Molecular dynamics of the rough sphere fluid. II. Kinetic models of partially sticky spheres, structured spheres, and rough screwballs

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The rough sphere model is extended and suitably generalized to collisions between partially rough spheres, "spheres" with anisotropic mass distributions, and spheres with domains of roughness and smoothness distributed in such a way as to model polyatomic models. These models are used to compute various relaxation and correlation times. In addition, a model is devised for the interaction of a chiral molecule and nonchiral solvent molecules. This model is used to compute the couplings between translations and rotations. In treating the chiral systems we extend the independent binary collision model to the multivariate case.

I. INTRODUCTION

There is a long history in the kinetic theory of gases and in statistical mechanics of constructing very simple models for the collision between molecules.[1] The perfectly smooth elastic sphere has been used to describe atomic fluids, whereas the rough and loaded sphere models have been used to describe polyatomic fluids. These models have played an important role in our present understanding of the structure and dynamics of simple gases and liquids and in the discovery of new phenomena. This success is remarkable given the crudeness of the models. Recent applications of statistical perturbation theories using some of these model fluids as zero order reference systems have been successful in incorporating the detailed features of more realistic intermolecular potentials.[2]

Given the foregoing, it would be interesting to retain many of the simple features of the smooth and rough sphere models while at the same time extending them so that they can account for some of the properties of real polyatomic molecules. For example, in symmetric tops there is an anisotropic mass distribution. This is not properly accounted for by the rough sphere model. In addition, in polyatomic molecules, because of the space filling nature of molecular groups, collisions involving different regions of the molecule will be relatively more "slippery" than others. This is likewise not properly accounted for in the rough sphere model. Both of these features are rather easily incorporated into a generalization of the collision model.

The basic philosophy of this paper is to devise the simplest models consistent with the more pervasive properties of polyatomic molecules. These models are then used to study translational and rotational relaxation processes in polyatomic fluids. All of the results are simple to derive and, moreover, are physically transparent. The models lend themselves rather easily to study by molecular dynamics. In devising these models, attention is given to boundary conditions intermediate between slip and stick boundary conditions.

Much work has already been done on molecular modeling. Particularly noteworthy is the work on general convex shaped bodies and the particular applications to spherocylinders and prolate and oblate elipsoids.[3] The chief advantage of these models is that they are anisotropic space filling models, whereas the models devised in this paper are all isotropic with respect to their space filling properties. The chief disadvantage of these more realistic models is that they are much more cumbersome to use.

The properties of gases and liquids containing optically active molecules should be different from those containing inactive molecules. For example, in chiral systems there should be a direct coupling between translational and rotational motion with the consequence that a forced translation will lead to a forced rotation and vice versa. To our knowledge, there exists no simple kinetic models for chiral molecules that are analogous to those for nonchiral molecules. Much work exists in hydrodynamics on chiral systems.[4] The simplest hydrodynamic object with chirality is the isotropic helicoid. In this paper, we propose a very simple model for the interaction between a chiral and a nonchiral molecule—a model we call the rough screwball model. This model is then applied to a study of the coupling between translations and rotations.

The major points in this paper are: (1) a generalization of the smooth and rough sphere models to the case of collisions between partially sticky spheres, (2) a new model for collisions between symmetric top molecules, which we call the "sturctured sphere model," (3) a binary collision model of angular velocity and linear velocity relaxation in fluids of structured spheres, (4) a simple kinetic model for collisions between a chiral molecule and nonchiral model which we call the rough screwball model, and, finally, (5) a study of the coupling between translations and rotations in a fluid containing a rough screwball in a host consisting of ordinary rough spheres.

II. LINEAR AND ANGULAR VELOCITY RELAXTION TIMES

It is of interest to study rotational and translational relaxation in fluids defined by the foregoing models. In particular, we are interested in the autocorrelation functions of the total linear $\mathbf{c}_1$ and angular ω_1 velocity of a given sphere

$$C_v(t) \equiv \langle \mathbf{c}_1 \circ e^{tLt} \mathbf{c}_1 \rangle / \langle c_1^2 \rangle \quad , \tag{2.1}$$

$$C_\omega(t) \equiv \langle \omega_1 \circ e^{iLt}\omega_1\rangle / \langle \omega_1^2\rangle \quad . \tag{2.2}$$

In the binary collision model,[5-7] the trajectory is approximated by a trajectory consisting of an infinite sequence of uncorrelated binary collisions. All collisions are then independent, and in this event it can be shown that the correlation functions are exponential functions with time constants

$$\frac{1}{\tau_v} = -\sum_\beta \frac{n_\beta g_{1\beta}^{(2)}(\sigma_{1\beta})\sigma_{1\beta}^2}{\langle c_1^2\rangle}\left\langle \int d\Omega v_{\beta 1}\mathbf{c}_1 \circ (\mathbf{c}_1' - \mathbf{c}_1)\right\rangle_{1\beta} \tag{2.3}$$

$$\frac{1}{\tau_\omega} = -\sum_\beta \frac{n_\beta g_{1\beta}^{(2)}(\sigma_{1\beta})\sigma_{1\beta}^2}{\langle \omega_1^2\rangle}\left\langle \int d\Omega v_{\beta 1}\boldsymbol{\omega}_1 \cdot (\omega_1' - \boldsymbol{\omega}_1)\right\rangle_{1\beta} \tag{2.4}$$

where the sum goes over all components β in the system, n_β is the number density of component β, $g_{1\beta}^{(2)}(\sigma_{1\beta})$ is the contact pair correlation function between particles of type 1 and β, $\sigma_{1\beta} = (\sigma_1 + \sigma_\beta)/2$ is the distance of closest approach in the collision, $\mathbf{v}_{\beta 1}$ is the relative velocity of a sphere of type β with sphere 1, and $d\Omega$ is the solid angle. The brackets indicate an average over a Maxwell distribution of the initial linear and angular velocities and the subscripts 1β indicate that the values c_1' and ω_1' after collision are to be calculated using the dynamical law for a collision between sphere 1 and a sphere of type β.

Given its anisotropy with respect to its mass distribution and force center distribution, a symmetric top should experience more or less drag from the bath depending on whether it translates in a direction parallel ($\parallel$) or perpendicular ($\perp$) to its molecular axis $\mathbf{u}_1$. Likewise, the molecule should experience different drag torques depending on whether it rotates about an axis parallel to $\mathbf{u}_1$ or perpendicular to $\mathbf{u}_1$. This leads us to investigate the following variables:

$$\mathbf{c}_\parallel = (\mathbf{c}_1 \circ \mathbf{u}_1)\mathbf{u}_1 \ , \tag{2.5a}$$

$$\mathbf{c}_\perp = (\delta - \mathbf{u}_1\mathbf{u}_1) \circ \mathbf{c}_1 \ , \tag{2.5b}$$

$$\boldsymbol{\omega}_\parallel = (\boldsymbol{\omega}_1 \circ \mathbf{u}_1)\mathbf{u}_1 \ , \tag{2.5c}$$

$$\boldsymbol{\omega}_\perp = (\delta - \mathbf{u}_1\mathbf{u}_1) \cdot \mathbf{u}_1 \ , \tag{2.5d}$$

where $\mathbf{c}_1$ and $\boldsymbol{\omega}_1$ are the linear and angular velocities of the symmetric top molecules. The correlation times of these variables in the binary collision model are given, respectively,

$$\left(\frac{1}{\tau_v}\right)_\parallel = -\frac{3n_2 g_{12}(\sigma_{12})\sigma_{12}^2}{\langle c_1^2\rangle} \times \left\langle \int d^2\mathbf{u}_1 \int d\Omega v_{21}\mathbf{c}_1 \cdot \mathbf{u}_1\mathbf{u} \cdot (\mathbf{c}_1' - \mathbf{c}_1)\right\rangle, \tag{2.6a}$$

$$\left(\frac{1}{\tau_v}\right)_\perp = -\frac{3n_2 g_{12}(\sigma_{12})\sigma_{12}^2}{\langle c_1^2\rangle} \times \left\langle \int d^2\mathbf{u}_1 \int d\Omega v_{21}[\mathbf{c}_1 \circ (\delta - \mathbf{u}_1\mathbf{u}_1) \circ (\mathbf{c}_1' - \mathbf{c}_1)]\right\rangle, \tag{2.6b}$$

$$\left(\frac{1}{\tau_\omega}\right)_\parallel = -\frac{3n_2 g_{12}(\sigma_{12})\sigma_{12}^2}{\langle \omega_1^2\rangle} \times \left\langle \int d^2\mathbf{u}_1 \int d\Omega v_{21}\boldsymbol{\omega}_1 \circ \mathbf{u}_1\mathbf{u}_1 \circ (\boldsymbol{\omega}_1' - \boldsymbol{\omega}_1)\right\rangle \tag{2.6c}$$

$$\left(\frac{1}{\tau_\omega}\right)_\perp = -\frac{3n_2 g_{12}(\sigma_{12})\sigma_{12}^2}{\langle \omega_1^2\rangle} \times \left\langle \int d^2\mathbf{u}_1 \int d\Omega v_{21}\boldsymbol{\omega}_1 \circ (\delta - \mathbf{u}_1\mathbf{u}_1) \circ (\boldsymbol{\omega}_1' - \boldsymbol{\omega}_1)\right\rangle \tag{2.6d}$$

for the case where there is one anisotropic sphere in a fluid of perfectly rough spheres.

The correlation times of the total linear and angular velocities $\mathbf{c}_1$ and ω_1 are, respectively, given in terms of their parallel and perpendicular component

$$\frac{1}{\tau_v} = \frac{1}{3}\left[\left(\frac{1}{\tau_v}\right)_\parallel + 2\left(\frac{1}{\tau_v}\right)_\perp\right], \tag{2.7a}$$

$$\frac{1}{\tau_\omega} = \frac{1}{3}\left[\left(\frac{1}{\tau_\omega}\right)_\parallel + 2\left(\frac{1}{\tau_\omega}\right)_\perp\right]. \tag{2.7b}$$

Structured spheres, like other structured molecules, diffuse anisotropically both with respect to translations and rotations. For symmetric tops, the translational dynamics is given by the diffusion tensor $\mathbf{D}$, and the rotational diffusion tensor Θ. In the principle axis frame of the molecule

$$\mathbf{D} = \begin{pmatrix} D_\parallel & 0 & 0 \\ 0 & D_\perp & 0 \\ 0 & 0 & D_\perp \end{pmatrix}, \tag{2.8a}$$

$$\Theta = \begin{pmatrix} \Theta_\parallel & 0 & 0 \\ 0 & \Theta_\perp & 0 \\ 0 & 0 & \Theta_\perp \end{pmatrix}, \tag{2.8b}$$

where $D_\parallel$ and $D_\perp$ are, respectively, translational diffusion coefficients parallel and perpendicular to the symmetry axis and correspondingly where $\Theta_\parallel$ and $\Theta_\perp$ are, respectively, rotational diffusion coefficients around the axis parallel and perpendicular to the symmetry axis.

The components of these diffusion tensors are related to the various linear and angular velocity correlation times already introduced. Explicitly,

$$D_\parallel = \frac{K_B T}{m_1}(\tau_v)_\parallel \ ; \quad D_\perp = \frac{K_B T}{m_1}(\tau_v)_\perp \tag{2.9a}$$

and

$$\Theta_\parallel = \frac{K_B T}{I_\parallel}(\tau_\omega)_\parallel \ ; \quad \Theta_\perp = \frac{K_B T}{I_\perp}(\tau_\omega)_\perp \ . \tag{2.9b}$$

Molecular reorientations are often discussed in terms of the orientational correlation functions[8,9]

$$C_l(t) = \langle P_l[\mathbf{u}(0) \circ \mathbf{u}(t)]\rangle \ , \tag{2.10}$$

where $\mathbf{u}$ is a unit vector embedded in the molecule, and $P_l(x)$ is the Legendre polynomial of rank l. $\mathbf{u}$ can be taken either parallel to the symmetry axis $\mathbf{u} = \mathbf{u}_\parallel$ or perpendicular to the symmetry axis $\mathbf{u} = \mathbf{u}_\perp$ depending on the case of interest. As pointed out in Ref. 7 it is easier to work with the irreducible tensorial set

$$\boldsymbol{\alpha}_{(u)}^{(l)} \equiv \mathbf{Y}_l(\mathbf{u}) \ , \tag{2.11}$$

where $Y_l(\mathbf{u})$ is an irreducible tensorial set consisting of the $2l+1$ spherical harmonics $\{Y_{lm}(\mathbf{u})\}$. In addition the tensor dot product $\odot$ is defined such that $Y_l(\mathbf{u}_1)\odot Y_l(\mathbf{u}_2) = P_l(\mathbf{u}_1 \circ \mathbf{u}_2)$. From this it is clear that Eq. (2.1) can be written as

$$C_l(t) = \langle (e^{iLt}\boldsymbol{\alpha}^{(l)}) \odot \boldsymbol{\alpha}^{(l)} \rangle , \tag{2.12}$$

where L is the Liouville operator. The aim is to compute these correlation functions. A binary collision approximation scheme has been developed[5,7] according to which the Laplace transform of $C_l(t)$ can be expressed as

$$\tilde{C}_l(s) = \frac{\tilde{C}_l^{(0)}(s+\beta_l)}{1-\beta_l \tilde{C}_l^{(0)}(s+\beta_l)} , \tag{2.13}$$

where the parameter β_l is by definition

$$\beta_l = \frac{\langle \dot{\boldsymbol{\alpha}}^{(l)} \odot T\mathring{\boldsymbol{\alpha}}^{(l)} \rangle}{\langle \mathring{\boldsymbol{\alpha}}^{(l)} \odot \mathring{\boldsymbol{\alpha}}^{(l)} \rangle} . \tag{2.14}$$

An explicit derivation of Eq. (2.14) is given in Ref. 7. T is the total binary collision operator. It is convenient to evaluate the parameter β_l using the representation for the rate of change of $\dot{\boldsymbol{\alpha}}_l$,

$$\dot{\boldsymbol{\alpha}}^{(l)} = i\boldsymbol{\omega} \cdot \mathrm{I}\boldsymbol{\alpha}^{(l)} . \tag{2.15}$$

Here $\boldsymbol{\omega}$ is the angular velocity of the molecule and $\mathrm{I} = i(\mathbf{u}\times\nabla_u)$ is the generator of the rotations of $\mathbf{u}$ about an axis perpendicular to $\mathbf{u}$, that is, the angular momentum operator perpendicular to $\mathbf{u}$. It should be noted that $\mathbf{u} \circ \mathrm{I} = 0$. Writing Eq. (2.15) in Cartesian form and substituting into Eq. (2.14) gives

$$\beta_l = \frac{\langle [(I_i\boldsymbol{\alpha}^{(l)}) \odot (I_j\boldsymbol{\alpha}^{(l)})]\, \omega_i T\omega_j \rangle}{\langle [(I_{i'}\boldsymbol{\alpha}^{(l)}) \odot (I_{j'}\boldsymbol{\alpha}^{(l)})]\, \omega_{i'}\omega_{j'} \rangle} . \tag{2.16}$$

This follows from the fact that instantaneous collisions do not change the orientation but only the angular and linear velocity so that T commutes with $I_j\boldsymbol{\alpha}^{(l)}$.

It follows from the transformation properties of angular momentum operators that (see the Appendix)

$$(I_i\boldsymbol{\alpha}^{(l)}) \odot (I_j\boldsymbol{\alpha}^{(l)}) = \frac{l(l+1)}{2}(\delta_{ij} - u_iu_j) . \tag{2.17}$$

Substitution of this into Eq. (6.7) then gives

$$\beta_l = \frac{\langle \boldsymbol{\omega} \circ (\delta - \mathbf{uu}) \circ T\boldsymbol{\omega} \rangle}{\langle [\omega^2 - (\mathbf{u} \circ \boldsymbol{\omega})^2] \rangle} . \tag{2.18}$$

Certain experiments probe only the reorientation of the symmetry axis $\mathbf{u}_1$. Taking $\underline{u} = \mathbf{u}_1$ in Eq. (2.18) and comparing the results with Eqs. (2.6c) and (2.6d) gives for this case

$$\beta_l = \left(\frac{1}{\tau_\omega}\right)_\perp , \quad \mathbf{u} = \mathbf{u}_1 . \tag{2.19}$$

Other experiments probe the reorientations of vectors perpendicular to the symmetry axis. There are three orthogonal unit vectors $\mathbf{u}_1$, $\mathbf{u}_{\perp 1}$, and $\mathbf{u}_{\perp 2}$ that specify the orientation of the symmetric top. $\mathbf{u}_1$ is along the symmetry axis whereas $\mathbf{u}_{\perp 1}$ and $\mathbf{u}_{\perp 2}$ lie in the plane perpendicular to $\mathbf{u}_1$. If we look at the reorientations of the unit vector $\mathbf{u}_{\perp 1}$, then the relaxation time that characterizes this reorientation is given by Eq. (2.18) with $\delta - \mathbf{u}_{\perp 1}\mathbf{u}_{\perp 1} = \mathbf{u}_1\mathbf{u}_1 + \mathbf{u}_{\perp 2}\mathbf{u}_{\perp 2}$. Substitution into Eq. (2.18) and comparison of the result with Eq. (2.6) shows that

$$\beta_l^\perp = \frac{1}{2}\left[\left(\frac{1}{\tau_\omega}\right)_\parallel + \left(\frac{1}{\tau_\omega}\right)_\perp\right] , \quad \mathbf{u} = \mathbf{u}_{\perp 1}, \mathbf{u}_{\perp 2} . \tag{2.20}$$

It is clear from a comparison of Eqs. (2.19) and (2.20) that parameters β_l and $\beta_l^\perp$, respectively, characterizing the reorientations of the symmetry axis $\mathbf{u}_1$ and a vector $\mathbf{u}_{\perp 1}$ orthogonal to this are clearly different. For linear molecules there is no rotation about the symmetry axis and there is no need to consider the reorientation of $\mathbf{u}_\perp$.

The remaining sections will be devoted to the evaluation of these various relaxation times for different kinetic models.

III. GENERAL CONSIDERATIONS

In the ordinary rough sphere model,[1] a sphere of type 1 is characterized by several parameters: its diameter σ_1, its mass m_1, its moment of inertia I_1, or equivalently its dimensionless moment of inertia

$$\kappa_1 = 4I_1/m_1\sigma_1^2 , \tag{3.1}$$

where $\kappa_1 = 0$ when the mass is concentrated completely at the center of the sphere, $\kappa_1 = 2/5$ if the mass is uniformly distributed throughout the sphere, and κ_1 reaches its maximum value $\kappa_1 = 0.6$ when all of the mass is distributed on the surface of the sphere. In a collision between two impenetrable spheres of type 1 (σ_1, m_1, κ_1) and type 2(σ_2, m_2, κ_2) initially translating with center of mass velocities $\mathbf{c}_1$ and $\mathbf{c}_2$ and rotating with angular velocities ω_1 and ω_2, the relative velocities of the point of contact of sphere 1 and sphere 2 changes from its initial value of

$$\mathbf{g}_{21} = \mathbf{c}_2 - \mathbf{c}_1 - \tfrac{1}{2}\mathbf{n}\times(\sigma_1\omega_1 + \sigma_2\omega_2) \tag{3.2}$$

to a value $\mathbf{g}'_{21}$ after collision. In the following a prime will always denote the properties of the two molecules after collision. The vector $\mathbf{n}$ is defined in Fig. 1. It

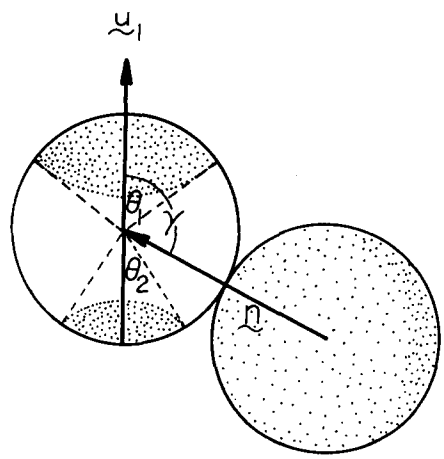

FIG. 1. The shaded areas on sphere 1 indicate domains of roughness and are characterized by polar angles θ_1 and θ_2. Sphere 2 is a perfectly rough sphere. The collision is rough only if the point of tangency lies in the shaded areas of sphere 1, that is, if $x_1 = \cos\theta_1 \le (n \cdot u_1) \le 1$ or $-1 \le (n \cdot u_1) \le -\cos\theta_2 = -x_2$; otherwise it is smooth.

is a unit vector pointing along a line from the center of sphere 1 to the center of sphere 2 and passing through the point of contact. This is called the apse line.

The relative velocity vector $\mathbf{g}_{21}$ can be resolved into a vector parallel to $\mathbf{n}$ denoted by $\mathbf{g}_{\parallel} = (\mathbf{n} \cdot \mathbf{g}_{21})\mathbf{n}$ and a vector $\mathbf{g}_{\perp}$ perpendicular to $\mathbf{n}$. The dynamical model is completely specified by how $\mathbf{g}_{\parallel}$ and $\mathbf{g}_{\perp}$ change upon collision. Towards this end it is important to consider the constraints imposed by energy conservation.

In a collision between two spheres as depicted in Fig. 1 the linear and angular velocities of the two spheres after collision (primed quantities) are related to those before collision by

$$m_1\mathbf{c}_1' = m_1\mathbf{c}_1 - \mathbf{J} \quad , \tag{3.3a}$$

$$m_2\mathbf{c}_2' = m_2\mathbf{c}_2 + \mathbf{J} \quad , \tag{3.3b}$$

$$I_1\boldsymbol{\omega}_1' = I_1\boldsymbol{\omega}_1 + \tfrac{1}{2}\sigma_1(\mathbf{n}\times\mathbf{J}) \quad , \tag{3.3c}$$

$$I_2\boldsymbol{\omega}_1 = I_2\boldsymbol{\omega}_2 + \tfrac{1}{2}\sigma_2(\mathbf{n}\times\mathbf{J}) \quad , \tag{3.3d}$$

where $\mathbf{n}$ is a unit vector along the apse line as specified in Eq. (3.1) and $\mathbf{J}$ is the impulse. The rest of the parameters are specified in the text. These equations conserve linear and total angular momentum.

The relative velocity of the points of contact before collision are given by Eq. (3.2).

The collision changes $\mathbf{g}_{21}$ to $\mathbf{g}_{21}'$, resulting in the change $\Delta\mathbf{g} = \mathbf{g}_{21}' - \mathbf{g}_{21}$. Equation (3.3) can be solved for $\mathbf{J}$ in terms of $\Delta\mathbf{g}$,

$$\mathbf{J} = \frac{m_1 m_2}{m_0}(\Delta\mathbf{g}_{\parallel} + \kappa_{12}\Delta\mathbf{g}_{\perp}) \quad , \tag{3.4}$$

where $\Delta\mathbf{g}_{\parallel}$ denotes the component of $\Delta\mathbf{g}$ along $\mathbf{n}$ and $\Delta\mathbf{g}_{\perp}$ is that part of $\Delta\mathbf{g}$ perpendicular to $\mathbf{n}$. The parameters are the total mass $m_0 = m_1 + m_2$, and

$$\kappa_0 \equiv \frac{m_1\kappa_1 + m_2\kappa_2}{m_1 + m_2} \quad , \qquad \kappa_{12} \equiv \frac{\kappa_1\kappa_2}{\kappa_1\kappa_2 + \kappa_0} \quad . \tag{3.5}$$

The change in total energy on collision can be computed from Eqs. (3.3) and (3.4):

$$\Delta E = E' - E = \frac{1}{2}\left(\frac{m_1 m_2}{m_0}\right) \times[\Delta\mathbf{g}_{\parallel}^2 + 2\mathbf{g}_{\parallel}\cdot\Delta\mathbf{g}_{\parallel} + \kappa_{12}(\Delta\mathbf{g}_{\perp}^2 + 2\mathbf{g}_{\perp}\cdot\Delta\mathbf{g}_{\perp})] \quad . \tag{3.6}$$

Thus, the energy is conserved only if the term in parenthesis is zero. Now if the dynamical law is to be the same for different choices of κ_1 and κ_2 and therefore κ_{12}, it follows that energy is conserved only if the following two conditions are satisfied by the dynamical law:

$$\Delta\mathbf{g}_{\parallel}[\Delta\mathbf{g}_{\parallel} + 2\mathbf{g}_{\parallel}] = 0 \quad , \tag{3.7a}$$

$$\Delta\mathbf{g}_{\perp}\cdot[\Delta\mathbf{g}_{\perp} + 2\mathbf{g}_{\perp}] = 0 \quad . \tag{3.7b}$$

Introducting the definition $\Delta\mathbf{g} = \mathbf{g}' - \mathbf{g}$ into Eqs. (3.7a) and (3.7b) gives, respectively, two conditions for energy conservation

$$\mathbf{g}_{\parallel}'^2 = \mathbf{g}_{\parallel}^2 \quad , \tag{3.8a}$$

$$\mathbf{g}_{\perp}'^2 = \mathbf{g}_{\perp}^2 \quad . \tag{3.8b}$$

Because two riged spheres are completely impenetrable $\mathbf{g}_{\parallel}$ is always inverted by a collision, that is,

$$\mathbf{g}_{\parallel}' = -\mathbf{g}_{\parallel} \quad . \tag{3.9}$$

This clearly satisfies Eq. (3.8a), and typifies all models considered here.

The two models used most often in kinetic theory are the smooth hard sphere model (SHSM)

$$(\text{SHSM}) = \begin{cases} \mathbf{g}_{\parallel}' = -\mathbf{g}_{\parallel} \\ \mathbf{g}_{\perp}' = \mathbf{g}_{\perp} \end{cases}$$

and the rough hard sphere model (RHSM)

$$(\text{RHSM}) = \begin{cases} \mathbf{g}_{\parallel}' = -\mathbf{g}_{\parallel} \\ \mathbf{g}_{\perp}' = -\mathbf{g}_{\perp} \end{cases}$$

These two dynamical laws satisfy momentum and energy conservation.

It is clear, however, that Eqs. (3.8a) and (3.8b) admit of a greater variety of dynamical laws. For example, any transformation that preserves the length of $\mathbf{g}'$ will suffice. Thus, there may be a collection of dynamical laws that are consistent with energy conservation. These all correspond to rotations and inversions of $\mathbf{g}$. Suffice it to say that in accepting or rejecting a given dynamical law, other symmetries must be considered.

IV. PARTIALLY STICKY COLLISIONS–THE KINETIC SLIP MODEL

The trouble with the rough sphere model is best summarized by Chapman and Cowling: "Because of the reversal of the relative velocity of the points coming into contact, even a grazing collision can produce a large deflection. Finally, experiment suggests a relatively slow interchange between translatory and rotational energies; such a slow interchange is obtained by taking κ_1, κ_2 small, but (contrary to what one would expect of actual molecules) this still permits free interchange of rotational energy between molecules."

If the rough sphere model is to be useful, it must be generalized in such a way that grazing collisions are somewhat less effective. This can be done in a variety of ways. Towards this end we define an intermediate model in which

$$\Delta\mathbf{g}_{\perp} = -2f\mathbf{g}_{\perp} \quad , \tag{4.1}$$

where f is a function that can either be 0 or 1 depending on the physical model. Then Eq. (2.4) becomes

$$\mathbf{J} = \frac{-2m_1 m_2}{m_0}(\mathbf{g}_{\parallel} + \kappa_{12} f\,\mathbf{g}_{\perp}) \quad . \tag{4.2}$$

When $f = 0$ we recover the smooth sphere result, whereas when $f = 1$ we recover the rough sphere result. Note that in either case $(\mathbf{g}_{\perp}')^2 = \mathbf{g}_{\perp}^2$ so that energy is conserved in the collision.

In our first model, we assume that when the relative kinetic energy $\epsilon_{\parallel}$ along the line of centers exceeds a certain energy E, the collision is rough, whereas, when it is less than E the collision is smooth, that is,

$$f = \begin{cases} 0, & \epsilon_{\parallel} \equiv \frac{1}{2}\frac{m_1 m_2}{m_0}\mathbf{g}_{\parallel}^2 \le E \ , \\ 1, & \epsilon_{\parallel} > E \ . \end{cases} \tag{4.3}$$

This model springs from our notion that when two real spheres collide their "depth of penetration" increases with their speed along their line of centers with a concomittant increase in their tangential friction. We call this the *kinetic stick model.*

The factor f defined in Eq. (3.3) for the kinetic stick model can be expressed in terms of the total relative translational kinetic energy $\epsilon \equiv \frac{1}{2}\mu v_{21}^2$. From Fig. 2 it follows that $(\mathbf{n}\cdot v_{21})^2 = v_{21}^2\cos^2\alpha$ so that Eq. (4.3) can be expressed as

$$f(\epsilon) = \begin{cases} 0, & \epsilon \le E/\cos^2\alpha \ , \\ 1, & \epsilon > E/\cos^2\alpha \ , \end{cases} \tag{4.4}$$

where E is the cut off energy, that is, the energy above which the collision is sticky.

Combining Eqs. (3.3) and (4.2)–(4.4) then gives

$$\frac{1}{\tau_v} = \frac{ng(\sigma)\sigma^2}{2\langle c_1\rangle^2}\left\langle \int_0^{2\pi} d\phi \int_0^{\pi/2} d\alpha \sin\alpha\cos\alpha\, v_{21} \times \left\{\left[1 - \frac{\kappa}{\kappa+1}f(\epsilon)\right](\underline{n}\cdot v_{21})^2 + \frac{\kappa}{\kappa+1}f(\epsilon)v_{21}^2\right\}\right\rangle \tag{4.5}$$

and

$$\frac{1}{\tau_\omega} = \frac{ng(\sigma)\sigma^2}{3\langle\omega_1^2\rangle(\kappa+1)}\left\langle \int_0^{2\pi} d\phi \int_0^{\pi/2} d\alpha \sin\alpha\cos\alpha\, v_{21} f(\epsilon)\right\rangle . \tag{4.6}$$

These correlation times can be expressed in terms of three parameters

$$\beta \equiv \frac{2}{\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\alpha \sin\alpha\cos^3\alpha \langle f(\epsilon) v_{21}^3\rangle / \langle v_{21}^3\rangle \ , \tag{4.7a}$$

$$\gamma \equiv \frac{1}{\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\alpha \sin\alpha\cos\alpha \langle f(\epsilon) v_{21}^3\rangle / \langle v_{21}^3\rangle \ , \tag{4.7b}$$

$$\delta \equiv \frac{1}{\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\alpha \sin\alpha\cos\alpha \langle f(\epsilon) v_{21}\rangle / \langle v_{21}\rangle \ , \tag{4.7c}$$

where the brackets indicate an average over a Maxwellian distribution of relative velocities. Then Eqs. (4.5) and (4.6) become

$$\frac{1}{\tau_v} = \frac{1+1+(2\gamma-\beta)}{1+\kappa}\frac{1}{\tau_E} \ , \tag{4.8a}$$

$$\frac{1}{\tau_\omega} = \frac{\delta}{1+\kappa}\frac{1}{\tau_E} \ , \tag{4.8b}$$

where τ_E is defined by

$$\frac{1}{\tau_E} = \frac{8}{3}\left(\frac{\pi K_B T}{m}\right)^{1/2} ng(\sigma)\sigma^2 \ . \tag{4.8c}$$

Letting $\lambda \equiv 2\gamma - \beta$ and transforming to $x = \cos\alpha$, the relevant parameters are

$$\lambda = 2\gamma - \beta = \frac{2}{\langle v_{21}^3\rangle}\int_0^1 dx\, x(1-x^2)\int d\epsilon p(\epsilon) f(\epsilon) v_{21}^3 \ , \tag{4.9a}$$

$$\delta = \frac{2}{\langle v_{21}\rangle}\int_0^1 dx\, x \int d\epsilon p(\epsilon) f(\epsilon) v_{21} \ , \tag{4.9b}$$

where $p(\epsilon)$ is the Maxwell distribution function of relative energies and the integrals go over all energies from 0 to ∞. Note, however, the presence of the factor $f(\epsilon)$ defined by Eq. (4.4),

$$f(\epsilon) = \begin{cases} 0, & \epsilon \le E/x^2 \ , \\ 1, & \epsilon > E/x^2 \ . \end{cases} \tag{4.10}$$

This factor merely places a lower limit on the integrals which now read $\int_{E/x^2}^{\infty} d\epsilon \cdots$. Substituting the explicit form of the Maxwell energy distribution function gives after some simple manipulations

$$\lambda \equiv 1 - \frac{\int_0^1 dx\, x(1-x^2)\int_0^{(1/x)(2E/u)^{1/2}} dv\, v^5 e^{-\beta\mu v^2/2}}{\int_0^1 dx\, x^3 \int_0^{\infty} dv\, v^5 e^{-\beta\mu v^2/2}} \ , \tag{4.11a}$$

$$\delta \equiv 1 - \frac{\int_0^1 dx\, x \int_0^{(1/x)(2E/u)^{1/2}} dv\, v^3 e^{-\beta\mu v^2/2}}{\int_0^1 dx\, x \int_0^{\infty} dv\, v^3 e^{-\beta\mu v^2/2}} \ . \tag{4.11b}$$

Now transforming to $z = v^2$ enables us to express the inner integrals in terms of

$$I_n(x) = \int_0^{b(x)} dz\, z^n e^{-az} \ ,$$

where $a \equiv \beta\mu/2$ and $b(x) \equiv 2E/\mu x^2$. Evaluation of the integrals $I_n(x)$ and substitution into Eqs. (4.11a) and (4.11b) then gives upon transformation to $y \equiv x^{-2}$,

$$\lambda \equiv 2[(1-x)\omega_2(x) + x\omega_1(x) - \omega_3(x)] \ , \tag{4.12a}$$

$$\delta = [\omega_2(x) + x\omega_1(x)] \ , \tag{4.12b}$$

where $x = \beta E$ and where $\omega_n(x)$ is

$$\omega_n(x) \equiv \int_1^{\infty} dy\, y e^{-yx} \ . \tag{4.12c}$$

Integration by parts then gives

$$\lambda = e^{-\beta E} = \delta \ . \tag{4.13}$$

Substitution into Eqs. (4.8a) and (4.8b) then yields the final results

$$\frac{1}{\tau_v} = \frac{1+[1+\lambda(\beta)\kappa]}{1+\kappa}\frac{1}{\tau_E} \ , \tag{4.14a}$$

$$\frac{1}{\tau_\omega} = \frac{\lambda(\beta)}{1+\kappa}\frac{1}{\tau_E} \ , \tag{4.14b}$$

where $\lambda(\beta)$, the coefficient of stick, depends on $\beta[\equiv (k_B T)^{-1}]$ and on the cut off energy E, above which the collisions are sticky

$$\lambda(\beta) \equiv e^{-\beta E} \ . \tag{4.15}$$

Thus, because $\lambda \to 0$ as $E \to \infty$, and $\lambda \to 1$ as $E \to 0$, we recover the smooth and rough sphere results in these two limits. $\lambda(\beta)$ is a temperature dependent quantity so that the fluid becomes stickier as $T \to \infty$.

The kinetic stick model easily lends itself to molecular dynamics calculations, where a test is readily made to see whether the kinetic energy along the line of centers exceeds the cutoff E. If it does, the collision is treated as perfectly rough; otherwise, it is treated as smooth. We present the results of these calculations in a subsequent paper in this series.

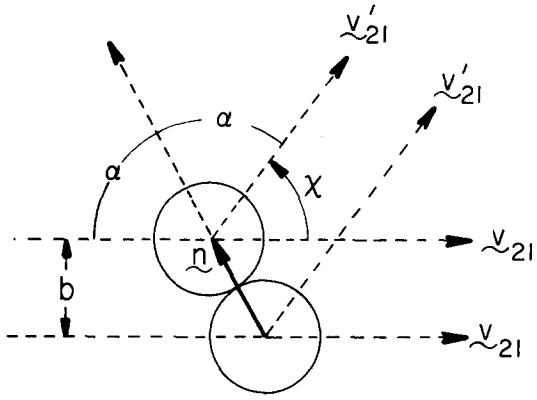

FIG. 2. Two spheres 1 and 2 of diameters σ_1 and σ_2 and masses m_1 and m_2 collide with impact parameter b. v_{21} is the initial relative velocity of 2 with respect to 1 before collision and $\mathbf{v}'_{21}$ is the relative velocity after collision. χ is the scattering angle. The angle α is by construction $\alpha = \frac{1}{2}\pi - x$. From the diagram it is obvious that $b = \frac{1}{2}(\sigma_1 + \sigma_2)\sin\alpha$. The angular integration in Eq. (2.3) is given by $d\Omega = d\epsilon d\alpha \sin\alpha\cos\alpha$, where $0 \le \epsilon \le 2\pi$ and $0 \le \alpha \le \pi/2$.

V. PARTIALLY STICKY SPHERES–THE ROUGH DOMAIN MODEL

Another approach to intermediate boundary conditions is the one that we recently proposed in a paper on the coupling between translational and rotational motion.[7] In this case, we imagine that the surface of each sphere of type 1 is covered by domains of roughness between which there are domains of perfect smoothness. These domains are randomly distributed and are such that the fraction of surface area that is rough will be denoted α_1 whereas the fraction that is smooth is $(1 - \alpha_1)$. Contact between the rough domain of one sphere and the smooth domain of another sphere must give rise to a perfectly slippery collision, whereas contact between two rough domains gives rise to a perfectly rough collision. The probability p of a rough collision between two spheres of types 1 and 2 is therefore equal to

$$p \equiv \lambda_{21} \equiv \alpha_1 \alpha_2 \tag{5.1}$$

and the probability of a smooth collision is obviously $1 - \alpha_1 \alpha_2$.

To generalize, we substitute into Eq. (4.2) $f \equiv b_{21}$, where $b_{21} = 1$ for a rough contact and $b_{21} = 0$ for a smooth contact. Now it should be clear from the foregoing that when b_{21} is averaged over all collisions between a sphere of type 1 and a sphere of type 2

$$\langle f \rangle = \langle b_{21} \rangle = \lambda_{21} = \alpha_1 \alpha_2 \tag{5.2}$$

Thus, for a semisticky sphere there is a stick parameter $\lambda_{21} = \alpha_1 \alpha_2$, which can vary between 0 and 1. All properties will depend on λ_{21}. The explicit calculations for mixtures is found in Ref. 7. The results for a neat fluid of semisticky spheres are

$$\frac{1}{\tau_v} = \left[\frac{1 + (1+\lambda)\kappa}{1+\kappa}\right]\frac{1}{\tau_E} , \tag{5.3a}$$

$$\frac{1}{\tau_\omega} = \left[\frac{\lambda}{1+\kappa}\ \frac{1}{\tau_E}\right], \tag{5.3b}$$

where now

$$\lambda \equiv \alpha^2 , \tag{5.3c}$$

α being the fraction of the surface area that is rough.

This model also lends itself very easily to computer experiments.[10] In this case a collision is either sticky or slippery depending on a sampling of random numbers in accordance with the probability $\lambda = \alpha^2$.

This model gives results that are quite similar to Eq. (4.14) except that λ is now temperature independent.

Real polyatomic molecules, unlike the foregoing models, have discrete centers of force. It is possible to devise a model that is closer to this reality. Such a model is indicated in Fig. 1. Sphere 1 has different size caps of roughness distributed such that there is axial symmetry about the unit vector $\mathbf{u}_1$—the unit vector specifying the orientation of the sphere. We call this a *structured sphere*. The structured sphere can be used as an elementary model for a heteronuclear diatomic molecule. Obviously, other distributions of domains of roughness can be used to simulate other molecules. For example, equal size domains located at the vertices of a hexagon inscribed in a sphere can be used to simulate benzene.

A collision between one structured sphere and a perfectly rough sphere is indicated in Fig. 1. In this case, the function f is defined as

$$f(\mathbf{n}\cdot\mathbf{u}_1) = \begin{cases} 1, & x_1 \le (\mathbf{n}\cdot\mathbf{u}_1) \le 1 \text{ or } -1 < (\mathbf{n}\cdot\mathbf{u}_1) \le -x_2 , \\ 0, & \text{otherwise} , \end{cases} \tag{5.4}$$

where f is a function of the projection of $\mathbf{u}_1$ on the apse line and $x_1 = \cos\theta_1$, $x_2 = \cos\theta_2$. This follows immediately from the fact that the collisions are rough only when the point of contact n passes through the shaded areas in Fig. 1. Collisions between two structured spheres can also be treated, but the results are beyond the scope of this paper. Before giving the explicit formulas for this model we best turn to the question of the moment of inertia anisotropy that is found in symmetric top molecules.

VI. THE STRUCTURED SPHERE MODEL

The structured sphere model presented in Sec. IV clearly involves an anisotropic mass distribution. For the case presented in Fig. 1, the mass distribution is axially symmetric and the particle is a symmetric top with moment of inertia tensor

$$\mathbf{I}_1 = I_{\parallel}\mathbf{u}_1\mathbf{u}_1 + I_{\perp}(\delta - \mathbf{u}_1\mathbf{u}_1) ,$$

where $I_{\parallel}$ and $I_{\perp}$ are, respectively, the components of the moment of inertia parallel and perpendicular to the symmetry axis whose orientation is completely specified by the unit vector $\mathbf{u}_1$.

In addition, the mass distribution is such that in general the center of mass is displaced along $\mathbf{u}_1$ from the center of the sphere; then the object is a loaded sphere. For simplicity we restrict our attention to the case

where the center of mass coincides with the center of the sphere, and where $\theta_1 = \theta_2$ or equivalently $x_1 = x_2$.

It is convenient to express the two components $I_1^{\parallel}$, $I_1^{\perp}$ of the moment of inertia tensor in the dimensionless form $\kappa_1^{\parallel} \equiv 4I_1^{\parallel}/m_1\sigma_1^2$ and $\kappa_1^{\perp} \equiv 4I_1^{\perp}/m_1\sigma_1^2$.

To proceed, we must compute the impulse experienced by the molecule. In the case of an anisotropic mass distribution Eqs. (3.3a), (3.3b), and (3.3d) remain the same but Eq. (3.3c) must be changed to

$$\mathbf{I}_1 \circ \boldsymbol{\omega}_1' = \mathbf{I}_1 \cdot \boldsymbol{\omega}_1 + \frac{\sigma_1}{2}(\mathbf{n}\times\mathbf{J}) \ . \tag{6.1}$$

Equations (3.3a), (3.3b), (3.3d), and (6.1) together with (3.2) can be solved for the impulse J in a collision between the structured sphere and a completely rough sphere 2:

$$\mathbf{J} = \frac{m_1 m_2}{m_0}\left(\Delta\mathbf{g}_{\parallel} + \kappa_{12}^{\perp} \times\left\{\Delta\mathbf{g}_{\perp} - \frac{\gamma}{1+\gamma[1-(\mathbf{n}\circ\mathbf{u}_1)^2]}(\mathbf{n}\times\mathbf{u}_1)\cdot\Delta\mathbf{g}_{\perp}\right\}\right), \tag{6.2}$$

where the parameters are

$$\kappa_{12}^{\perp} \equiv \frac{\kappa_1^{\perp}\cdot\kappa_2}{\kappa_1^{\perp}\kappa_2 + \kappa_0^{\perp}} \ , \qquad \kappa_0^{\perp} = \frac{m_1\kappa_1^{\perp} + m_2\kappa_2}{m_1+m_2} \ , \tag{6.3a}$$

and

$$\gamma \equiv \frac{m_2\kappa_{12}^{\perp}}{m_1+m_2}\left(\frac{1}{\kappa_1^{\parallel}} - \frac{1}{\kappa_1^{\perp}}\right) \ . \tag{6.3b}$$

The parameter γ measures the anisotropy of the moment of distribution. For a spherical top $\gamma = 0$, whereas for a prolate ellipsoid $\gamma > 0$ and for an oblate ellipsoid $\gamma < 0$.

Although tedious, it is not difficult to establish for this case that energy is still conserved if $\mathbf{g}_{\parallel}' = -\mathbf{g}_{\parallel}$ and $\mathbf{g}_{\perp}'^2 = \mathbf{g}_{\perp}^2$. Thus, we may once again take the dynamical law to be

$$\Delta\mathbf{g}_{\parallel} = -2\mathbf{g}_{\parallel} \ , \tag{6.4a}$$

$$\Delta\mathbf{g}_{\perp} = -2f\,\mathbf{g}_{\perp} \ , \tag{6.4b}$$

where f is defined in Eq. (5.4). This gives the impulse

$$\mathbf{J} = \frac{-2m_1m_2}{m_0}\{\mathbf{g}_{\parallel} + \kappa_{12}^{\perp} f(x) \times[\mathbf{g}_{\perp} - h_{\gamma}(x)(\mathbf{n}\times\mathbf{u}_1)(\mathbf{n}\times\mathbf{u}_1)\cdot\mathbf{g}_{\perp}]\}, \tag{6.5a}$$

where for simplicity we define

$$h_{\gamma}(x) \equiv \frac{\gamma}{1-\gamma[1-(\mathbf{n}\cdot\mathbf{u}_1)^2]} \tag{6.5b}$$

and where $x \equiv \mathbf{n}\circ\mathbf{u}_1$. Equations (6.5a) and (6.5b) together with Eqs. (3.3a), (3.3b), (3.3d), and (6.1) completely specify the effects of the collision.

In a linear molecule $I_{\parallel} = 0$. This means that no angular momentum is transferred around the symmetry axis. Thus, in Eq. (6.1) we only consider the angular velocity perpendicular to the symmetry axis $\boldsymbol{\omega}_{\perp} = (\delta - \mathbf{u}_1\mathbf{u}_1)\mathbf{u}_1$. This gives

$$I_{\perp}\boldsymbol{\omega}_{\perp}' = I_{\perp}\omega_{\perp} + \tfrac{1}{2}\sigma_1(\mathbf{n}\times\mathbf{J}) \ . \tag{6.6}$$

The same treatment used before then gives Eqs. (6.5a) and (6.5b) with the simple change that

$$\gamma = -\frac{m_2\kappa_{12}^{\perp}}{m_0\kappa_1^{\perp}} \tag{6.7}$$

and $\omega_{\parallel} \to \omega_{\perp}$. This gives a very simple prescription for extracting the linear molecule result from the general symmetric top results: *drop all terms involving* $I_{\parallel}$ and $1/I_{\parallel}$ *or equivalently* $\kappa_1^{\parallel}$ and $1/\kappa_1^{\parallel}$.

It is a straightforward but tedious exercise to evaluate the various relaxation times that enter the rough sphere model. These are

$$\left(\frac{1}{\tau_v}\right)_{\parallel} = [1 + 3\kappa_{12}^{\perp}\lambda_-(0)]\frac{1}{\tau_E(1,2)} \tag{6.8a}$$

$$\left(\frac{1}{\tau_v}\right)_{\perp} = \{1 + \tfrac{3}{2}\kappa_{12}^{\perp}[\lambda_+(0) - \gamma\lambda_-(\gamma)]\}\frac{1}{\tau_E(1,2)} \ , \tag{6.8b}$$

$$\left(\frac{1}{\tau_\omega}\right)_{\parallel} = 3\frac{\kappa_{12}^{\perp}}{\kappa_1^{\parallel}}\lambda_-(\gamma)\frac{1}{\tau_E(1,2)} \ , \tag{6.8c}$$

$$\left(\frac{1}{\tau_\omega}\right)_{\perp} = \frac{3}{2}\frac{\kappa_{12}^{\perp}}{\kappa_1^{\perp}}[\lambda_+(0) + \lambda_-(0) - \lambda_-(\gamma) - \gamma\lambda_-(\gamma)]\frac{1}{\tau_E(1,2)} \ , \tag{6.8d}$$

where the Enskog time constant is by definition

$$\frac{1}{\tau_E(1,2)} = \frac{16}{3}\frac{m_2}{m_0}\left(\frac{\pi K_B T}{2\mu_{12}}\right)^{1/2} n_2 g^{(2)}(\sigma_{12})\sigma_{12}^2 \ . \tag{6.9a}$$

This is simply $(16m_2/3m_0)$ times the collision rate between the symmetric top and the bath particles. The only other dynamic parameters that enter are

$$\lambda_{\pm}(\gamma) \equiv \frac{1}{4}\int_{-1}^{1} dx f(x)\frac{(1\pm x^2)}{1+\gamma(1-x^2)} \ , \tag{6.9b}$$

where γ is a parameter specifying the moment of inertia anisotropy [see Eq. (6.3b)], $x \equiv (\mathbf{n}\circ\mathbf{u}_1)$, and $f(x)$ is defined by Eq. (5.4). Actually $f(x)$ can be defined to take into account more general symmetric top force center distributions. $\lambda_{\pm}(\gamma)$ are two coefficients of slip that depend on the precise form of $f(x)$ and the moment of inertia anisotropy. If $\gamma = 0$ and $f(x) = 1$ for all x, $\lambda_+(0) = 2/3$ and $\lambda_-(0) = 1/3$ and the formulas reduce to the case of a mixture of perfectly isotropic rough spheres where the $\parallel$ and $\perp$ components are all equal.

Let us consider the case of a linear molecule. As mentioned at the end of Sec. V all terms involving $\kappa_1^{\parallel}$ should be ignored. In addition, there is no relaxation involving $\omega_{\parallel}$. Equations (6.8a)–(6.9b) change only in that γ must be replaced by Eq. (6.7). Equations (5.8c) and (5.8d) however become

$$\left(\frac{1}{\tau_\omega}\right)_{\parallel} \equiv 0 \ , \tag{6.10a}$$

$$\left(\frac{1}{\tau_\omega}\right)_{\perp} = \frac{3}{2}\frac{\kappa_{12}^{\perp}}{\kappa_1^{\perp}}\lambda_+(0)\frac{1}{\tau_E}(1,2) \ . \tag{6.10b}$$

For a linear molecule with $f = 1$, $\lambda_+(0) = 2/3$. If $\kappa_2 = \kappa_1^{\perp}$, Eq. (6.9b) reduces to the value used by Chandler in his computations on liquid Nitrogen.[5]

In the case of symmetric top molecules the $\parallel$ and $\perp$ components are generally different. The parameters β_l and $\beta_l^{\perp}$ given in Eqs. (2.19) and (2.20) will therefore be

different.

In general when dealing with $f \neq 1$, the results will depend on the precise geometrical distributions of the rough domains.

VII. A KINETIC MODEL FOR CHIRAL MOLECULES–THE ROUGH SCREWBALL

In this section we present a very simple dynamical model for the interaction between a chiral molecule and a nonchiral solvent, a model that we call the rough screwball model. This model possesses a parameter λ, which varies between 0 and 1, which we call the screw coefficient. When λ is zero the model reduces to the rough sphere model, but when $\lambda \neq 0$ the molecular interaction possesses chirality.

The relative velocity vector $\mathbf{g}_{21}$ can be resolved into a vector parallel to $\mathbf{n}$ denoted by $\mathbf{g}_{\parallel}$ and a vector perpendicular to $\mathbf{n}$ denoted by $\mathbf{g}_{\perp}$. Because the two rigid spheres are completely impenetrable $\mathbf{g}_{\parallel}$ is always inverted by a collision. Energy conservation requires that the magnitude of $\mathbf{g}_{\perp}$ must remain unchanged by a collision. The most general dynamical law consistent with energy conservation is that one in which $\mathbf{g}_{\perp}$ is rotated through an angle γ, that is,

$$\mathbf{g}_{\perp}' = [\cos\beta\, \mathbf{g}_{\perp} + \sin\beta(\mathbf{n}\times\mathbf{g}_{\perp})] \quad . \tag{7.1}$$

In this section we explore the consequences of this dynamical law when β varies between 0 rad, where it gives the smooth sphere results, and π rad, where it gives the rough sphere result.

β should be regarded as a parameter in this model. When $0 < \beta < \pi$, the dynamical law has a right hand screw sense, whereas when $-\pi < \beta < 0$ it has a left hand screw sense. Obviously, the dynamical law has chirality.

It is convenient to define two parameters λ and μ for the collision such that

$$\lambda = \tfrac{1}{2}(1 + \cos\beta) \quad , \tag{7.2a}$$

$$\mu = |\sin\beta| = 2[\lambda(1-\lambda)]^{1/2} \quad . \tag{7.2b}$$

λ is a parameter that measures the strength of the chirality. The smaller the parameter the weaker the effects. In terms of these parameters Eq. (7.1) becomes

$$\mathbf{g}_{\perp}' = (1 - 2\lambda)\,\mathbf{g}_{\perp} \pm \mu(\mathbf{n}\times\mathbf{g}_{\perp}) \quad , \tag{7.3}$$

where the + and − sign defines the chirality. This result reduces to a smooth sphere when $\lambda = 0$ and to a rough sphere when $\lambda = 1$.

Substitution of Eq. (7.3) into Eq. (3.4) then gives

$$\mathbf{J}_{\pm} = \frac{-2m_1m_2}{m_1+m_2}\{(\mathbf{n}\cdot\mathbf{g})\,\mathbf{n} + \kappa_{12}[\lambda\mathbf{g}_{\perp} \pm \mu(\mathbf{n}\times\mathbf{g}_{\perp})]\} \quad . \tag{7.4}$$

New features appear in translational and rotational relaxation due to chirality. For simplicity, in this section attention is restricted to one dextrorotory or levorotary molecule in a solvent consisting of rough spheres. The various couplings are computed in the approximation defined in Sec. II.

The properties of interest are $A_1 \equiv \mathbf{c}_1$ and $A_2 \equiv \boldsymbol{\omega}_1$, where $\mathbf{c}_1$ and $\boldsymbol{\omega}_1$ are the center of mass velocity and the angular velocity, respectively, of the chiral sphere in a solvent consisting of rough spheres.

We now define a scalar product as

$$(A_i, A_j) = \langle A_i \circ A_j^* \rangle \quad , \qquad i, j = 1, 2 \quad , \tag{7.5}$$

where $\langle \circ\circ\circ \rangle$ denotes an ensemble average and the * denotes a complex conjugate. Given the definitions of A_1 and A_2 the various scalar products are $\langle c_1^2 \rangle$, $\langle \omega_1^2 \rangle$, $\langle \mathbf{c}_1 \circ \boldsymbol{\omega}_1 \rangle$, $\langle \boldsymbol{\omega}_1 \circ \mathbf{c}_1 \rangle$. The first two are given by equipartition as $\langle c_1^2 \rangle = 3kT/m_1$, $\langle \omega_1^2 \rangle = 3kT/I_1 = \langle c_1^2 \rangle / 4\kappa_1\sigma_1^2$, whereas the last two are zero because the linear and angular momentum are independent in an equilibrium ensemble. The quantity (A_i, A_j) forms a 2×2 matrix which we denote

$$(\mathbf{A}, \mathbf{A}^+) = \begin{pmatrix} \langle c_1^2 \rangle & 0 \\ 0 & \langle \omega_1^2 \rangle \end{pmatrix} \quad . \tag{7.6}$$

There is a corresponding matrix of equilibrium time correlation functions $(\mathbf{A}(t), \mathbf{A}^+(0))$, whose components are the velocity correlation function $\langle \mathbf{c}_1(t) \cdot \mathbf{c}_1(0) \rangle$, the angular velocity correlation function $\langle \boldsymbol{\omega}_1(t) \circ \boldsymbol{\omega}_1(0) \rangle$, and the two cross correlation function $\langle \mathbf{c}_1(t) \circ \boldsymbol{\omega}_1(0) \rangle$ and $\langle \boldsymbol{\omega}_1(t) \circ \mathbf{c}_1(0) \rangle$. The cross correlation functions are rigorously zero only for nonchiral interactions. The matrix

$$\mathbf{C}(t) = (\mathbf{A}(t), \mathbf{A}^+(0)) \cdot (\mathbf{A}, \mathbf{A}^+)^{-1} \tag{7.7a}$$

is the normalized correlation matrix [$\mathbf{C}(0) = \mathbf{I}$, where $\mathbf{I}$ is the 2×2 identity matrix]. Explicitly,

$$\mathbf{C}(t) = \begin{pmatrix} \dfrac{\langle \mathbf{c}_1(t) \cdot \mathbf{c}_1(0) \rangle}{\langle c_1^2 \rangle} & \dfrac{\langle \mathbf{c}_1(t) \cdot \boldsymbol{\omega}_1(0) \rangle}{\langle \omega_1^2 \rangle} \\ \dfrac{\langle \boldsymbol{\omega}_1(t) \cdot \mathbf{c}_1(0) \rangle}{\langle c_1^2 \rangle} & \dfrac{\langle \boldsymbol{\omega}_1(t) \cdot \boldsymbol{\omega}_1(0) \rangle}{\langle \omega_1^2 \rangle} \end{pmatrix} \quad . \tag{7.7b}$$

The independent binary collision (IBC) limit must be generalized to the multivariate case. In the IBC limit the correlation matrix must have the form

$$\mathbf{C}(t) = \exp(-\boldsymbol{\gamma} t) \quad , \tag{7.8}$$

where $\boldsymbol{\gamma}$ is a 2×2 matrix of damping rates. $\boldsymbol{\gamma}$ can be determined from the initial time derivative of $\mathbf{C}(t)$ so that

$$\boldsymbol{\gamma} = -\dot{\mathbf{C}}(0) = (T\mathbf{A}, \mathbf{A}^+) \cdot (\mathbf{A}, \mathbf{A}^+)^{-1} \quad , \tag{7.9}$$

where T is the total "T" operator

$$T = \sum_{ij} T_{ij} \quad , \tag{7.10}$$

where T_{ij} is the T operator for the collision between sphere (i, j) and the sum is over all collision pairs. Thus, the damping matrix is explicitly

$$\boldsymbol{\gamma} = \begin{pmatrix} \dfrac{\langle \mathbf{c}_1 \cdot T\mathbf{c}_1 \rangle}{\langle c_1^2 \rangle} & \dfrac{\langle \boldsymbol{\omega}_1 \cdot T\mathbf{c}_1 \rangle}{\langle \omega_1^2 \rangle} \\ \dfrac{\langle \mathbf{c}_1 \cdot T\boldsymbol{\omega}_1 \rangle}{\langle c_1^2 \rangle} & \dfrac{\langle \boldsymbol{\omega}_1 \cdot T\boldsymbol{\omega}_1 \rangle}{\langle \omega_1^2 \rangle} \end{pmatrix} \quad . \tag{7.11}$$

It is a simple matter to compute the individual matrix elements given that the equations of change are explicitly given by Eq. (3.3a)–(3.3d) and Eq. (7.4). For the case

where $m_1 = m_2$ and $\kappa_1 = \kappa_2$,

$$\gamma = \begin{pmatrix} \frac{1}{\tau_v} & \pm \frac{\kappa\sigma}{2} \frac{\mu}{\kappa+1} \frac{1}{\tau_E} \\ \mp \frac{2}{\sigma} \frac{\mu}{\kappa+1} \frac{1}{\tau_E} & \frac{1}{\tau_\omega} \end{pmatrix}, \tag{7.12}$$

where λ and μ and κ have been defined, the + sign corresponds to + enantiomers and the − sign corresponds to − enantiomers. The correlation times τ_v and τ_ω are the velocity and angular velocity relaxation times and can be expressed in terms of the Enskog correlation time τ_E given by Eq. (4.8c) as

$$\frac{1}{\tau_v} = \left[\frac{1+(1+\lambda)\kappa}{1+\kappa}\right]\frac{1}{\tau_E}, \tag{7.13a}$$

$$\frac{1}{\tau_\omega} = \left[\frac{\lambda}{\kappa+1}\frac{1}{\tau_E}\right]. \tag{7.13b}$$

Let us now explicitly evaluate the correlation matrix $\mathbf{C}(t)$. From Eq. (7.8) it immediately follows that the Laplace transform of $\hat{\mathbf{C}}(t)$ is

$$\hat{\mathbf{C}}(s) = (s\mathbf{I}+\gamma)^{-1}, \tag{7.14}$$

where $\mathbf{I}$ is the 2×2 indentity matrix. The reciprocal of the matrix $s\mathbf{I}+\gamma$ is

$$\hat{\mathbf{C}}(s) = \frac{1}{\|s\mathbf{I}+\gamma\|}\begin{pmatrix} s+\gamma_{22} & -\gamma_{12} \\ -\gamma_{21} & s+\gamma_{11} \end{pmatrix}. \tag{7.15}$$

To Laplace invert Eq. (7.15) it is necessary to determine the roots of the dispersion equation

$$\|s\mathbf{I}+\gamma\| = (s+\gamma_{11})(s+\gamma_{22}) - \gamma_{12}\gamma_{21} = 0, \tag{7.16}$$

which are

$$s_\pm = -\frac{(\gamma_{11}+\gamma_{22})}{2} \pm \tfrac{1}{2}[(\gamma_{11}-\gamma_{22})^2 + 4\gamma_{12}\gamma_{21}]^{1/2}, \tag{7.17}$$

a straightforward inversion gives

$$\mathbf{C}(t) = \frac{1}{(s_+ - s_-)}\begin{pmatrix} [(s_+ + \gamma_{22})e^{s_+t} - (s_- + \gamma_{11})e^{s_-t}] - \gamma_{12}[e^{s_+t} - e^{s_-t}] \\ [-\gamma_{21}[e^{s_+t} - e^{s_-t}]][(s_+ + \gamma_{11})e^{s_+t} - (s_- + \gamma_{11})e^{s_-t}] \end{pmatrix} \tag{7.18}$$

Substitution of the explicit forms of γ_{ij} from Eq. (7.12) into Eq. (7.17) gives the various correlation functions. It is clear from this that chirality introduces couplings between the linear and angular velocity in such a way that the velocity and angular velocity autocorrelation functions are not single exponentials but both decay on two different time scales determined by the parameters in Eq. (7.12). In addition, the cross correlation functions are nonzero, so that there is a direct coupling between linear and angular velocity.

An alternative point of view that is consistent with the foregoing is that $\mathbf{c}_1$, ω_1 evolve according to the Langevin equation

$$\frac{d}{dt}\begin{pmatrix}\mathbf{c}_1 \\ \omega_1\end{pmatrix} = -\gamma\cdot\begin{pmatrix}\mathbf{c}_1 \\ \omega_1\end{pmatrix} + \begin{pmatrix} \mathbf{a}_1 + \frac{\mathbf{F}_1}{m_1} \\ \mathbf{a}_1 + \frac{\mathbf{N}_1}{I_1}\end{pmatrix}, \tag{7.19}$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are random accelerations and $\mathbf{F}_1$ and $\mathbf{N}_1$ are applied forces and torques. In steady flow these reduce to

$$\begin{pmatrix} \frac{1}{m_1}\mathbf{F}_1 \\ \frac{1}{I_1}\mathbf{N}_1 \end{pmatrix} = \gamma\cdot\begin{pmatrix}\mathbf{c}_1 \\ \omega_1\end{pmatrix}, \tag{7.20}$$

from which we find that

$$\mathbf{c}_1 = \frac{\gamma_{22}}{m_1\|\gamma\|}\mathbf{F}_1 - \frac{\gamma_{12}}{I_1\|\gamma\|}\mathbf{N}_1, \tag{7.21a}$$

$$\omega_1 = -\frac{\gamma_{21}}{m_1\|\gamma\|}\mathbf{F}_1 - \frac{\gamma_{11}}{I_1\|\gamma\|}\mathbf{N}_1. \tag{7.21b}$$

In the absence of applied torques we see that a particle acted upon by an external torque is induced to rotate, whereas in the absence of forces we see that a particle acted upon by an external torque is induced to translate. These are phenomena that occur when particles have a particular screw sense. If $\lambda = 1$, γ becomes diagonal and these cross effects disappear.

Although the model introduced here has chirality we have not been entirely successful in satisfying ourselves that it satisfies all symmetries. In this context it should be noted that the various coupling tensors introduced in the hydrodynamic treatment of isotropic helicoids may have different symmetries than would be generated by this model.

APPENDIX: ORIENTATIONAL DYNAMICS AND IRREDUCIBLE TENSORS

The quantity $[I_i\boldsymbol{\alpha}^{(l)}]\odot[I_j\boldsymbol{\alpha}^{(l)}]$ can be evaluated as follows. This has the explicit form

$$[I_i\boldsymbol{\alpha}^{(l)}(\mathbf{u})]\odot[I_j\boldsymbol{\alpha}^{(l)}(\mathbf{u})] = \frac{4\pi}{2l+1}\sum_{m=-l}^{+l}[I_i Y_{lm}(\mathbf{u})]^*[I_j Y_{lm}(\mathbf{u})]. \tag{A1}$$

Since the sum goes over all projections m, it follows that this must transform like a second rank Cartesian tensor, that is,

$$I_i\boldsymbol{\alpha}^{(l)}(\mathbf{u})\odot I_j\boldsymbol{\alpha}^{(l)}(\mathbf{u}) = a\delta_{ij} + bu_iu_j. \tag{A2}$$

Contraction gives

$$b+3a = I_i\boldsymbol{\alpha}^{(l)}(\mathbf{u})\odot I_i\boldsymbol{\alpha}^{(l)}(\mathbf{u}). \tag{A3}$$

Contraction with u_iu_j together with $\mathbf{u}\cdot\mathbf{I}\boldsymbol{\alpha}^{(l)} = 0$ gives

$$b+a = 0. \tag{A4}$$

To continue we note that because $\boldsymbol{\alpha}^{(l)}(\mathbf{u})\odot\boldsymbol{\alpha}^{(l)}(\mathbf{u})$ is a "scalar"

$$I_i^2[\boldsymbol{\alpha}^{(l)}(\mathbf{u})\odot\boldsymbol{\alpha}^{(l)}(\mathbf{u})] = 0. \tag{A5}$$

Applying the operator serially then gives

$$2(I_i^2\boldsymbol{\alpha}^{(l)}\odot(I_i\boldsymbol{\alpha}^{(l)}) = (I_i^2\boldsymbol{\alpha}^{(l)})\odot\boldsymbol{\alpha}^{(l)} + \boldsymbol{\alpha}^{(l)}\odot(I_i^2\boldsymbol{\alpha}^{(l)}). \tag{A6}$$

Now since we are using the Einstein summation convention $I_i^2 = \mathbf{I}\cdot\mathbf{I}$, and it follows from the properties of irreducible tensorial sets that $I^2\boldsymbol{\alpha}^{(l)} = l(l+1)\boldsymbol{\alpha}^{(l)}$. Equation (A6) thus becomes

$$(I_i\boldsymbol{\alpha}^{(l)})\odot(I_i\boldsymbol{\alpha}^{(l)}) = l(l+1). \tag{A7}$$

Combining Eqs. (A2)–(A4) and (A6) then gives

$$I_i\alpha^{(l)}(\underline{u})\odot I_j\alpha^{(l)}(\underline{u}) = \frac{l(l+1)}{2}[\delta_{ij} - \underline{u}_i\underline{u}_j] \quad . \tag{A8}$$

This is identical to Eq. (2.17).

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