Translational and rotational diffusion in liquids. II. Orientational single-particle correlation functions

David Chandler

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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This is the second of two articles concerned with the translational and rotational motion in molecular liquids. In this paper, orientational single-particle correlation functions are considered. By applying the approximations developed in Paper I of this series, Gordon's J diffusion model theory is derived. The analysis does not require one to adopt the unrealistic views of the liquid state that are usually attributed to that theory. The range of validity of the J diffusion model approximation is ascertained. Further, a microscopic expression is derived for the relaxation time which Gordon introduced phenomenologically. The expression leads naturally to a simple method for calculating \( \tau_J \).

These predictions are tested against results obtained from recent computer simulations of liquid \( \text{N}_2 \).

The comparison shows that the theory is qualitatively accurate.

I. INTRODUCTION

In this article we extend the analysis developed in Paper I and discuss the orientational single-particle correlation functions in molecular liquids. The theory we present is motivated by Gordon's imaginative paper in which he derives the J diffusion model approximation for rotational motion and his explanation of the measured density dependence of the NMR \( T_1 \) for dense \( \text{H}_2 \) gas.

In Sec. II, the approximation to the binary collision expansion introduced in Paper I is applied to orientational correlation functions for a rough hard sphere fluid. From the relationship between real liquids and the rough hard sphere fluid that was developed in Paper I, one can show that the equations derived for rough hard spheres are also valid for real liquids when the rough hard sphere model is chosen correctly. In the absence of a derivation of the relationship between rough hard spheres and real fluids, previous workers have assumed either that a connection exists or that the perfectly rough sphere system provides some sort of bound for properties of real systems. References 6 and 7 provide two examples of this research as applied to rotational motion.

A principal result of our analysis in Sec. II is a systematic derivation of Gordon's J diffusion model theory. The benefits of our approach are twofold: First, the approximations necessary to derive Gordon's theory are clearly seen within the context of a microscopic analysis. As a result, the range of validity of the theory can be understood. Second, a microscopic expression is obtained for the relaxation time which Gordon introduced phenomenologically. The expression is amenable to computations, and from it we are able to determine the density and temperature dependence of the relaxation time.

In Sec. III, some numerical consequences of our theory are investigated. The article is concluded in Sec. IV with a discussion of the relationship between the theoretical methods used herein and the physical ideas presented by Gordon. The Appendix contains a calculation that is relevant to the discussion in the main text.

For the sake of brevity, this article has been written under the assumption that the reader has already read Paper I of the series. The principal concepts and notation used herein are defined in Paper I.

II. APPROXIMATE THEORY FOR SINGLE-PARTICLE ORIENTATIONAL CORRELATION FUNCTIONS

We assume the rotational motion in the liquid is related to that in a rough hard sphere fluid. The justification for this assumption is given in Sec. V of Paper I. For simplicity, consider liquids composed of linear molecules. Let \( u_i \) denote the unit vector that is parallel to the axis of molecule \( i \). The angular momentum is given by \( J_i = \langle u_i \rangle \times \langle \vec{u}_i \rangle \), where \( \langle \cdot \rangle \) stands for the moment of inertia. In the rough hard sphere fluid associated with the liquid, the mass and moment of inertia of the \( i \)th sphere is the same as that for the \( i \)th molecule in the liquid, and the angular momentum is also given by \( J_i = \langle u_i \rangle \times \langle \vec{u}_i \rangle \).

Let \( u(t) \) denote \( u_i \) at time \( t \), and let \( J(t) = \langle u(t) \rangle \) denote \( J_i \) at time \( t \). The specific correlation functions considered in this article are

\[
C_1(t) = \langle u \cdot u(t) \rangle = \langle P_2[\vec{u} \cdot \vec{u}(t)] \rangle,
\]

\[
C_2(t) = \langle P_2[\vec{u} \cdot \vec{u}(t)] \rangle,
\]

and

\[
C_4(t) = \langle J \cdot J(t) \rangle / \langle J^2 \rangle.
\]

In these equations, \( u = u(t = 0), J = J(t = 0), \) and \( P_n(x) \) is the \( n \)th Legendre polynomial of \( x \).

In Sec. II.A we analyze \( C_1(t) \) and \( C_2(t) \). The angular momentum (or angular velocity) autocorrelation function, \( C_2(t) \), is treated in Sec. II.B, and contact is made with Gordon's J diffusion model theory in Sec. II.C.

A. Theory for \( C_1(t) \) and \( C_2(t) \) for rough hard spheres

Consider the fluid composed of rough hard spheres. The binary collision expansion for the system was reviewed in Sec. II of Paper I. In Sec. III of that paper, an approximation was devised to calculate correlation functions of the form \( \langle A^* A(t) \rangle \) where the dynamical vari-
able $A$ must satisfy the following conditions: $A$ is a function of coordinates (and not the momenta) of particle 1; $\langle A \rangle = 0$; and $\langle A \rangle^2 = 1$. The principal approximation for such a correlation function is given by Eq. (3.17) of Paper I. This result can be directly applied to calculate $C_t(t)$. Let $A = \sqrt{3} n_3$, where $n_3$ is one of the three components of $n$ in a Cartesian coordinate system. It is obvious that $A$ satisfies the requirements listed above. Further, $\langle A^* A(t) \rangle = C_t(t)$. Thus, the approximation to the binary collision expansion introduced in Paper I gives [see Eq. (3.17) in that article]

$$\tilde{C}_t(s) \approx \tilde{C}_1^{(0)}(s + \tau^2)/(1 - \tau^2 \tilde{C}_2^{(0)}(s + \tau^2)),$$

(2.4)

where $\tilde{C}_1^{(0)}(s)$ is the Laplace transform of the ideal gas (free rotor) expression for $C_t(t)$, and

$$\tau^2 = (N - 1)/(\omega \cdot (T_1 \omega)), (\omega \cdot (T_1 \omega)) \approx \tau^2_0.$$

(2.5)

The second equality follows from Eq. (2.11) of Paper I.

The calculation of $C_t(t)$ is not quite as direct. One must now consider a torsional correlation function. Let $A(t)$ stand for a $3 \times 3$ matrix of dynamical variables with the $\alpha \gamma$ element given by

$$A_{\alpha \gamma}(t) = \langle \tilde{A}_{\alpha \gamma}(s) \rangle = \frac{3}{2} n_3(n_3),$$

(2.6)

Here, $\delta_{\alpha \gamma}$ is the Kronecker delta function. It can be shown that $\langle A A \rangle = 1$, where $I$ is the identity matrix. It can also be verified that $\langle A \rangle = 0$. Furthermore,

$$C_{\alpha \gamma}(t) = \text{Tr}(A \langle A(t) \rangle),$$

(2.7)

where $\text{Tr}$ stands for the trace of the matrix.

The formalism given in Sec. III of Paper I for a scalar $A(t)$ can be generalized to apply to $A(t)$. The details are straightforward, but the algebra is tedious. The final result for $C_{\alpha \gamma}(t)$ is the same as that given in Eqs. (2.4) and (2.5) with the subscript 1 replaced by 2, i.e.,

$$\tilde{C}_t(s) \approx \tilde{C}_2^{(0)}(s + \tau^2)/(1 - \tau^2 \tilde{C}_2^{(0)}(s + \tau^2)).$$

(2.8)

From the properties of the binary collision operator for rough hard spheres, it can be shown that

$$\tau^2_0 = a(t) \tau^{2\alpha}_0,$$

(2.9)

where $a(t)$ is dependent on temperature but not density. In the Appendix, this formula is derived explicitly for two specific rough hard sphere models.

Equations (2.4) and (2.8) are Gordon's $^8$ $J$ diffusion model approximations for $C_t(t)$ and $C_{\alpha \gamma}(t)$ if $\tau^2_0 = \tilde{C}_t(s = 0)$. To investigate the validity of this equality we now proceed with an analysis of $C_t(t)$.

B. Approximate calculation of $C_t(t)$ for rough hard spheres

In Paper I, the principal result for the self-correlation function implied that the velocity autocorrelation function for the rough hard sphere fluid is given by 

$$\exp(-t/\tau_v).$$

When the hard spheres are smooth, $\tau_v = \tau_{\omega}$, and thus the exponential is the Enskog result for the correlation function.

There is an alternative method for obtaining this formula; the method can also be used to derive an approximate expression for $C_t(t)$. The approach taken below is that the approximation which produces the Enskog expression (which is known to be fairly accurate) should also be useful when it is applied to calculate the angular velocity autocorrelation function for the rough hard sphere fluid.

To derive the exponential form for the velocity autocorrelation function without first calculating the self-correlation function, we use an approximation which is similar to the one used in Sec. III of Paper I. Following the scheme introduced there, we define the generalized average $\langle \langle G \rangle \rangle = \langle v \cdot (G \nu) \rangle / \langle v^2 \rangle$ where $G$ stands for any dynamical variable or operator. Then

$$C_t(t) = \langle \langle e^{i t \nu} \rangle \rangle.$$

To obtain Eq. (4.7) of Paper I, simply neglect second- and higher-order cumulants of $L$, i.e.,

$$\langle L(t) \rangle_{\text{rough hard sphere}} \approx \exp((-L_t)_{\text{rot}})$$

$$= \exp\{-[(N - 1)(\nu \cdot (T_1 \nu))/\langle (\nu^2) \rangle]\}$$

$$= \exp(-t/\tau_{\omega}).$$

(2.10)

The physical meaning of the approximation in Eq. (2.10) is that the dynamical events contributing to $C_t(t)$ can be approximated by sequences of uncorrelated nearest-neighbor binary collisions. Let us assume that the same approximation to the dynamics provides an accurate description of the angular velocity autocorrelation function. Then $C_t(t)$ can be approximated as follows:

$$\langle J_t(t) \rangle_{\text{rough hard spheres}} = \langle (J_t \cdot (e^{itJ})) / (J^2) \rangle$$

$$= \langle (e^{itJ}) \rangle_J$$

$$\approx \exp\{(-t/L)_{\text{rot}}\}$$

$$= \exp\{-[(N - 1)(J \cdot (T_1 J))/\langle (J^2) \rangle]\}.$$

(2.11)

For a linear rotor, the term in brackets is $\tau^{1\alpha}_0$. Thus, we predict that

$$\langle J_t(t) \rangle_{\text{rough hard spheres}} \approx \exp(-t/\tau_{\omega}).$$

(2.12)

Further, according to Eq. (2.12),

$$\tau_{\omega_{\alpha \gamma}} \approx \tau_{\omega},$$

(2.13)

where $\tau_{\omega}$ is defined by

$$\tau_{\omega} = \int_0^\infty C_t(t) dt.$$ 

(2.14)

If the accuracy of the Enskog theory for smooth hard spheres is indicative (and we believe it is), then $C_t(t)$ for rough hard spheres is given by Eq. (2.12) with an error that is never larger in magnitude than 0.03. However, the errors in Eq. (2.13) can be significantly larger than 3%. Indeed, at very high densities, $\tilde{C}_t(s = 0)$ for smooth hard spheres differs from $\tau_{\omega}$ by more than 20%.

[The reason for the discrepancy is that small errors in the Enskog formula for $C_t(t)$ persist for very long times.] Thus, one must expect that Eq. (2.13) can contain errors that are at least as large as 10%.

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C. J diffusion model theory

In Sec. II A and II B, we have derived equations to describe the rotational motion of particles in a rough hard sphere fluid. From the analysis given in Sec. V of Paper I, these equations can be adopted to describe C(t) and C(t) in a real liquid provided: (1) the liquid is composed of molecules that are only slightly nonspherical; (2) the density is high (>\frac{3}{2} the triple point density); and (3) the rough hard sphere model is chosen to satisfy

\[ \tau^\text{J}_{\text{real liquid}} = [(N-1)(\omega \cdot [T_{21}(s=0)\omega])]/(\omega^2)_{\text{ref}}. \]  

(2.15)

[See the derivation of Eq. (5.5) in Paper I.] Further, the zero frequency parts of C(t) for the real liquid and for the rough hard sphere fluid are the same. Thus, if we accept Eq. (2.13),

\[ \langle \tau_J \rangle_{\text{real liquid}} \approx \tau_\omega, \]  

(2.16)

Equations (2.16), (2.8), and (2.4) comprise Gordon’s J diffusion model theory for C(t) and C(t). It should be noted that Eqs. (2.4), (2.8), and (2.15) provide a complete theory for C(t) and C(t). There is no need to assume that \( \tau_J = \tau_\omega \).

The present derivation of the J diffusion model reveals that it should be accurate when the density is high (so that the repulsive forces dominate the dynamics) and when the molecules in the liquid are fairly spherical (so that \( \epsilon_0 \) is relatively small). It also provides an explicit expression for the relaxation time, \( \tau_\omega \), from which quantitative calculations can be made. These calculations are the subject of the next section.

III. NUMERICAL CONSEQUENCES OF THE THEORY

A. Density dependence of \( \tau_J \)

Equations (2.16) and (2.9) imply that at constant temperature the density dependence of \( \tau_J \) is given by

\[ \tau_J \propto \eta \propto \frac{\eta g_{d}(d+)}{(d^+)^{2}}. \]  

(3.1)

In the second proportionality, we have used Eq. (2.9) of Paper I, \( \eta \equiv \frac{\tau_0}{\rho_0} \) in which \( \rho \) is the particle density, and \( g_{d}(d+) \) is accurately given by

\[ g_{d}(d+) = (2 - \eta)/(2(1 - \eta)^2). \]  

(3.2)

This particular simple relationship is certainly amenable to experimental tests. Gordon et al., developed a physical argument for Eq. (3.1) and showed that it provided a semiquantitative description of constant temperature measurements of the NMR relaxation time for dense H2 gas.

B. Comparison of theory with computer “experiments” on a model for liquid N2

In a recent publication, Barajas et al., presented the results of computer simulations performed on a model for liquid N2. In the model, the intermolecular potential is given by

\[ w_{ij} = \frac{1}{2} \sum_{a=1}^{\infty} w_{ij}(r_{ij}^2 - r_{ij}^3), \]  

(3.3)

where \( r_{ij} \) denotes the position of the \( j \)th nucleus in the \( i \)th N2 molecule. \[ r_{ij} - r_{ij}^3 = 1.100 \text{ Å is the N–N internuclear separation in a molecule, and } w_{ij}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \text{ is a Lennard–Jones potential. For the N2 model, } \epsilon = 6.067 \times 10^{-19} \text{ erg and } \sigma = 3.341 \text{ Å. The mass of a molecule is 28 amu.} \]

The parameters \( \epsilon \) and \( \sigma \) form the natural units of energy and length, respectively. With them it is convenient to define the reduced thermodynamic variables \( T^* = (\epsilon k)^4 \) and \( \rho^* = \rho a^3 \). The triple point density is \( \rho T^* = 0.70 \). The triple point temperature is \( T^*_T = 1.4 \). The critical point is at \( T^*_c = 2.8 \).

While the results discussed below are specifically for this model for N2, they are indicative of what would be found for any molecular fluid in which the shape of the molecules is linear, and the length-to-width ratio is roughly \( (3.341 + 1.100)/(3.341) = 1.33 \).

To apply our theory to this system, the intermolecular potential must be separated into a reference part and a perturbation. The reference interaction must contain all the shape-determining harsh repulsive interactions so that the effects of the perturbation on the liquid structure can be neglected. The separation of \( w_{ij}(r) \) which satisfies this condition breaks \( w_{ij}(r) \) into the following two parts:

\[ w_{ij}(r) = w_{ij}^{(0)}(r) + u_{ij}(r), \]  

(3.4a)

where

\[ w_{ij}^{(0)}(r) = w_{ij}(r) - \epsilon, \quad \rho < \rho_0 \]

\[ = 0, \quad \rho \geq \rho_0 \]  

(3.4b)

and

\[ u_{ij}(r) = - \epsilon, \quad \rho < \rho_0 \]

\[ = w_{ij}(r), \quad \rho \geq \rho_0 \]  

(3.5)

In these equations, \( \rho_0 = 2^{1/3} \) is the location of the minimum in the Lennard–Jones potentials. Then, the reference intermolecular interaction is

\[ u_{L}(1, 2) = \sum_{a, a=1}^{\infty} u_{ij}^{(0)}(r_{ij}^2 - r_{ij}^3). \]  

(3.5)

The reader is referred to Refs. 1–3 and 24 of Paper I for detailed discussions of the physical and mathematical motivation which leads to the potential separation given in Eqs. (3.4) and (3.5).

With the reference system defined by Eq. (3.5), we could determine the optimum rough hard sphere model (the diameter and the roughness) by finding (at each density and temperature) the hard sphere system which satisfies Eq. (2.15) of the present paper and Eq. (5.5) of Paper I. Instead of doing this, we employ an approximation which avoids the necessity of calculating the two-body collision dynamics for the reference system molecules. We assume that the diameter \( d \) can be approximately determined by the condition which relates the static properties of the reference system to those in a hard sphere fluid. This condition is

\[ 0 = \int dR dG u(R)(f_0(1, 2) - f_2(1, 2)), \]  

(3.6)

where we have used the notation of Ref. 12. Further,
we assume that the roughness is such that \( a(T) \) in Eq. (2.9) is approximately a constant for all thermodynamic states. The constant is the one free parameter in the calculations. The value we choose is (2.3)^{4/3}, i.e.,

\[
  a(T) \approx a = (2.3)^{4/3}.
\]  

(3.7)

[The analysis in the Appendix of the perfectly rough hard sphere gives \( a(T) = (1.2)^{2/3} \). If the spheres are smooth, \( a(T) = 0 \). Our choice for \( a(T) \) is approximately halfway between the two extremes.]

The values of \( d \) obtained from Eq. (3.6) at the different thermodynamic states are listed in Table I. It is seen that for \( T^* < T^\ast \), \( d \) is essentially independent of density and can be represented (with errors less than 0.3\%) by

\[
d(T^*) \approx d(T^\ast)[1 - B(T^* - T^\ast)]
\]

where we have chosen \( T^\ast = 1.43 \) so that \( d(T^\ast) = 3.756 \, \text{Å} \), and we find \( B = 0.015 \). Thus, in the absence of any detailed knowledge of the intermolecular potentials, the theory discussed in this paper can be used to interpret a great deal of experimental data with just three parameters: \( a, d(T^\ast), \) and \( B \).

With the diameter determined from Eq. (3.6), \( \tau_F \) is calculated directly from Eq. (2.9) of Paper I. The results for several thermodynamic states are given in Table I. Then \( \tau_F \) is calculated from Eqs. (3.7), (2.16), and (2.9), i.e., \( \tau_F \approx \tau_0 = 2 \cdot 3 \cdot \tau_s \). The results are obtained are also shown in Table I and compared with those obtained from the molecular dynamics computer experiments. (The molecular dynamics results for \( \tau_F \) contain errors that can be as large as 0.01\%.) The agreement between theory and experiment satisfies our expectation that the theory is accurate to within 10\%.

It may be noticed that at constant density, \( \tau_F \) is very nearly temperature independent. This need not be the case for all liquids. In fact, if the associated hard sphere diameter did not decrease with temperature, we would predict that \( \tau_F \approx T^{-1/3} \). The 1\% decrease in \( d \) between \( T^\ast \) and \( T^\ast \) essentially cancels this temperature dependence. If the diameter decreased by 10\% going from the triple point temperature to the critical temperature, we would predict a \( \tau_F \) that increases over the interval by a factor of 2.

We can also calculate the "relaxation times" \( \tau_1 \) and \( \tau_2 \)

which are defined by

\[
\tau_1 = \int_0^\infty dC_i(t), \quad i = 1, 2.
\]

(3.8)

By applying the theory developed in Sec. III, in particular Eqs. (2.4) and (2.8), we obtain

\[
\tau_1 \approx \tau_n x e^x E_1(x) / [1 - x e^x E_1(x)],
\]

(3.9)

where \( x = (2 \tau_n^{1/3} / \beta)^{-1} \)

\[
\tau_2 \approx \tau_n^{-1} \left[ 1 + 3 ye^y E_1(y) / [1 - 3 ye^y E_1(y)] \right],
\]

(3.10)

where \( y = (3 \tau_n^{1/3} / \beta)^{-1} \). In both of these equations,

\[
E_1(z) = \int_z^\infty \frac{du e^{-u}}{u}.
\]

The results obtained from Eqs. (3.9) and (3.10) are shown in Table I and compared with the molecular dynamics results. The agreement between experiment and theory for \( \tau_2 \) is within the expected 10\% range. However, experiment and theory predict significantly different values for \( \tau_1 \). We are puzzled by the differences because the other comparisons (for \( \tau_F \) and \( \tau_2 \)) work out so well. Incidentally, the agreement does not improve if we replace \( \tau_n \) in Eq. (3.9) with the experimental \( \tau_F \) (which would correspond precisely to Gordon's \( J \) diffusion model result).

If we discount the possibility that there are large uncertainties in the molecular dynamics results, then there are two explanations for the disagreement between the theoretical and experimental values for \( \tau_1 \). One is that \( \delta n \) is not small enough (i.e., the molecule is not spherical enough) for the relationship between hard spheres and the reference system to be reliable. The other is that our theory for rough hard spheres, which approximates the dynamics by sequences of uncorrelated binary collisions, is not accurate. Whichever is the case, we find it strange that the inadequacies of the theory are manifested in \( \tau_1 \) only.

IV. DISCUSSION

In this paper we have studied the microscopic approximations which must be made to arrive at Gordon's \( J \) diffusion model theory for rotational motion in liquids. The physical ideas presented by Gordon to derive the theory are summarized as follows: between collisions, molecules move freely (as if they are in an ideal gas); collisions completely randomize the angular momentum of a molecule; collisions occur instantaneously, and

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**TABLE I.** Relaxation times for liquid N\(_2\) obtained from the molecular dynamics experiments of Ref. 11 (MD) and from the theory presented in this paper (this work).

| Thermodynamic state \( \rho^\ast \) | \( T^\ast \) | \( d (\text{Å}) \) | \( \tau_F (10^{12} \text{ sec}) \) | \( \tau_1 (10^{12} \text{ sec}) \) | \( \tau_2 (10^{12} \text{ sec}) \)
<table>
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<tr>
<td>0.622</td>
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<td>3.766</td>
<td>0.106</td>
<td>0.24</td>
<td>0.24</td>
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<td>3.48</td>
<td>3.702</td>
<td>0.097</td>
<td>0.22</td>
<td>0.24</td>
</tr>
<tr>
<td>0.696</td>
<td>1.43</td>
<td>3.796</td>
<td>0.080</td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td>0.696</td>
<td>1.83</td>
<td>3.797</td>
<td>0.077</td>
<td>0.18</td>
<td>0.17</td>
</tr>
<tr>
<td>0.696</td>
<td>4.03</td>
<td>3.666</td>
<td>0.068</td>
<td>0.16</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*The associated hard sphere diameter calculated from Eq. (3.6).*

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Here, we use the notation established in Appendix B of Paper I. Equation (A.1) is derived from the definition of a perfectly rough sphere (i.e., the vector $g_{h}$ is reversed by a collision) and the conservation laws for linear momentum, angular momentum, and kinetic energy.\(^{1}\)

For hard spheres which collide impulsively,\(^{15}\)

\[
(N-1)|\omega_{1} + [T_{21} \omega_{1}]| = \rho \sigma n \bar{d} \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \omega_{2} \phi(\tau_{1}, \tau_{2}, \tau_{3}) d\tau_{1} d\tau_{2} d\tau_{3} \,
\]

where we have used the notation defined after Eq. (B.3) in Paper I. By combining Eqs. (A.1) and (A.2) and performing the integrations, one finds

\[
(N-1)|\omega_{1} + [T_{21} \omega_{1}]| = \frac{2}{3} \left( \frac{a}{2m} \right)^{1/2} \rho \sigma n \bar{d} \int_{0}^{\infty} \tau_{1} \phi(\tau_{1}, \tau_{2}, \tau_{3}) d\tau_{1} d\tau_{2} d\tau_{3} \,
\]

Thus, for perfectly rough spheres, one has

\[
\tau_{1} \sim (\kappa + 1)^{-1/2} \,
\]

For $N_{2}$, $\kappa = 0.2$. As a result, the coefficient $a(7)$ in Eq. (2.9) is probably between zero (the value if the spheres were smooth) and $(1.2)^{1}$. In Sec. III the value of $a(7)$ used to fit the data for $N_{2}$ is $a(7) = a(2.3)^{1}$ which is approximately halfway between the two extremes.

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\(^{11}\)This assumes that the density dependence of the hard sphere diameter is very small compared to the temperature dependence. For the specific molecular model of $N_{2}$ studied in this paper, it is seen from Table 1 that $\sigma(1.4)/\sigma(1.4) = \sigma(1)/\sigma(2)$.


\(^{15}\)D. Levesque (private communicaion).

\(^{16}\)See Footnote 28 of Paper I. We estimate there that the size of $t_{4}$ causes 10% errors in the theory.

\(^{17}\)See Refs. 1-6, 9, 10, 12, 24, and 27 of Paper I.

\(^{18}\)See Refs. 15 and 16 of Paper I.

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APPENDIX

An explicit calculation of $\tau_{1}$ is given here for perfectly rough spheres. For simplicity, we consider only linear rotors and spherical tops since then the angular momentum is proportional to the angular velocity.

Consider two spheres 1 and 2. If they collide, the angular velocity changes according to the equation\(^{4}\)

\[
\omega_{1} - \omega_{2} = (a/d)(\kappa + 1)\tau_{1} \phi(\tau_{1}, \tau_{2}, \tau_{3}) d\tau_{1} d\tau_{2} d\tau_{3} \,
\]

Use the notation established in Appendix B of Paper I. Equation (A.1) is derived from the definition of a perfectly rough sphere (i.e., the vector $g_{h}$ is reversed by a collision) and the conservation laws for linear momentum, angular momentum, and kinetic energy.\(^{1}\)

For hard spheres which collide impulsively,\(^{15}\)

\[
(N-1)|\omega_{1} + [T_{21} \omega_{1}]| = \frac{2}{3} \left( \frac{a}{2m} \right)^{1/2} \rho \sigma n \bar{d} \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \omega_{2} \phi(\tau_{1}, \tau_{2}, \tau_{3}) d\tau_{1} d\tau_{2} d\tau_{3} \,
\]

where we have used the notation defined after Eq. (B.3) in Paper I. By combining Eqs. (A.1) and (A.2) and performing the integrations, one finds

\[
(N-1)|\omega_{1} + [T_{21} \omega_{1}]| = \frac{2}{3} \left( \frac{a}{2m} \right)^{1/2} \rho \sigma n \bar{d} \int_{0}^{\infty} \tau_{1} \phi(\tau_{1}, \tau_{2}, \tau_{3}) d\tau_{1} d\tau_{2} d\tau_{3} \,
\]

Thus, for perfectly rough spheres, one has

\[
\tau_{1} \sim (\kappa + 1)^{-1/2} \,
\]

For $N_{2}$, $\kappa = 0.2$. As a result, the coefficient $a(7)$ in Eq. (2.9) is probably between zero (the value if the spheres were smooth) and $(1.2)^{1}$ In Sec. III the value of $a(7)$ used to fit the data for $N_{2}$ is $a(7) = a(2.3)^{1}$ which is approximately halfway between the two extremes.