theta_{12}$. To order $\beta^{3/2}$,

$$\delta = \frac{4\pi^2 a^3}{3} \int_{\substack{u_{31}^0 > \frac{1}{2}(u_{11}^0 + u_{21}^0) \\ \vec{X}^0 \in V_0(\beta)}} du_{11}^0 \, du_{21}^0 \, du_{31}^0 \, 4\pi\beta g_{12c}(\vec{u}^0, \vec{u}^0; \beta)$$
$$= \frac{4\pi^2 a^3}{3} \int_{\vec{X}^0 \in V_0(\beta)} du_{11}^0 \, du_{21}^0 \, du_{31}^0 \, 4\pi\beta g_{12c}(\vec{u}^0, \vec{u}^0; \beta) - \frac{2\pi^2 a^3}{3} \int_0^\infty du_{11}^0 \int_0^\infty du_{21}^0 \, (u_{11}^0 + u_{21}^0) 4\pi\beta g_{12c}(\vec{u}^0, \vec{u}^0; \beta). \tag{5.11}$$

In the last integral, to order $\beta^{3/2}$, the wedge angle can be given its value on S_0, i.e., $\Theta=\cos^{-1}(-\frac{1}{4})$; also, the integration ranges for u_{11}^0 and u_{21}^0 can be extended to ∞, with a negligible error. Therefore, the last term in (5.11) is $-(\frac{4}{3}\pi^2a^3)A_2(\Theta)$.

Consider now $b_0^{(0)}$. Using (2.6), (4.15), and (4.18), and taking as integration variables the distances $p_i^0=x_i^0-a$, we obtain, to order $\beta^{3/2}$,

$$b_0^{(0)}=\frac{4\pi^2a^3}{3}\int_{\vec{X}^0\in V_0(\beta)} dp_1^0\,dp_2^0\,dp_3^0\left((4\pi\beta)^{3/2}h(\vec{p}^0,\vec{p}^0;\beta)-\sum_{i=1}^{3}(4\pi\beta)^{1/2}k_i(p_i^0,p_i^0;\beta)+2\right). \tag{5.12}$$

The variables u_{i1}^0 in (5.11) are identical with the variables p_i^0. We can therefore combine (5.11) and (5.12) into

$$b_0^{(0)}-3\delta=4\pi^2a^3A_2(\Theta)+\frac{4\pi^2a^3}{3}\int_0^\infty dp_1^0\int_0^\infty dp_2^0\int_0^\infty dp_3^0(4\pi\beta)^{3/2}\bar{h}(\vec{p}^0,\vec{p}^0;\beta), \tag{5.13}$$

where

$$(4\pi\beta)^{3/2}\bar{h}(\vec{p}^0,\vec{p}^0;\beta)=(4\pi\beta)^{3/2}h(\vec{p}^0,\vec{p}^0;\beta)-\sum_{1\le i<j\le 3}4\pi\beta g_{ij}(\vec{p}^0,\vec{p}^0;\beta)+\sum_{i=1}^{3}(4\pi\beta)^{1/2}k_i(p_i^0,p_i^0;\beta)-1. \tag{5.14}$$

The combination of Green's functions $\bar{h}$ depends upon the angles φ_{ij} between the faces of the trihedral Ω. To order $\beta^{3/2}$, however, these angles can be given the value $\varphi_{ij}=\Theta=\cos^{-1}(-\frac{1}{4})$, for the evaluation of the integral (5.13); also, the integration ranges for the p_i^0 can be extended to ∞.

Let us finally come to the curvature term $b^{(1)}$. Using (4.9), (4.10), and their analogs for G_i, we obtain

$$b^{(1)}=b_1^{(1)}+b_2^{(1)}, \tag{5.15}$$

where

$$b_1^{(1)}=\frac{(4\pi\beta)^3}{a}\int_{V_{12}(\beta)} d\vec{X}_1^0\,d\vec{X}_2^0\frac{1-4\cos^2\varphi_{12}}{8\sin^2\varphi_{12}}\int_0^\beta d\tau\left[\int_{\mathcal{S}_1} dS\,u_{12}^2\left(\frac{\partial G^{(0)}(\vec{X}^0,\vec{X};\beta-\tau)}{\partial u_{11}}\frac{\partial G^{(0)}(\vec{X},\vec{X}^0;\tau)}{\partial u_{11}}\right)_{u_{11}=0}\right.$$
$$\left.-\int_{\mathcal{S}_1} dS\,u_{12}^2\left(\frac{\partial G_1^{(0)}(\vec{X}^0,\vec{X};\beta-\tau)}{\partial u_{11}}\frac{\partial G_1^{(0)}(\vec{X},\vec{X}^0;\tau)}{\partial u_{11}}\right)_{u_{11}=0}\right] \tag{5.16}$$

and

$$b_2^{(1)}=\frac{(4\pi\beta)^3}{a}\int_{V_{12}(\beta)} d\vec{X}_1^0\,d\vec{X}_2^0\int_0^\beta d\tau\left[\int_{\mathcal{S}_1} dS\left(\frac{3v_{12}^2}{8\sin^2\varphi_{12}}+\frac{v_{11}^2}{2}\right)\left(\frac{\partial G^{(0)}(\vec{X}^0,\vec{X};\beta-\tau)}{\partial u_{11}}\frac{\partial G^{(0)}(\vec{X},\vec{X}^0;\tau)}{\partial u_{11}}\right)_{u_{11}=0}\right.$$
$$\left.-\int_{\mathcal{S}_1} dS\left(\frac{3v_{12}^2}{8\sin^2\varphi_{12}}+\frac{v_{11}^2}{2}\right)\left(\frac{\partial G_1^{(0)}(\vec{X}^0,\vec{X};\beta-\tau)}{\partial u_{11}}\frac{\partial G_1^{(0)}(\vec{X},\vec{X}^0;\tau)}{\partial u_{11}}\right)_{u_{11}=0}\right] \tag{5.17}$$

[the term $u_{12}v_{12}$ from (4.9) gives an odd integrand and no contribution to (5.15)]. When the decomposition (4.11) of $G^{(0)}$ and its analog for $G_1^{(0)}$ are used, dS becomes $d\vec{v}du_{12}$. The integrations on $\vec{v}$ are easily performed. One finds, to order $\beta^{3/2}$,

$$b_1^{(1)}=8\pi^3a^3\beta\int_{\pi/3}^{\Theta} d\varphi_{12}(1-4\cos^2\varphi_{12})Q(\varphi_{12})+\Delta_1; \tag{5.18}$$

$Q(\varphi_{12})$ is an integral on the wedge Green's functions:

$$Q(\varphi_{12})=\int_0^\beta d\tau\int_{\omega_{12}} d\vec{u}^0\int_{\mathcal{S}_1} du_{12}\,u_{12}^2\left(\frac{\partial g_{12}(\vec{u}^0,\vec{u};\beta-\tau)}{\partial u_{11}}\frac{\partial g_{12}(\vec{u},\vec{u}^0;\tau)}{\partial u_{11}}-\frac{\partial g_1(\vec{u}^0,\vec{u};\beta-\tau)}{\partial u_{11}}\frac{\partial g_1(\vec{u},\vec{u}^0;\tau)}{\partial u_{11}}\right)_{u_{11}=0}, \tag{5.19}$$

where g_1 is the two-dimensional Green's function which satisfies zero-boundary conditions on $\tilde{\mathcal{S}}_1$,

$$g_1(\vec{u}, \vec{u}^0; \beta) = [e^{-u_{12}^2/4\beta}/(4\pi\beta)^{1/2}]\, k_1(u_{11}, u_{11}^0; \beta). \tag{5.20}$$

The term Δ_1 arises because the term of (5.19) containing g_1 must actually be integrated on the whole domain $\tilde{\mathcal{S}}_1$. The explicit expression (4.19) of k_1 permits the calculation of Δ_1. It is convenient to take polar coordinates (r, φ) and (r_0, φ_0) for $\vec{u}$ and $\vec{u}^0$, respectively, with the origin at the summit of the wedge ω_{12}, and to use the variable $t = r/r_0$ rather than the variable r. One finds, after some work,

$$\Delta_1 = -\tfrac{9}{32}\pi^{5/2}a^3\beta^{3/2}(\tfrac{2231}{1280} - 2\ln 2) = -0.0813 \times \tfrac{5}{36}\pi^2 a^3\lambda^3. \tag{5.21}$$

Similarly, after integration on $\vec{v}$ in (5.17), one obtains, to order $\beta^{3/2}$,

$$b_2^{(1)} = 64\pi^3 a^3 \int_{\pi/3}^{\Theta} d\varphi_{12}(\tfrac{3}{4} + \sin^2\varphi_{12}) \int_0^\beta d\tau\, \tau(\beta - \tau) \int_{\omega_{12}} d\vec{u}^0 \bigg[\int_{\mathcal{S}_1} du_{12} \left(\frac{\partial g_{12}(\vec{u}^0, \vec{u}; \beta - \tau)}{\partial u_{11}} \frac{\partial g_{12}(\vec{u}, \vec{u}^0; \tau)}{\partial u_{11}} \right)_{u_{11}=0} - \int_{\tilde{\mathcal{S}}_1} du_{12} \left(\frac{\partial g_1(\vec{u}^0, \vec{u}; \beta - \tau)}{\partial u_{11}} \frac{\partial g_1(\vec{u}, \vec{u}^0; \tau)}{\partial u_{11}} \right)_{u_{11}=0} \bigg]. \tag{5.22}$$

This expression can be simplified by using the closure properties

$$\int_{\omega_{12}} d\vec{u}^0 g_{12}(\vec{u}^0, \vec{u}; \beta - \tau) g_{12}(\vec{u}, \vec{u}^0; \tau) = g_{12}(\vec{u}, \vec{u}; \beta) \tag{5.23}$$

and

$$\int_{\pi_+} d\vec{u}^0 g_1(\vec{u}^0, \vec{u}; \beta - \tau) g_1(\vec{u}, \vec{u}^0; \tau) = g_1(\vec{u}, \vec{u}; \beta), \tag{5.24}$$

where π_+ is the half-plane $u_{11}^0 > 0$. Adding and subtracting in (5.24) the integration domain $\bar{\omega}_{12}$, the complement of ω_{12} in π_+, we find

$$b_2^{(1)} = \tfrac{32}{3}\pi^3 a^3 \beta^3 \int_{\pi/3}^{\Theta} d\varphi_{12}(\tfrac{3}{4} + \sin^2\varphi_{12}) T(\varphi_{12}) + \Delta_2, \tag{5.25}$$

where

$$T(\varphi_{12}) = \int_{\mathcal{S}_1} du_{12} \left(\frac{\partial^2 g_{12}(\vec{u}, \vec{u}'; \beta)}{\partial u_{11} \partial u_{11}'} - \frac{\partial^2 g_1(\vec{u}, \vec{u}'; \beta)}{\partial u_{11} \partial u_{11}'} \right)_{\substack{u_{12} = u_{12}' \\ u_{12} = u_{11}' = 0}} \tag{5.26}$$

The term Δ_2 arises from the contribution to the term of (5.22) containing g_1 of the whole domain $\tilde{\mathcal{S}}_1$, and from the contribution to (5.24) of the domain $\bar{\omega}_{12}$. This term Δ_2 can be explicitly computed along the same lines as Δ_1, with the result

$$\Delta_2 = \tfrac{9}{64}\pi^{5/2}a^3\beta^{3/2}(1 + 4\ln\tfrac{5}{4}) = 0.2157 \times \tfrac{5}{36}\pi^2 a^3 \lambda^3. \tag{5.27}$$

Our remaining task is to perform the integrals on g_{ij} and h in (5.8), (5.13), (5.18), and (5.25).

VI. WEDGE AND TRIHEDRAL GREEN'S FUNCTIONS

We have shown how to express the third cluster integral in terms of the Green's functions of a wedge and of a trihedral. These Green's functions however cannot be expressed in terms of elementary functions, and we shall have to bypass this difficulty.

The term $A_1(\varphi_{12})$ has already been evaluated in Ref. 1. We represent $\vec{u}^0$ by polar coordinates (r, φ); the origin is taken at the wedge summit, and φ is the angle between $\vec{u}^0$ and one edge of the wedge. The wedge Green's function has the expression

$$g_{12}(\vec{u}^0, \vec{u}^0; \beta) = \frac{1}{\beta\varphi_{12}} \sum_{n=1}^{\infty} e^{-r^2/2\beta} I_{n\pi/\varphi_{12}}\left(\frac{r^2}{2\beta}\right) \sin^2\left(\frac{n\pi\varphi}{\varphi_{12}}\right), \tag{6.1}$$

where I is a Bessel function of imaginary argument. Using (6.1), it is possible to compute $A_1(\varphi_{12})$, with the result

$$A_1(\varphi_{12}) = \beta[\tfrac{1}{6}(\pi^2/\varphi_{12} - \varphi_{12})\sin\varphi_{12} - \cos\varphi_{12}]. \tag{6.2}$$

The expression (6.1) of g_{ij} unfortunately turns out to be of no help for the computation of (5.10), (5.19), (5.26). Also, we have no explicit expression of h for the computation of (5.13). We must now resort to approximations. On the one hand, we shall compute (5.10), (5.19), and (5.26) for special values of φ_{12}. On the other hand, we shall expand these quantities and (5.13) in powers of $\cos\varphi_{12}$. Approximate expressions will be derived from the combination of these results.

A. Special values of φ_{12}

The method of images gives simple expressions for g_{12} and g_{12c} when φ_{12} is a submultiple of π. We have considered the cases $\varphi_{12} = \frac{1}{2}\pi$ and $\varphi_{12} = \frac{1}{3}\pi$.

1. $\varphi_{12}=\frac{1}{2}\pi$

For brevity we put $u_{11}=u_1$, $u_{21}=u_2$, $u_{11}^0=u_1^0$, $u_{21}^0=u_2^0$. Then

$$g_{12}(\vec{u},\vec{u}^0;\beta)=\frac{1}{4\pi\beta}\prod_{i=1,2}\left(e^{-(u_i-u_i^0)^2/4\beta}-e^{-(u_i+u_i^0)^2/4\beta}\right). \tag{6.3}$$

From (6.3), one easily finds $A_2(\frac{1}{2}\pi)=\frac{1}{4}\pi^{1/2}\beta^{3/2}$ and $T(\frac{1}{2}\pi)=-1/(8\pi^{1/2}\beta^{3/2})$. A more tedious calculation gives $Q(\frac{1}{2}\pi)=-(3/128)(\beta/\pi)^{1/2}$.

2. $\varphi_{12}=\frac{1}{3}\pi$

In terms of polar coordinates (r,φ) for $\vec{u}$ and (r_0,φ_0) for $\vec{u}^0$,

$$4\pi\beta g_{12}(\vec{u},\vec{u}^0;\beta)=\sum_{n=0}^{2}e^{-(r\cos\varphi-x_n)^2/4\beta}\left(e^{-(r\sin\varphi-y_n)^2/4\beta}-e^{-(r\sin\varphi+y_n)^2/4\beta}\right), \tag{6.4}$$

where $x_n=r_0\cos(\varphi_0+n\frac{2}{3}\pi)$, $y_n=r_0\sin(\varphi_0+n\frac{2}{3}\pi)$. One finds rather easily $A_2(\frac{1}{3}\pi)=\frac{5}{24}\pi^{1/2}\beta^{3/2}$ and $T(\frac{1}{3}\pi)=-\sqrt{3}/(8\pi^{1/2}\beta^{3/2})$, and after a very tedious calculation (using the variable $t=r/r_0$ rather than r) $Q(\frac{1}{3}\pi)=-(403/18\,432)(3\beta/\pi)^{1/2}$.

B. $\cos\varphi_{12}$ expansions

The Green's function $g_{12}(\vec{u},\vec{u}^0;\beta)$, in a wedge of angle φ_{12}, can be expanded in powers of $\cos\varphi_{12}$. We use as (nonorthogonal) coordinates the distances u_1, u_2 to the edges. The differential equation (4.12) becomes

$$\left(\frac{\partial}{\partial\beta}-\frac{\partial^2}{\partial u_1^2}-\frac{\partial^2}{\partial u_2^2}-2\cos\varphi_{12}\frac{\partial^2}{\partial u_1\partial u_2}\right)g_{12}(\vec{u},\vec{u}^0;\beta)=\sin\varphi_{12}\,\delta(\beta)\delta(u_1-u_1^0)\delta(u_2-u_2^0), \tag{6.5}$$

and g_{12} obeys zero-boundary conditions for $u_1=0$ and $u_2=0$. When $\cos\varphi_{12}=0$, g_{12} reduces to the expression (6.3), which will be called here $g_{12}^{(0)}$. Considering the term $\partial^2/\partial u_1\partial u_2$ in (6.5) as a perturbation, we obtain for g_{12} the expansion

$$g_{12}(\vec{u},\vec{u}^0;\beta)=\sin\varphi_{12}\left(g_{12}^{(0)}(\vec{u},\vec{u}^0;\beta)-2\cos\varphi_{12}\int_0^\beta d\tau\int_0^\infty du_1'\int_0^\infty du_2'\,g_{12}^{(0)}(\vec{u},\vec{u}';\beta-\tau)\frac{\partial^2 g_{12}^{(0)}(\vec{u}',\vec{u}^0;\tau)}{\partial u_1'\partial u_2'}+\cdots\right). \tag{6.6}$$

Using (6.6), and keeping the integration upon τ for the end, we obtain from (5.10)

$$A_2(\varphi_{12})=\tfrac{1}{4}\pi^{1/2}\beta^{3/2}(1-\tfrac{3}{8}\cos\varphi_{12}+\cdots), \tag{6.7}$$

and from (5.26)

$$T(\varphi_{12})=-(1/8\pi^{1/2}\beta^{3/2})(1+\cos\varphi_{12}+\cdots). \tag{6.8}$$

The expansion of $Q(\varphi_{12})$ was found too complicated for being carried on.

A similar method of expansion can be used for the Green's function h in a trihedral, in terms of the Green's function $h^{(0)}$ in a rectangular trihedral. One finds for the integral in (5.13)

$$\int_0^\infty dp_1^0\int_0^\infty dp_2^0\int_0^\infty dp_3^0\,\bar{h}(\vec{p}^0,\vec{p}^0;\beta)=-\tfrac{1}{64}[1-(2/\pi)\cos\Theta-(\tfrac{3}{2}+2/\pi-16/\pi^2)\cos^2\Theta+\cdots]; \tag{6.9}$$

here $\cos\Theta=-\frac{1}{4}$. The calculation of the coefficient of $\cos^2\Theta$ in (6.9) involves an integrand which turns out to be an even function of the p_i^0, and this allows an extension of the integration range to $(-\infty,+\infty)$; the calculation is nevertheless cumbersome, and we omit its details here.

C. Fit and integration of functions of φ_{12}

We fit $A_2(\varphi_{12})$ by the approximate expression

$$A_2(\varphi_{12})\approx\tfrac{1}{4}\pi^{1/2}\beta^{3/2}(1-\tfrac{3}{8}\cos\varphi_{12}+\tfrac{1}{12}\cos^2\varphi_{12}), \tag{6.10}$$

which takes account of (6.7) and the value of A_2 at $\varphi_{12}=\frac{1}{3}\pi$. Using (6.2) and (6.10) in (5.8), we find

$$3b_{12}^{(0)}+3\delta=0.731\,878\,2\pi^2a^4\lambda^2+4.6591\tfrac{5}{36}\pi^2a^3\lambda^3. \tag{6.11}$$

Using (6.9) and (6.10) in (5.13), we find

$$b_0^{(0)}-3\delta=0.4124\times\tfrac{5}{36}\pi^2a^3\lambda^3. \tag{6.12}$$

We fit the values of $Q(\varphi_{12})$ at $\varphi_{12}=\frac{1}{2}\pi$, $\varphi_{12}=\frac{1}{3}\pi$, and $\varphi_{12}=\pi$ [for $\varphi_{12}=\pi$, $Q=0$, since the integrand of (5.19) vanishes], by

$$Q(\varphi_{12})\approx-\tfrac{3}{128}(\beta/\pi)^{1/2}\times(1+1.154\,372\cos\varphi_{12}+0.154\,372\cos^2\varphi_{12}). \tag{6.13}$$

Using (6.13) in (5.18), we find

$$b_1^{(1)}=\Delta_1-0.0943\tfrac{5}{36}\pi^2a^3\lambda^3. \tag{6.14}$$

We fit $T(\varphi_{12})$ by

$$T(\varphi_{12}) \approx -(1/8\pi^{1/2}\beta^{3/2}) \times[1+\cos\varphi_{12}+(4\sqrt{3}-6)\cos^2\varphi_{12}], \quad (6.15)$$

which takes account of (6.8) and the value of T at $\varphi_{12}=\frac{1}{3}\pi$. Using (6.15) in (5.25), we find

$$b_2^{(1)} = \Delta_2 - 1.6705 \times \tfrac{5}{36}\pi^2 a^3 \lambda^3. \quad (6.16)$$

Collecting (6.11), (6.12), (6.14), (5.21), (6.16), (5.27) in (5.2) and (5.15), we obtain

$$b_V = 0.731\,878\,2\pi^2 a^4 \lambda^2 + 3.441\tfrac{5}{36}\pi^2 a^3 \lambda^3. \quad (6.17)$$

VIII. RESULT

Using (2.11) and (6.17) in (2.12), we find for the third cluster integral

$$b_3 = \frac{5\pi^2 a^6}{36}\left[\frac{27}{5} + \frac{81\sqrt{2}}{10}\frac{\lambda}{a} + 9.566\,707\left(\frac{\lambda}{a}\right)^2 + 3.871\left(\frac{\lambda}{a}\right)^3 + \cdots\right]. \quad (7.1)$$

The second virial coefficient is[5]

$$B_2 = \frac{2\pi a^3}{3}\left[1 + \frac{3}{2\sqrt{2}}\frac{\lambda}{a} + \frac{1}{\pi}\left(\frac{\lambda}{a}\right)^2 + \frac{1}{16\pi\sqrt{2}}\left(\frac{\lambda}{a}\right)^3 + \cdots\right]. \quad (7.2)$$

Using (7.1) and (7.2) in (1.1), we obtain for the third virial coefficient

$$B_3 = \frac{5\pi^2 a^6}{18}\left[1 + \frac{3\sqrt{2}}{2}\frac{\lambda}{a} + 1.707\,660\left(\frac{\lambda}{a}\right)^2 + 0.63\left(\frac{\lambda}{a}\right)^3 + \cdots\right]. \quad (7.3)$$

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