JOURNAL OF COMPUTATIONAL PHYSICS 7, 515–527 (1971)

Molecular Dynamics of Rough Disks Assemblies and Dielectric Relaxation

E. KESTEMONT AND A. BELLEMANS

Free University of Brussels, Belgium

Received December 10, 1970

As a simple model of dielectric relaxation we study two-dimensional assemblies of *rough disks* at various densities ρ by the method of molecular dynamics. The electric moment autocorrelation function $\psi(t)$ as well as its Fourier transform $\tilde{\psi}(\omega)$ and the dynamic dielectric function $\epsilon(\omega)$ are determined. A clear change from inertial behavior towards Debye relaxation is observed as ρ increases. The angular velocity autocorrelation function is also considered and the results are compared to a simple stochastic model.

1. INTRODUCTION

The dielectric relaxation of an isotropic and homogeneous assembly of polar molecules is related to the time-dependent autocorrelation function of the total electric moment of the system

$$\psi(t) = \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle / \langle \mathbf{M}^2 \rangle, \tag{1}$$

where $\langle \cdots \rangle$ represents the canonical average over all configurations for zero external field. For a spherical sample of unpolarizable molecules, the frequency-dependent dielectric constant $\epsilon(\omega)$ is given by [1]

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{\epsilon_s - 1}{\epsilon_s + 2} \int_0^\infty [-\dot{\psi}(t)]\, e^{-i\omega t}\, dt$$

or alternatively

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{\epsilon_s - 1}{\epsilon_s + 2} [1 - i\omega\tilde{\psi}(\omega)], \tag{2}$$

where ϵ_s is the static dielectric constant and $\tilde{\psi}(\omega)$ is the Fourier transform of $\psi(t)$,

$$\tilde{\psi}(\omega) = \int_0^\infty \psi(t)\, e^{-i\omega t}\, dt. \tag{3}$$

The function $\psi(t)$ is of course related to the rotational relaxation of the molecules. At infinitely weak coupling, $\psi(t)$ results essentially from the inertial motion and corresponds approximately to a Gaussian function with a characteristic time $(I/kT)^{1/2}$, where I is the moment of inertia of a molecule [2–4]. In dense liquids or highly compressed gases, experiments show that $\psi(t)$ roughly behaves like an exponential function with a microscopic relaxation time τ_R,

$$\psi(t) \simeq e^{-t/\tau_R}, \qquad \tilde{\psi}(\omega) \simeq \frac{\tau_R}{1 + i\omega\tau_R}, \tag{4}$$

in reasonable agreement with the theory of Debye [5], so that

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \simeq \frac{\epsilon_s - 1}{\epsilon_s + 2} \frac{1}{1 + i\omega\tau_R}. \tag{5}$$

Of course deviations from this formula are bound to occur at sufficiently high frequencies on account of inertial effects which predominate at short times [6, 7].

Starting from an initially dilute system and increasing steadily its density, one expects $\psi(t)$ to change approximately from a Gaussian to an exponential function in a smooth manner, depending of course on the nature of the orientational intermolecular forces involved, and it would be interesting to know the relative effectiveness of the various types of forces. Although this question can in principle be settled by statistical studies of "model hamiltonians," the difficulties are considerable and rather few results are available yet. One could, roughly speaking, classify angular-dependent forces into:

(a) Weak ones acting at long or medium ranges, such as dipolar interactions;

(b) Strong ones acting at short range only and related to the precise shape of the molecules.

The role of weak forces in dielectric relaxation has been discussed by several authors. On the basis of semimacroscopic models Scaife [8] and Zwanzig [9] concluded that dipolar interactions play a minor role only. This was confirmed by Kestemont [10] who studied analytically an array of dipoles on a rigid lattice, using Prigogine's statistical theory of irreversible processes in the weak coupling limit. Bellemans *et al* [4] amplified these conclusions by studying this same model on a computer by the *method of molecular dynamics*, originally devised by Alder and Wainwright [11] for investigating hard disks and hard spheres assemblies. In agreement with Kestemont they observed that dipolar interactions did not lead to a Debye relaxation but that even at relatively high coupling, $\psi(t)$ remained approximately Gaussian and that no other characteristic time than $(I/kT)^{1/2}$ did appear. This relative independence of dielectric relaxation on weak forces was also observed for quadrupolar effects and confirmed by other authors [12]. One noticeable exception is the classical spin–spin interaction favoring parallel alignment of the dipoles, which lead approximately to a Debye relaxation; this interaction seems however rather unrealistic [4].

From the preceding discussion we may expect that the essential role in dielectric relaxation is played by strong interactions. These however are extremely difficult to handle theoretically because perturbation methods usually fail completely. Only a few calculations have been made, mainly based on stochastic models of collisions [2, 13], and it is clear that computer experiments would be extremely valuable for exploring this field. Although, many sophisticated strong potentials could be handled by the method of molecular dynamics (such as dumb-bell Lennard–Jones molecules [14]), we believe it wiser to limit ourselves at first to the very simple model of *rough spheres* which is well known in the kinetic theory of gases [15] and may be easily treated stochastically.

2. ROUGH SPHERES AND ROUGH DISKS ASSEMBLIES

Consider an assembly of N rough spheres of mass M, inertial momentum I and diameter D. The trajectory of the center of each sphere between two successive collisions is a straight line so that the kinematics of this system is as simple as that of smooth spheres. The dynamics is however different: When two rough spheres collide, they grip each other at their points of contact without slipping; each of them is at first strained by the other, then this strain energy is released and transformed into translational and rotational kinetic energies in such a way that the relative velocities of the points of contact are exactly reversed. As a result each collision entails an energy transfer between rotational and translational degrees of freedom, depending on the dimensionless quantity

$$R = 4I/MD^2 \tag{6}$$

In order to discuss dielectric relaxation with this model we consider that an electric dipole μ is located at the center of each sphere. We however assume μ to be vanishingly small so that neither do these dipoles influence the trajectories of the spheres nor are they correlated to each other. (This seems justified by our previous observations that dipolar forces are relatively unimportant). Hence, we have

$$\langle \mathbf{M}^2 \rangle = \sum_i \sum_j \langle \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \rangle = N\mu^2,$$

$$\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle = \sum_i \sum_j \langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_j(t) \rangle = N \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle,$$

so that

$$\psi(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle, \tag{7}$$

where **u** is the unit vector pointing in the direction of the dipole of a molecule. Hence, $\psi(t)$ is identical in the present case to the orientational autocorrelation function of a molecule. Also, in the limit $\mu \rightarrow 0$, both ϵ_s and $\epsilon(\omega)$ tend to unity so that (2) may be rewritten as

$$\frac{\epsilon(\omega) - 1}{\epsilon_s - 1} = 1 - i\omega\tilde{\psi}(\omega). \tag{8}$$

Up to now we limited our investigation to two-dimensional systems of *rough disks* instead of spheres. This simplifies the problem without altering too much its physical relevance and saves about 50% of computing time. The application of the method of molecular dynamics to hard disks and hard spheres has been extensively discussed by Alder and Wainwright [11] and will not be described here. We shall however quote the equations determining the change of velocities of a pair of colliding rough disks, denoted [15] as 1 and 2:

$$\begin{aligned}
\mathbf{v}_1' &= \mathbf{v}_1 + \frac{R}{1+R}\left[\mathbf{V} + \frac{1}{R}\mathbf{k}(\mathbf{k}\cdot\mathbf{V})\right],\\
\mathbf{v}_2' &= \mathbf{v}_2 - \frac{R}{1+R}\left[\mathbf{V} + \frac{1}{R}\mathbf{k}(\mathbf{k}\cdot\mathbf{V})\right],\\
\mathbf{\Omega}_1' &= \mathbf{\Omega}_1 - \frac{2}{(1+R)D}\mathbf{k} \wedge \mathbf{V},\\
\mathbf{\Omega}_2' &= \mathbf{\Omega}_2 - \frac{2}{(1+R)D}\mathbf{k} \wedge \mathbf{V}.
\end{aligned} \tag{9}$$

Here $\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_1'$, $\mathbf{v}_2'$ and $\mathbf{\Omega}_1$, $\mathbf{\Omega}_2$, $\mathbf{\Omega}_1'$, $\mathbf{\Omega}_2'$ are, respectively, the translational and rotational velocities, where the *prime* variables correspond to the situation after collision; **V** is the relative velocity of the points of contact before collision

$$\mathbf{V} = \mathbf{v}_2 - \mathbf{v}_1 - \tfrac{1}{2}D\mathbf{k} \wedge (\mathbf{\Omega}_1 + \mathbf{\Omega}_2) \tag{10}$$

and **k** is the unit vector in the direction of the line from the center of the second molecule to that of the first at collision. Note that in the present case the translational velocities are two-dimensional vectors while the angular velocities, normal to the plane of the disks, are actually algebraic numbers.

We end this section with the derivation of $\psi(t)$ in the limit of infinitely weak coupling. Each disk rotates independently with a constant velocity Ω distributed according to the normalized Boltzmann law

$$(2\pi I/kT)^{-1/2}\exp(-\tfrac{1}{2}I\Omega^2/kT). \tag{11}$$

It follows that

$$\langle \mathbf{u}(0)\cdot\mathbf{u}(t)\rangle = \langle\cos\Omega t\rangle = \exp(-\tfrac{1}{2}t^2kT/I).$$

From now on we shall put $(I/kT)^{1/2}$ equal to unity so that the autocorrelation function at infinitely weak coupling may be written as

$$\psi_0(t) = \exp(-\tfrac{1}{2}t^2) \tag{12}$$

and its Fourier transform is given by

$$\tilde{\psi}_0(\omega) = \int_0^\infty e^{-t^2/2}\,e^{-i\omega t}\,dt. \tag{13}$$

3. Results of The Computer Experiments

Several systems of approximately one hundred disks have been studied on the computer of the Free University of Brussels (IBM 7040 — 32 K) by the method of molecular dynamics, at various densities and for two particular values of the parameter R defined by (6). The functions $\psi(t)$ which were subsequently deduced from these "experiments," are plotted on Figs. 1 and 2 and their main characteristics are summarized in Table I. Note that we use the following reduced units:

$$I/kT = 1, \qquad D = 1,$$

so that the equilibrium averages $\langle\Omega^2\rangle$ and $\langle v^2\rangle$ assume the following values:

$$\begin{aligned}\langle\Omega^2\rangle &= kT/I \equiv 1,\\ \langle v^2\rangle &= 2kT/M = \tfrac{1}{2}(kT/I)\,D^2(4I/MD^2) \equiv \tfrac{1}{2}R.\end{aligned}$$

For each experiment we checked the equilibrium state of the system by verifying not only that

$$\langle v^2\rangle/\langle\Omega^2\rangle \simeq \tfrac{1}{2}R,$$

but also

$$\langle\Omega^4\rangle/\langle\Omega^2\rangle^2 \simeq 3, \qquad \langle v^4\rangle/\langle v^2\rangle^2 \simeq 2$$

as implied by the Botzmann distribution.

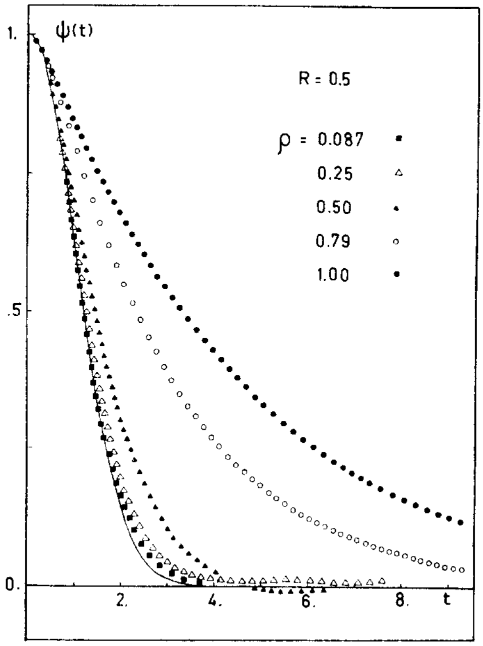

FIG. 1. Autocorrelation function $\psi(t)$ for various densities and for $R = 0.5$. The solid line corresponds to $\psi_0(t)$ (zero coupling).

TABLE I

Results of the various computer experiments; τ is the average time interval between collisions and N is the number of disks of the experiment

R	ρ	τ	τ^{-1}	τ_R	τ_Ω	N
0.5	0.087	8.3	0.120	—	—	100
	0.25	2.61	0.383	—	3.8 ± 0.3	120
	0.50	0.83	1.20	—	1.3 ± 0.2	120
	0.79	0.204	4.90	2.9 ± 0.1	0.39 ± 0.08	100
	1.00	0.126	7.96	3.6 ± 0.2	0.24 ± 0.05	120
0.05	0.087	26.3	0.038	—	—	100
	0.25	8.3	0.121	—	9 ± 1	120
	0.50	2.64	0.380	—	3.00 ± 0.3	120
	0.79	0.65	1.55	—	—	100
	1.00	0.397	2.52	2.9 ± 0.1	0.46 ± 0.09	120

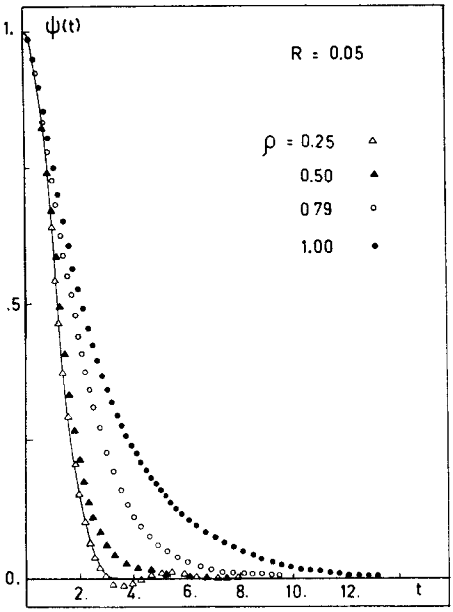

FIG. 2. Autocorrelation function $\psi(t)$ for various densities and for $R = 0.05$. The solid line corresponds to $\psi_0(t)$ (zero coupling). (The density 0.087 is not shown as the corresponding points fall allmost exactly on the curve $\psi_0(t)$.)

Figure 1 shows the various curves of $\psi(t)$ for $R = 0.5$ and for five densities ρ equal to

$$0.087, \quad 0.25, \quad 0.50, \quad 0.79, \quad 1.00$$

(the density of close-packing is $2/\sqrt{3} \simeq 1.15$); the first four values correspond to fluid states, the last one falls in the solid region. As ρ increases a clear change is seen in $\psi(t)$: At the lowest density it is practically identical to the function $\psi_0(t)$ given by (13) and corresponding to zero coupling; in contrast $\psi(t)$ appears approximately exponential for the highest density, with a small Gaussian region at very short times, due to inertial effects.

The behavior of $\psi(t)$ for $R = 0.05$, shown on Fig. 2, is qualitatively the same, though not so well marked. This can be interpreted as follows. The role of R is two-fold:

(a) The frequency of collision is proportional to $\langle v \rangle$, i.e., to $R^{1/2}$; this tends to reduce inertial effects as R increases and to lengthen the relaxation time.

(b) The efficiency of an individual collision for changing Ω decreases as R increases (as I and R are directly proportional); this on the contrary enhances inertial effects.

It finally turns out that of these two conflicting influences of R, the first one is predominant. (For simple real molecules R may reasonably be expected to lay between 0.2 and 0.01).

It seems thus that this model system nicely illustrates the evolution from inertial behavior to Debye relaxation. Further insight in the problem can be obtained by taking the Fourier transform $\tilde{\psi}(\omega)$ and calculating $\epsilon(\omega)$ from (8). Figures 3–6 show the real and imaginary parts of $\epsilon(\omega)$ for the two values of R considered here. In all cases there is a systematic shift of the curves towards lower frequencies as ρ increases. Moreover, the negative part of $\epsilon'(\omega) - 1$, occuring at high frequencies

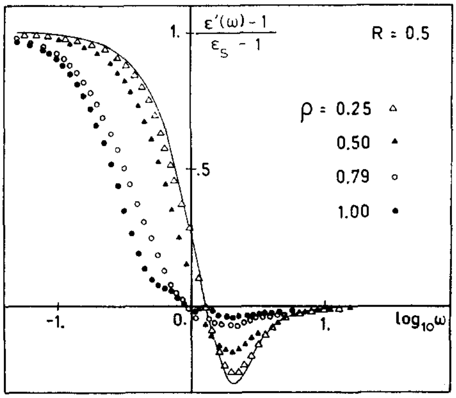

FIG. 3. Real part of $\epsilon(\omega)$ for various densities and for $R = 0.5$ ($\rho = 0.087$ not shown). The solid line corresponds to zero coupling.

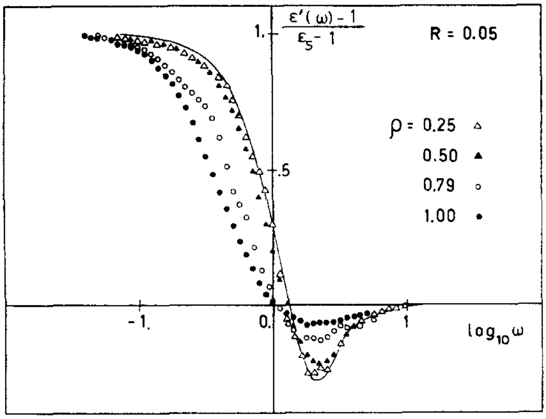

FIG. 4. Real part of $\epsilon(\omega)$ for various densities and for $R = 0.05$ ($\rho = 0.087$ not shown). The solid line corresponds to zero coupling.

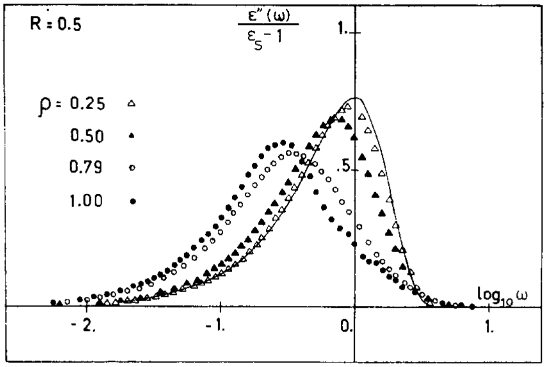

FIG. 5. Imaginary part of $\epsilon(\omega)$ for various densities and for $R = 0.5$ ($\rho = 0.087$ not shown). The solid line corresponds to zero coupling.

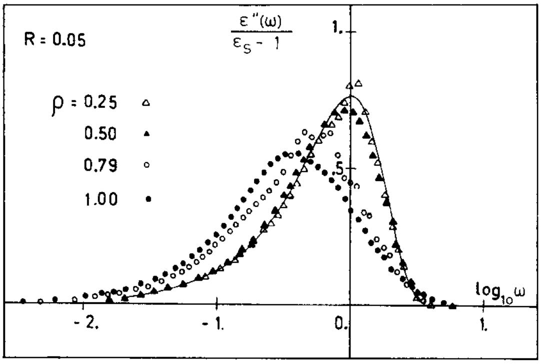

FIG. 6. Imaginary part of $\epsilon(\omega)$ for various densities and for $R = 0.05$ ($\rho = 0.087$ not shown). The solid line corresponds to zero coupling.

on account of inertial effects, is progressively destroyed, while the maximum of $\epsilon''(\omega)$ becomes more flat and more symmetrical. Unfortunately the accuracy of the Fourier transforms is not altogether satisfactory. There is nevertheless a clear evolution of $\epsilon''(\omega)$ towards the Debye symmetrical curve with maximum height equal to 0.5 [5]. Three cases, namely $\rho = 1.0$ and 0.79 for $R = 0.5$ and $\rho = 1.0$ for $R = 0.05$, seem not too far from the Debye picture and we have accordingly evaluated their corresponding relaxation times τ_R from the location of the maximum of $\epsilon''(\omega)$; see Table I.

To complete this study we also determined the autocorrelation function of the angular velocity of a molecule

$$\varphi(t) = \langle \Omega(0)\, \Omega(t) \rangle / \langle \Omega^2 \rangle \tag{14}$$

which is, in a sense, complementary to $\psi(t)$. It turns out that this function is exponential to a good approximation

$$\varphi(t) \simeq e^{-t/\tau_\Omega} \tag{15}$$

and the estimated values of τ_Ω are listed in Table I for the various "experiments"; one will notice the parallel behavior of τ_Ω and τ as ρ increases, τ being the average time interval between successive collisions.

4. STOCHASTIC MODEL OF COLLISIONS

It will be interesting to compare the above results with a simple stochastic model. Consider one particular disk with angular velocity Ω_0 at time 0 and assume that this disk suffers a series of n collisions during the time interval $(0, t)$, occuring at $t_1, t_2, ..., t_n$ so that its angular velocity successively takes the values $\Omega_1, \Omega_2, ..., \Omega_n$. We have

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \cos\{\Omega_0 t_1 + \Omega_1(t_2 - t_1) + \cdots + \Omega_n(t - t_n)\}$$

the statistical average of which gives $\psi(t)$. Following Gordon [2] we evaluate $\psi(t)$ approximately by making three assumptions:

(a) Given the mean frequency of collisions τ^{-1}, the probability for n collisions in the interval $(0, t)$ is given by the Poisson distribution

$$e^{-t/\tau}(t/\tau)^n/n!$$

(b) The collision times $t_1, t_2, ..., t_n$ are randomly distributed between 0 and t.

(c) $\Omega_0, \Omega_1, ..., \Omega_n$ are completely uncorrelated and distributed according to (11).

Combining assumptions (a)–(c), we get for $\psi(t)$;

$$\psi(t) = e^{-t/\tau} \sum_0^\infty \tau^{-n} \int_0^t dt_n \int_0^{t_n} dt_{n-1} \cdots \int_0^{t_2} dt_1 \, T(t; t_1, ..., t_n),$$

where

$$\begin{aligned} T(t; t_1, ..., t_n) &= (2\pi)^{-(n+1)/2} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} d\Omega_0 \cdots d\Omega_n \, e^{-\frac{1}{2}(\Omega_0^2 + \cdots + \Omega_n^2)} \\ &\quad \times \cos\{\Omega_0 t_1 + \Omega_1(t_2 - t_1) + \cdots + \Omega_n(t - t_n)\} \\ &= \exp(-\tfrac{1}{2}[t_1^2 + (t_2 - t_1)^2 + \cdots + (t - t_n)^2]). \end{aligned}$$

Rather than $\psi(t)$ itself we calculate its Fourier transform $\tilde{\psi}(\omega)$. We find easily that

$$\tilde{\psi}(\omega) = \frac{X(i\omega + \tau^{-1})}{1 - \tau^{-1}X(i\omega + \tau^{-1})}, \tag{16}$$

where

$$X(z) = \int_0^\infty e^{-t^2/2}\, e^{-zt}\, dt \tag{17}$$

and finally from (8) we get

$$\frac{\epsilon(\omega) - 1}{\epsilon_s - 1} = \frac{1 - (i\omega + \tau^{-1})\, X(i\omega + \tau^{-1})}{1 - \tau^{-1}X(i\omega + \tau^{-1})}. \tag{18}$$

For $\tau \to \infty$, we recover the infinitely weak coupling limit, i.e.,

$$\frac{\epsilon(\omega) - 1}{\epsilon_s - 1} = 1 - i\omega\tilde{\psi}_0(\omega)$$

by noticing that $X(i\omega) \equiv \tilde{\psi}_0(\omega)$. Consider now the opposite case $\tau^{-1} \gg 1$; we then have to turn to the asymptotic expansion of $X(z)$ [16],

$$X(z) = \frac{1}{z} - \frac{1}{z^3} + \frac{3}{z^5} + \cdots. \tag{19}$$

If we make the double assumption that $\tau^{-1} \gg 1$ and $\tau^{-1} \gg \omega$, we find from (18) that

$$\frac{\epsilon(\omega) - 1}{\epsilon_s - 1} \simeq \frac{1}{1 + i\omega/\tau}, \tag{20}$$

which is nothing else but the Debye expression (5) with

$$\tau_R \equiv 1/\tau. \tag{21}$$

(This last relation seems to have been established first by E. P. Gross [6]).

It is also instructive to look for $\varphi(t)$ in this same model. On account of assumption (c) one gets rather trivially

$$\varphi(t) = \langle \Omega_0^2 \rangle\, e^{-t/\tau} = e^{-t/\tau}. \tag{22}$$

Hence provided that the frequency of collisions τ^{-1} is much higher than the mean rotational frequency $(kT/I)^{1/2}$ (here equal to 1), and as long as one is interested in frequencies ω much lower than τ^{-1}, the Debye theory is approximately valid and the characteristic relaxation times τ_R, τ_Ω of $\psi(t)$ and $\varphi(t)$ are respectively given by

$$\tau_R \simeq \frac{1}{\tau}, \qquad \tau_\Omega \simeq \tau. \tag{23}$$

These predictions do not agree with the results of Table I, though there is a noticeable parallel between the variation of τ_R, τ^{-1} on one hand and τ_Ω, τ on the other hand, as ρ changes. Equations (23) however suggerates that a simple relation exists between τ_R and τ_Ω, namely

$$\tau_R \tau_\Omega \simeq 1. \tag{24}$$

The three cases of Table I for which both τ_R and τ_Ω have been estimated, give

$$R = 0.5, \qquad \rho = 0.79 : \tau_R\tau_\Omega = 1.1 \pm 0.2;$$
$$R = 0.5, \qquad \rho = 1.0 \;\; : \tau_R\tau_\Omega = 0.9 \pm 0.2;$$
$$R = 0.05, \qquad \rho = 1.0 \;\; : \tau_R\tau_\Omega = 1.3 \pm 0.3,$$

which makes indeed relationship (24) plausible.

The main origin of the failure of (23) is to be traced to assumption (c) of the stochastic model. There obviously exists a *persistence of velocity* for rotation similar to the one known for translation in the kinetic theory of gases [17]. From this effect one may, e.g., anticipate that the ratio τ_Ω/τ is larger than one and increases with R, in agreement with Table I.

5. FINAL REMARKS

It seems to us that the results obtained here are interesting enough to justify an extension of this work to three dimensions, i.e., to *rough spheres*. We also intend to refine the stochastic model of collisions of Section 4 by removing assumption (c), which probably is its essential weakness. This will be the object of a forthcoming article.

We want to express our deep appreciation to Mrs. M. Gillis–Festraets and Mr. M. Promenschenkel who collaborated to the computational part of the present work [18].

REFERENCES

1. S. H. GLARUM, *J. Chem. Phys.* **33** (1960), 1371.
2. R. G. GORDON, *J. Chem. Phys.* **44** (1966), 1831.
3. W. A. STEELE, *J. Chem. Phys.* **38** (1963), 2411.

4. A. Bellemans, M. Köhler, and M. Gancberg, *J. Chem. Phys.* **51** (1969), 2578.
5. P. Debye, "Polar Molecules," p. 89, Dover Publications, New York, 1945.
6. E. P. Gross, *J. Chem. Phys.* **23** (1955), 1415.
7. Y. Leroy and E. Constant, C. R. **264**, 533 (1967).
8. B. K. P. Scaife, *Proc. Phys. Soc. London* **84** (1964), 616.
9. R. Zwanzig, *J. Chem. Phys.* **38** (1963), 1605.
10. E. Kestemont, Doctoral dissertation, University of Brussels (1968) (to be published).
11. T. Wainwright and B. J. Alder, *Nuovo Cimento Suppl.* **9** (1958), 116.
12. G. D. Harp and B. J. Berne, *J. Chem. Phys.* **49** (1968), 1249.
13. C. Brot, *J. de Physique* **28** (1967), 789.
14. B. Quentrec and C. Brot, private communication.
15. S. Chapman and T. G. Cowling, "The Mathematical Theory of Nonuniform Gases," p. 199, Cambridge University Press, Cambridge, 1960.
16. B. D. Fried and S. D. Conte, "The Plasma Dispersion Function," Academic Press, New York, 1961.
17. J. Jeans, "The Dynamical Theory of Gases," p. 260, Dover, New York, 1954.
18. A preliminary account of this work has been given at "The Second Annual Conference on Computational Physics," London (1970); Conference Digest edited by the Institute of Physics and the Physical Society, p. 104.