Calculation of the Dipole Autocorrelation Function for a System of Weakly Coupled Electric Dipoles

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In this paper, we present a simple theoretical treatment of dipolar relaxation, essentially based on the autocorrelation formalism and derived from the general theory developed by Boon and Rice for the autocorrelation function of a dynamical variable. A simple model is introduced to derive analytical expressions for the dipolar autocorrelation function, from which other quantities, like the response function and the complex dielectric function, are calculated. These theoretical results are tested against the experimental data obtained from a molecular dynamics study by Bellemans, Köhler, and Gancberg on a two-dimensional system of electric dipoles on a rigid lattice, subject to dipole–dipole interactions. We also append some results concerning the memory function governing the evolution of the autocorrelation function as described by the master equation.

I. INTRODUCTION

In a recent article,[1] detailed results have been presented concerning the dynamics of a two-dimensional system of interacting electric dipoles. These data were obtained from molecular dynamics experiments performed on a finite number of dipoles, located at the sites of a rigid lattice and interacting through an angle-dependent potential, defined by[2]

$$V = - \sum_{j}\sum_{\neq k} (\mu^2/r_{jk}) \cos(\phi_j + \phi_k - 2\alpha_{jk}), \qquad (1)$$

with μ the dipole moment; r_{jk} and α_{jk} the relative polar coordinates of sites j and k; and ϕ_i the angular coordinate of the ith dipole (see, e.g., Ref. 1, Fig. 1). Such a system, although oversimplified as compared to realistic systems, presents, nevertheless, qualitative features characteristic of an actual physical assembly of a large number of dipoles, subject to dielectric relaxation when interacting through a weak (dipole–dipole) potential.

On the other hand, the theoretical study of dielectric relaxation in physical systems involves in principle the solution of the many-body problem, which presents in the present case the further difficulty of long-range interactions. There have been several attempts to bypass this formal difficulty, in particular by treating the case of weakly coupled systems or by using a Brownian-motion-type approximation.[3] It remains, nevertheless, quite difficult from these theoretical results to derive useful expressions for the prediction of the physical properties of systems, even as simple as the one considered above, without introducing further approximations.

In this paper, we first present a simple theoretical treatment of dipolar relaxation which is essentially an extension of the general theory developed by Boon and Rice[4] (BR) for the autocorrelation function (a.f.) of a dynamical variable. The main purpose of this theoretical analysis is the application to a simple system of electric dipoles, as described above.

In Sec. II, we briefly recall the principle of the BR method, as applied to the dipole-normalized autocorrelation function (d.a.f.) defined by

$$\psi(t) = \langle \mathbf{M}(0)\mathbf{M}(t)\rangle / \langle [\mathbf{M}(0)]^2\rangle, \qquad (2)$$

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[1] A. Bellemans, M. Köhler, and M. Gancberg, J. Chem. Phys. **51**, 2578 (1969).

[2] In the present paper we shall restrict ourselves to the analysis of the *experiment* performed on the largest number of dipoles (421), as presented in Ref. 1, and subject to dipole–dipole interaction only.

[3] See, e.g., A. Bellemans, J. C. Bernard, M. Köhler, and E. Kestemont, Physica **31**, 1291 (1965); E. Kestemont and A. Bellemans (unpublished); for a general account of the existing theories, see E. Kestemont, thesis, Brussels, Belgium, 1968.

[4] J. P. Boon and S. A. Rice, J. Chem. Phys. **47**, 2480 (1967) (hereafter referred to as BR).

with $\mathbf{M}(t)$, the total electric moment at time t, and where the bracket defines an average in the canonical ensemble. We show how the master equation governing the time evolution of the d.a.f., i.e.,

$$\psi(t) = -\int_0^t K(\tau)\psi(t-\tau)d\tau. \tag{3}$$

[where the kernel $K(\tau)$ is often interpreted as the memory function of the system[4]], can advantageously be exploited to compute quantities characterizing the system considered: e.g., the response function and the polarization, or the dielectric function (Sec. III).

However, as stated before, such calculation cannot be performed explicitly, in general, on the basis of the master Eq. (3) alone. We therefore introduce a model based on arguments similar to those characterizing the BR model for the computation of the linear momentum a.f. in a simple dense fluid. The model is primarily needed here to obtain an explicit analytical form for the kernel in Eq. (3). Although this is a model calculation, the memory function $K(t)$ presents the qualitative features required by the formal properties of the kernel of the master equation.[5] A more detailed analysis of the memory function is presented in the appendix, where the model kernel is compared to the kernel derived from the computer experiment. We also take advantage of our numerical analysis program to comment on the BR model kernel as compared to Rahman's[6] for the linear momentum a.f. in liquid argon.

Sec. IV is devoted to the application of the theoretical model to the simple system of electric dipoles on a rigid two-dimensional lattice, as defined in the first paragraph of the present section.

Despite the fact that the analysis presented in this paper does not constitute, by any means, a complete or rigorous theory of dielectric relaxation in *real* system, the advantage of the method is twofold: first, all the qualitative features of the physical properties considered are correctly reproduced by the theory; second, the computation is entirely performed analytically (in particular, no appeal is made to any parametrization procedure). Furthermore, an essential feature of the method is that it describes the evolution of the dipole system over the whole time scale. This implies that the inertial stage is accounted for while most theories are restricted to long-time approximations, which are certainly quite appropriate to describe complex dipolar systems. However, for simple molecular systems (in particular, the simplest ones as considered in molecular dynamics experiments) the inertial stage plays an essential role, as seen, for instance, from the high-frequency behavior of such systems.

Although there would hardly be any *a priori* rigorous justification for the model considered herein, the results are gratifying, as it is found that the d.a.f. and related functions obtained from the theory are in very good agreement with the results from the computer experiment by Bellemans, Köhler, and Gancberg.[1]

II. THE DIPOLE AUTOCORRELATION FUNCTION

We simply sketch here the derivation of the master equation describing the time evolution of the d.a.f., as the calculation follows exactly the general treatment of the a.f. of a dynamical variable presented by Boon and Rice.[4]

The BR derivation consists essentially in the convergence of two different-but-equivalent approaches to the theory of irreversible processes, following in this way Résibois' analysis[7] of the connection between the kinetic equation formalism (Prigogine and co-workers[8,9]) (PR) and the a.f. formalism (Nakajima[10] and Zwanzig[5]) (NZ) for the representation of the thermal transport coefficients.

The BR calculation proceeds essentially in five steps:

(1) The a.f. is Laplace transformed with respect to the time variable, which allows infinite perturbation expansion of the Liouville resolvent operator;

(2) The result is then Fourier transformed with respect to the position (or angle) coordinates, which permits us to separate off the contribution arising from initial correlations;

(3) Differentiation with respect to time of the double-transformed d.a.f. yields the master equation, which reads

$$d\psi(t)/dt = -\frac{1}{2\pi}\oint dz \exp(-izt)\langle [M(0)]^2\rangle^{-1}$$

$$\times \int dJ \langle 0 \mid \mathbf{M}(J) \mid 0\rangle\{z/[z+\Psi(z)]\}\{[\mathbf{M}(J)f^{(N)}]_{\{0\}}$$

$$+ \sum_{\{m\}\neq 0} \langle 0 \mid \mathfrak{D}(z) \mid \{m\}\rangle[\mathbf{M}(J)f^{(N)}]_{\{m\}}\}, \quad (4)$$

where J is the angular momentum, and z and m are the Laplace and Fourier variables, respectively. Here $f^{(N)}$ is the canonical distribution function and $\Psi(z)$ and $\mathfrak{D}(z)$ are the collision and destruction operators, respectively, as defined elsewhere.[4,7-9] Notice that the master equation for the d.a.f., Eq. (4), can straightforwardly be obtained from Eq. (12) of Ref. 4 by the following change of variables:

$$\mathbf{R}\rightarrow\phi,$$
$$\mathbf{p}\rightarrow J,$$
$$U(\mathbf{R}, \mathbf{p}, t)\rightarrow\mathbf{M}(\phi, J, t)/(\langle[M(0)]^2\rangle)^{1/2}. \tag{5}$$

[5] See, e.g., R. Zwanzig, in *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1961), Vol. 3, pp. 106–141; and also, B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. 45, 1086 (1966), Appendix A.

[6] A. Rahman, Phys. Rev. 136, A405 (1964).

[7] P. Résibois, J. Chem. Phys. 41, 2979 (1964).

[8] I. Prigogine and P. Résibois, Physica 27, 629 (1961).

[9] I. Prigogine, *Non Equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962); and P. Résibois, in *N-particle Physics*, E. Meeron, Ed. (Gordon and Breach Scientific Publishers, Inc., New York, 1968).

[10] S. Nakajima, Progr. Theoret. Phys. (Kyoto) 20, 948 (1 958)

(4) Some formal transformations of the operators in Eq. (4) are accomplished to rewrite the d.a.f. in Laplace representation as

$$\tilde{\psi}(s) = [1 + \tilde{G}(s)]/[s + \Phi(s)], \qquad (6)$$

where $\tilde{G}(s)$ and $\Phi(s)$ are now, respectively, the destruction and collision *functions* of the complex Laplace variable $s = \epsilon + i\omega$.

(5) Furthermore, Eq. (6) can be substituted into the Laplace-transformed NZ master equation, Eq. (3), to yield the following expression for the kernel $K(t)$ in Laplace space:

$$\tilde{K}(s) = \Phi(s) - \{s\tilde{G}(s)/[1 + \tilde{G}(s)]\}$$

$$- \{\Phi(s)\tilde{G}(s)/[1 + \tilde{G}(s)]\}. \qquad (7)$$

We next introduce a simple model to define explicitly the functions $\Phi(s)$ and $\tilde{G}(s)$. As this model has been discussed at some length elsewhere,[4] we merely give here, without any further comments, the analytical form of the functions defining the BR model:

$$\Phi(s) = \gamma^2/(s+\alpha), \qquad (8)$$

$$\tilde{G}(s) = \delta^2/(s+\beta)^2, \qquad (9)$$

where $\alpha, \beta, \gamma, \delta$ are constants to be defined subsequently. Equations (8) and (9) are substituted into Eq. (6) which is then Laplace inverted to yield the d.a.f.:

$$\psi(t) = (\mu - \nu)^{-1}(\mu \exp(\nu t)[1 + \delta^2/(\beta+\nu)^2]$$

$$- \nu \exp(\mu t)[1 + \delta^2/(\beta+\mu)^2]$$

$$- \delta \exp(-\beta t)\{[\mu/(\beta+\nu)][\delta/(\beta+\nu) + \delta t]$$

$$- [\nu/(\beta+\mu)][\delta/(\beta+\mu) + \delta t]\}), \qquad (10)$$

with

$$\mu = -\tfrac{1}{2}\alpha\{1 - [1 - (4\gamma^2/\alpha^2)]^{1/2}\}, \qquad (11)$$

$$\nu = -\tfrac{1}{2}\alpha\{1 + [1 - (4\gamma^2/\alpha^2)]^{1/2}\}. \qquad (12)$$

Similarly, the memory function $K(t)$ is obtained from Eqs. (7)–(9); one finds

$$K(t) = [(\beta-\alpha)^2 + \delta^2]^{-1}(\gamma^2(\beta-\alpha)^2 \exp(-\alpha t)$$

$$+ \delta^2 \exp(-\beta t)\{[\gamma^2 - \delta^2 - (\beta-\alpha)^2]\cos(\delta t)$$

$$+ [\delta^{-1}(\beta-\alpha)(\gamma^2+\beta^2-\alpha\beta) + \beta\delta]\sin(\delta t)\}). \qquad (13)$$

Now consider the formal expression for the d.a.f., Eq. (2): this is an even function and its successive moments are therefore

$$\psi^{(n)}(t=0) = c^i, \qquad \text{for } n \text{ even}$$

$$= 0, \qquad \text{for } n \text{ odd.} \qquad (14)$$

Explicitly, we have[11]

$$\frac{d^2\psi}{dt^2}(t=0) = -\frac{\langle[(dM/dt)(0)]^2\rangle}{\langle[M(0)]^2\rangle}, \qquad (15)$$

$$\frac{d^3\psi}{dt^3}(t=0) = 0, \qquad (16)$$

$$\frac{d^4\psi}{dt^4}(t=0) = \frac{\langle[(d^2M/dt^2)(0)]^2\rangle}{\langle[M(0)]^2\rangle}. \qquad (17)$$

Furthermore, the Laplace-transformed d.a.f. at the origin

$$\tilde{\psi}(0) = \int_0^\infty dt \psi(t) \qquad (18)$$

is just the surface defined by the d.a.f. and represents the equivalent of a "diffusion coefficient" in the electric moment space. It is thus a physical constant of the system and can be obtained from *experimental* data.

Now, the model defined above is a four-parameter model: to evaluate these parameters, we have at our disposal four conditional equations, Eqs. (15)–(18), which, when they are considered as such, means essentially that we require the knowledge of the coefficient

$$\lambda = \int_0^\infty dt \psi(t) \qquad (18')$$

and that we have some knowledge of the initial conditions of the system considered, i.e., that we know

$$\langle[(dM/dt)(0)]^2\rangle/\langle[M(0)]^2\rangle = A^2, \qquad (15')$$

$$\langle[(d^2M/dt^2)(0)]^2\rangle/\langle[M(0)]^2\rangle = C^4, \qquad (17')$$

and also that Eq. (16) is satisfied. It is then simply a matter of algebra to evaluate, from Eqs. (10), (15'), (16), (17'), and (18') the parameters $\alpha, \beta, \gamma, \delta$ which appear as the solutions of the following set of equations:

$$\gamma^2 - \delta^2 = A^2, \qquad (15'')$$

$$2\beta\delta^2 - \alpha\gamma^2 = 0, \qquad (16')$$

$$\gamma^2(\alpha^2 - \delta^2) + \delta^2(\delta^2 - 3\beta^2) = C^4, \qquad (17'')$$

$$\gamma^2\beta^2/[\alpha(\beta^2+\delta^2)] = \lambda^{-1} = B. \qquad (18'')$$

The justifying feature of this model as applied to the dipolar system considered in Sec. IV is that the quantities A, B, and C can be evaluated once the system is defined. Before we turn to this application, we first derive some important functions related to the d.a.f. which will be used for the computation displayed in Sec. IV.

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[11] The two first moments are immediate to verify: $\psi(t=0) = 1$, as the d.a.f. is normalized, and $d\psi/dt(t=0) = 0$ follows straightforwardly from Eq. (10).

III. RESPONSE FUNCTION, SUSCEPTIBILITY, AND PERMITTIVITY

We shall make use of the reduced variables t^* and ω^* defined by

$$t^* = t(kT/I)^{1/2}, \tag{19}$$

$$\omega^* = \omega(I/kT)^{1/2}, \tag{20}$$

where I is the moment of inertia and T is the temperature of the system. However, as it is understood that from here on all functions are expressed in terms of the reduced variables, we shall omit the star superscript for the sake of simplicity in the notation.

We consider a spherical, homogeneous, isotropic system; hence the tensor $\psi(t)$, Eq. (2), becomes a scalar, defined by

$$\psi(t) = \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle / \langle [M(0)]^2 \rangle, \tag{21}$$

and the response function $\phi(t)$ reads

$$\phi(t) = -d\psi(t)/dt = -\langle \mathbf{M}(0) \cdot (d\mathbf{M}/dt)(t) \rangle / \langle [M(0)]^2 \rangle. \tag{22}$$

The Fourier transform of the response functions defines the complex susceptibility (apart from a constant factor according to the usual literature)

$$\tilde{\phi}(\omega) = \phi'(\omega) - i\phi''(\omega), \tag{23}$$

with

$$\phi'(\omega) = \int_0^\infty dt\, \phi(t) \cos(\omega t), \tag{24}$$

$$\phi''(\omega) = \int_0^\infty dt\, \phi(t) \sin(\omega t). \tag{25}$$

Indeed, the polarization $P(\omega)$ is related to the electric field $E(\omega)$ through the permittivity $\epsilon(\omega)$ by (for a two-dimensional system[12])

$$2\pi[P(\omega)/E(\omega)] = [\epsilon(\omega)-1]/[\epsilon(\omega)+1] \tag{26}$$

and[13]

$$[\epsilon(\omega)-1]/[\epsilon(\omega)+1] = [(\epsilon_s-1)/(\epsilon_s+1)]\tilde{\phi}(\omega), \tag{27}$$

with ϵ_s the static dielectric constant, and $\epsilon(\omega)$ the complex dielectric function

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega). \tag{28}$$

From Eqs. (23), (27), and (28) one obtains

$$\epsilon'(\omega) = 1 + [2p/(1-p)](Q'/Q), \tag{29}$$

$$\epsilon''(\omega) = [2p/(1-p)](Q''/Q), \tag{30}$$

with

$$Q' = 1 + (1-p)^{-1}\{[\phi'(\omega)/|\phi|^2] - 1\}, \tag{31}$$

$$Q'' = (1-p)^{-1}[\phi''(\omega)/|\phi|^2], \tag{32}$$

$$Q = (Q')^2 + (Q'')^2, \tag{33}$$

[12] H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, England, 1958).
[13] S. H. Glarum, J. Chem. Phys. **33**, 1371 (1960).

and where the constant p is given by the zero-frequency characteristics of the system

$$p = 2\pi(P_0/E_0) = (\epsilon_s-1)/(\epsilon_s+1). \tag{34}$$

These functions can be derived from the d.a.f. as follows: Consider the normalized Fourier transform of the d.a.f.

$$\tilde{\psi}(\omega)/\tilde{\psi}(0) = G(\omega) - iH(\omega), \tag{35}$$

where $G(\omega)$ is simply the normalized power spectrum

$$G(\omega) = \lambda^{-1} \int_0^\infty dt\, \psi(t) \cos(\omega t) \tag{36}$$

and $H(\omega)$ is defined by

$$H(\omega) = \lambda^{-1} \int_0^\infty dt\, \psi(t) \sin(\omega t). \tag{37}$$

It is then easily shown that

$$\phi'(\omega) = 1 - \lambda\omega H(\omega), \tag{38}$$

$$\phi''(\omega) = \lambda\omega G(\omega). \tag{39}$$

All the quantities introduced in this section can thus straightforwardly be computed (either analytically or numerically) from the knowledge of the d.a.f. [we give in the Appendix a similar procedure for the computation of the memory function $K(t)$ from $\psi(t)$].

We conclude this section by displaying the analytical results obtained from the model described in Sec. II.[14] First, we notice that

$$\langle [(dM/dt)(0)]^2 \rangle / \langle [M(0)]^2 \rangle = kT/I; \tag{40}$$

hence the reduction coefficient, according to Eqs. (15'), (19), and (20) will be $(\gamma^2 - \delta^2)^{1/2}$. Furthermore, for the physical system considered in the next section, it was
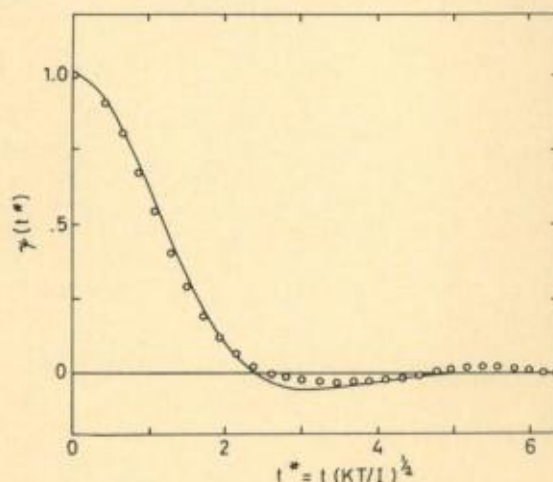

FIG. 1. The dipolar autocorrelation function, Eq. (41) (curve) compared to the experimental data (circles).

[14] We have also performed these calculations and computations for the exponential memory model introduced by Berne, Boon, and Rice (Ref. 5). However, these results will not be displayed in the present article, because we feel that the exponential memory function is less satisfactory than the BR kernel. Furthermore, the computation from the Berne, Boon, and Rice model provides poorer agreement with the experimental data, as compared to the results of Sec. IV.

found that $4\gamma^2 > \alpha^2$, whence we now rewrite the d.a.f., Eq. (10), in terms of the reduced time variable, as

$$\psi(t) = \psi_1(t)\,\exp[-\alpha t/2(\gamma^2-\delta^2)^{1/2}] + \psi_2(t)\,\exp[-\beta t/(\gamma^2-\delta^2)^{1/2}], \tag{41}$$

$$\psi_1(t) = 2I'\cos[\Omega_1 t/(\gamma^2-\delta^2)^{1/2}] + 2I''\sin[\Omega_1 t/(\gamma^2-\delta^2)^{1/2}], \tag{42}$$

$$\psi_2(t) = E + [\Omega_2 t/(\gamma^2-\delta^2)^{1/2}], \tag{43}$$

with

$$I' = \frac{1}{2} + \frac{\delta^2\{[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2 - \Omega_1^2 - [(\beta/\alpha)-\tfrac{1}{2}]\alpha^2\}}{2(\{[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2 - \Omega_1^2\}^2 + 4[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2\Omega_1^2)}, \tag{44}$$

$$I'' = \frac{\alpha}{4\Omega_1} + \frac{\delta^2((\alpha/4\Omega_1)\{[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2 - \Omega_1^2\} + [(\beta/\alpha)-\tfrac{1}{2}]\alpha\Omega_1)}{2(\{[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2 - \Omega_1^2\}^2 + 4[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2\Omega_1^2)}, \tag{45}$$

$$E = \frac{\delta^2\{[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2 - \Omega_1^2 - [(\beta/\alpha)-\tfrac{1}{2}]\alpha^2\}}{2(\{[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2 - \Omega_1^2\}^2 + 4[(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2\Omega_1^2)}, \tag{46}$$

$$\Omega_1 = (\gamma^2 - \tfrac{1}{4}\alpha^2)^{1/2}, \tag{47}$$

$$\Omega_2 = \delta^2\{-[(\beta/\alpha)-\tfrac{1}{2}]\alpha + \tfrac{1}{2}\alpha\}\{(\beta/\alpha)-\tfrac{1}{2}]^2\alpha^2 + \Omega_1^2\}^{-1}. \tag{48}$$

The corresponding response function reads

$$\phi(t) = \phi_1(t)\,\exp[-\alpha t/2(\gamma^2-\delta^2)^{1/2}] + \phi_2(t)\,\exp[-\beta t/(\gamma^2-\delta^2)^{1/2}], \tag{49}$$

$$\phi_1(t) = (\gamma^2-\delta^2)^{-1/2}\{(\alpha I' - 2\Omega_1 I'')\cos[\Omega_1 t/(\gamma^2-\delta^2)^{1/2}] + (\alpha I'' + 2\Omega_1 I')\sin[\Omega_1 t/(\gamma^2-\delta^2)^{1/2}]\}, \tag{50}$$

$$\phi_2(t) = (\gamma^2-\delta^2)^{-1/2}\{E\beta - \Omega_2 + [\beta\Omega_2 t/(\gamma^2-\delta^2)^{1/2}]\}, \tag{51}$$

wherefrom one obtains for the complex susceptibility

$$\phi'(\omega) = D^{-1}[1 - a\omega^2 - b\omega^4 - c\omega^6], \tag{52}$$

$$\phi''(\omega) = (\lambda\omega/D)\{1 - [(\alpha^2 - 2\beta^2 - \gamma^2 + \delta^2)/(\beta^2+\delta^2)][(\gamma^2-\delta^2)/\beta^2]\omega^2\}, \tag{53}$$

with

$$D = [1 - (2-\alpha^2/\gamma^2)(1-\delta^2/\gamma^2)\omega^2 + (1-\delta^2/\gamma^2)^2\omega^4]\{1 + [(\gamma^2-\delta^2)/\beta^2]\omega^2\}^2, \tag{53'}$$

$$a = (1-\delta^2/\gamma^2)\{1 - (2\gamma^2+\delta^2)/\beta^2 + (\delta^2/\gamma^2)[(\alpha^2+4\delta^2)/\beta^2]\}, \tag{54}$$

$$b = (1-\delta^2/\gamma^2)^2[\gamma^2/\beta^2(2-\gamma^2/\beta^2) + (\delta^2/\beta^2)[1 - (\alpha^2-\gamma^2)/\beta^2]\}, \tag{55}$$

$$c = (1-\delta^2/\gamma^2)^4(\gamma^4/\beta^4). \tag{56}$$

Finally, we mention for the sake of completeness, the low frequency and the asymptotic behavior, of the complex susceptibility:

low ω; $\quad \phi'(\omega) = 1 - (1-\delta^2/\gamma^2)\{[4\delta^4 + (\alpha^2-\gamma^2)(\delta^2+\beta^2)]/\gamma^2\beta^2\}\omega^2, \tag{57}$

low ω; $\quad \phi''(\omega) = \lambda\omega, \tag{58}$

high ω; $\quad \phi'(\omega) = -\omega^{-2}, \tag{59}$

high ω; $\quad \phi''(\omega) = (\{\alpha\gamma^2[(\gamma^2-\delta^2) - (\alpha^2-2\beta^2)]\}/(\gamma^2-\delta^2)^{5/2})\omega^{-5}. \tag{60}$

The theoretical model thus reproduces quite well the expected feature that $\phi''(\omega)$, at high frequencies, decreases much faster than $\phi'(\omega)$.

IV. APPLICATION

We consider a two-dimensional system of electric dipoles located at the sites of a rigid lattice, as discussed by Bellemans, Köhler, and Gancberg.[1] The sample is circular and contains 421 dipolar molecules, which rotate in the plane defined by the two-dimensional lattice and are subject to dipole–dipole interaction according to the potential defined by Eq. (1).

Once the system is defined by the above description

(for more details, see Ref. 1), we are in a position to evaluate the quantities which are needed for the computation of the d.a.f. and of the other related functions, as defined in the preceeding sections.

We obtain

$$\langle[(d^2M/dt^2)(0)]^2\rangle/\langle[M(0)]^2\rangle = 3(kT/I)^2$$
$$+ 2\{[M(0)]^4/I^2\}\sum_k r_{1k}^{-4} + \mathcal{O}([M(0)]^6), \tag{61}$$

and[1]

$$p = \pi\rho\langle[M(0)]^2\rangle/kT, \tag{62}$$
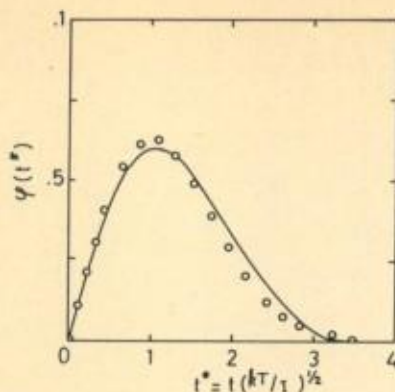
with ρ the number density of the system, and we

FIG. 2. The response function, Eq. (49) (curve) compared to the molecular dynamics results (circles).

evaluate the coefficient λ, Eq. (18′), by graphical integration of the *experimental* d.a.f. Notice that λ is the only quantity which is determined from experiment herein, as there is at present no way to calculate theoretically this coefficient. Whence the quantities A, B, C, Eqs. (15′)–(18′), are known from Eqs. (40), (61), and (62), and the set of conditional equations Eqs. (15′)–(18′) can now be solved for the system considered. One finds (in reduced units)

$$\alpha = 2.34,$$
$$\beta = 2.10,$$
$$\gamma^2 = 3.66,$$
$$\delta^2 = 2.04. \qquad (63)$$

These values of the parameters are substituted into
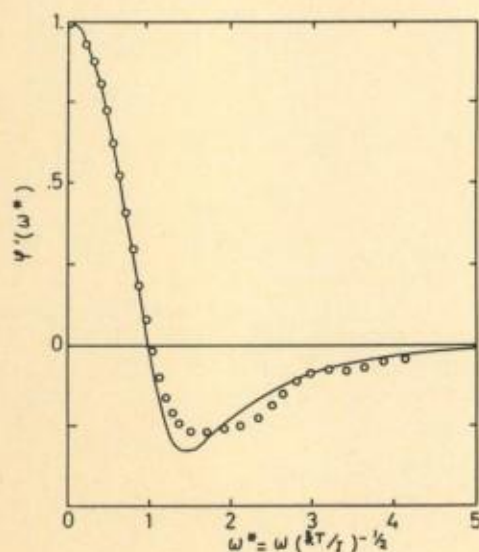

FIG. 3. The real part of the susceptibility, Eq. (52) (curve), compared to the Fourier analysis of the experimental response function (circles).
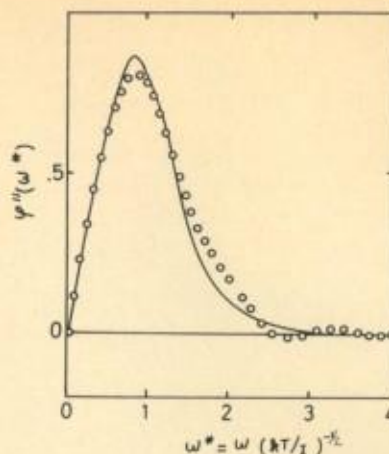

FIG. 4. The imaginary part of the susceptibility, Eq. (53) (curve), compared to the Fourier analysis of the experimental response function (circles).

the expressions of the d.a.f. and related functions (Sec. III) and the results are represented in Fig. 1–4, along with the experimental results of Bellemans, Köhler, and Gancberg.

As seen from Figs. 1 and 2, the agreement between theory and *experiment* is particularly good for the d.a.f and for the response function. That the theory leads to very good prediction in the present case follows essentially from the observation that, for a simple system of weakly coupled electric dipoles, the inertial stage plays an important role which is well accounted for in our theoretical analysis. Indeed—except for the coefficient λ—the parameters, Eqs. (15′)–(18′), are determined theoretically from the initial conditions of the system, namely, from the knowledge of the functions $\psi^{(n)}(0)$, $n = 0$, 2, 4, Eqs. (21), (40), and (61). As pointed out by Bellemans *et al.*,[1] the accuracy of the results from the computer experiment is good for short times ($t^* < 2$) and decreases for longer times: the oscillations which appear almost in every diagram from $t^* \sim 3$ seem to be fairly reliable in sign, although not in magnitude. Furthermore, there was no point in displaying the results for times larger than $t^* \sim 6$ as the
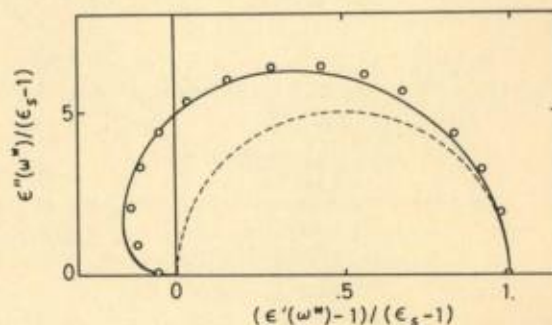

FIG. 5. Cole and Cole diagram, Eqs. (64) and (65) (curve), compared to the molecular dynamics results (circles). The dotted curve represents Debye's semicircle.
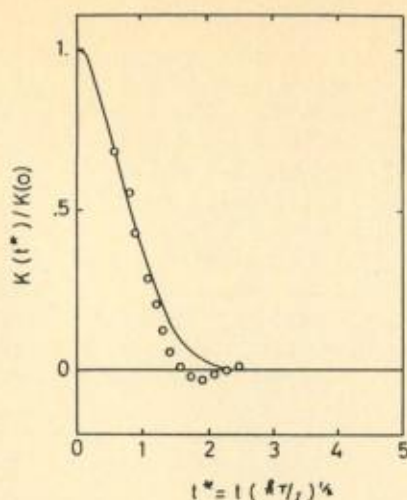
FIG. 6. The memory function, Eq. (13) (curve), compared to the "experimental" memory function obtained from the d.a.f. (circles).

uncertainty renders the data unreliable for long times ($t^* > 6$). This is certainly part of the reason why the results for $\phi'(\omega^*)$ and $\phi''(\omega^*)$, Figs. 3 and 4, present some larger discrepancies between theory and experiment, as the frequency-independent analysis appears to be much more sensitive. It should also be pointed out that the numerical procedure used for the Fourier analysis (Simpson method) is quite obviously partly responsible for oscillations at frequencies larger than $\omega^* \sim 3$.[15]

To represent the dielectric function $\epsilon(\omega)$, we have used the well-known Cole and Cole diagram method,[16] where $\epsilon''(\omega)[\epsilon_s - 1]^{-1}$ is plotted versus $[\epsilon'(\omega) - 1] \times [\epsilon_s - 1]^{-1}$. From Eqs. (29) and (30), it is easily seen that

$$[\epsilon'(\omega) - 1]/(\epsilon_s - 1) = Q'/Q. \tag{64}$$

$$\epsilon''(\omega)/(\epsilon_s - 1) = Q''/Q. \tag{65}$$

The results are presented in Fig. 5. The agreement between theory and experiment is particularly good, although it should be mentioned that the Cole and Cole representation is not extremely sensitive and tends therefore to smooth out the fluctuations observed in the Fourier analysis of the response function. Moreover, despite this fact our results are far off the Debye semicircle, which is obtained from the Brownian-motion approach to dielectric relaxation.[17] Our results agree

quite well in this sense (at least qualitatively[18]) with the theoretical analysis of Kestemont,[3] based on the theory of irreversible processes developed by Prigogine and co-workers.[9]

ACKNOWLEDGMENTS

APPENDIX

The memory function, namely, the kernel of the master equation, Eq. (3), can be formally derived from the knowledge of the a.f. by the following procedure.

We first introduce a new function $\mathcal{K}(\omega)$ [19] defined by

$$\mathcal{K}(\omega) = \omega^{-1} H(\omega), \tag{A1}$$

where $H(\omega)$ is given by Eq. (37); and we Fourier transform the kernel $K(t)$ as

$$\tilde{K}(\omega) = K'(\omega) + iK''(\omega), \tag{A2}$$

where $K'(\omega)$ and $K''(\omega)$ are easily related to $G(\omega)$ and $H(\omega)$, Eqs. (36) and (37), by Fourier transformation of the master equation, Eq. (3). One finds

$$K'(\omega)/\tilde{K}(0) = G(\omega)/\{[G(\omega)]^2 + [H(\omega)]^2\}, \tag{A3}$$

$$K''(\omega)/\tilde{K}(0) = (H(\omega)/\{[G(\omega)]^2 + [H(\omega)]^2\}) - \lambda\omega, \tag{A4}$$

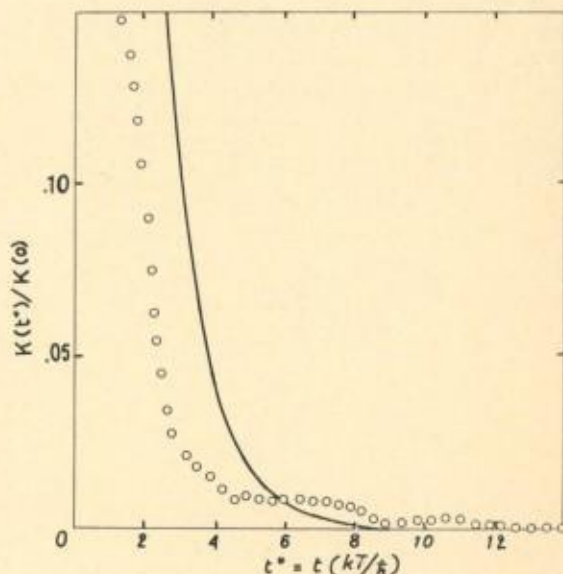where λ is defined by Eq. (18').

FIG. 7. The linear momentum memory function (curve), for liquid argon compared to the memory function obtained from Rahman's computer experiment (circles).

[15] As a test for this feature, we have performed a numerical Fourier analysis on the analytical functions and obtained oscillations which, when smoothed out by an envelope curve, coincide reasonably well with the analytical results.

[16] K. S. Cole and R. M. Cole, J. Chem. Phys. 9, 347 (1941).

[17] P. Debye, *Polar Molecules* (Dover Publications, Inc., New York, 1945).

[18] A more detailed analysis and quantitative comparison will be given in a forthcoming paper by E. Kestemont and A. Bellemans.

[19] We use the reduced variables defined by Eqs. (19) and (20) and normalize all the functions in what follows.

Then, by applying a theorem of complex variable analysis,[20] it is easily found that

$$K(t)/K(0) = I + II,$$ (A5)

$$I = \pi^{-1} \int_0^\infty d\omega \frac{1}{\lambda} \frac{G(\omega)}{[G(\omega)]^2 + [H(\omega)]^2} \cos(\omega t),$$ (A6)

$$II = \pi^{-1} \frac{d}{dt} \int_0^\infty d\omega \left(\frac{1}{\lambda} \frac{\mathfrak{IC}(\omega)}{[G(\omega)]^2 + [H(\omega)]^2} - 1 \right) \cos(\omega t).$$ (A7)

[The reason for introducing the function $\mathfrak{IC}(\omega)$, Eq. (A1), is the time derivative appearing in Eq. (A7), which permits us to eliminate the Fourier sine transform, a difficult function to handle in numerical analysis.]

As a test of internal consistency, we have derived from the molecular dynamics d.a.f. the experimental memory function by numerical analysis, according to the scheme presented above, and have compared this result with the model memory function of Sec. II.

The comparison is illustrated in Fig. 6. Although the agreement between the theoretical and the experimental kernels appears to be fairly poor, (especially because the experimental function seems to present oscillations, while the theoretical curve decays monotonically), it may be considered as satisfactory, when account is taken of the large uncertainty affecting this complicated numerical analysis. In particular, it is quite difficult to certify whether the oscillations really do exist or whether they should be ascribed to the numerical analysis.

The only positive conclusion that could be drawn from the preceding comparison is that the theoretical kernel overestimates somewhat the memory effects. However, this is probably a small effect, as very good agreement is obtained for the d.a.f. and related functions (Figs. 1–5).

The same feature was observed for the linear momentum memory function as computed for liquid argon

at 94.4°K. We performed a similar numerical analysis to derive the kernel from Rahman's experimental a.f.[6] The result is shown in Fig. 7 along with the BR model kernel.[4] Some fluctuations do appear in the *experimental* memory function around the "plateau" in the range $4 \lesssim t^* \lesssim 10$ (corresponding to values of t comprised between $t \simeq 0.3 \times 10^{-12}$ sec—for which the a.f. reaches the value zero for the first time—and $t \simeq 10^{-12}$ sec) but the function never becomes negative in this case. Here also the "theoretical kernel" is somewhat larger than the experimental, apart from the longer tail (plateau) obtained from molecular dynamics.

Our numerical analysis of Rahman's memory function is in agreement with the comments made in a recent article by Damle, Sjölander, and Singwi[21]: $K(t)$ drops to about 2% of its initial value after a duration of about 3×10^{-13} sec, after which a plateau value of about 1%–2% is maintained for about 10^{-12} sec and then gradually drops to zero.

Finally, a few comments should be made concerning the relative contributions of the destruction and collision terms appearing in the memory function, Eq. (7).

Rewriting Eq. (7) as

$$K(t) = K_C(t) + K_D(t) + K_{CD}(t),$$ (A8)

where the subscripts C and D refer to the collision and destruction functions, respectively, we find for the dipolar system considered in Sec. IV

$$|K_D{}^{max}/K_C{}^{max}| \cong 50\%,$$ (A9)

while for the case of liquid argon, this ratio is about 25%. Furthermore, it was found for liquid argon[4] that the destruction term contributes nothing ($\lesssim 1\%$) after the a.f. has reached the value zero for the first time, while we conclude, for the system of electric dipoles studied in the present article, that at the corresponding value of the time variable (i.e., for which the d.a.f.=0 for the first time), the collision and destruction functions contributions are equivalent ($\sim 7\%$). Both functions then decay together gradually to zero.

[20] See, e.g., R. V. Churchill, *Operational Mathematics* (McGraw-Hill Book Co., New York, 1958), Chap. 6.

[21] P. S. Damle, A. Sjölander, and K. S. Singwi, Phys. Rev. **165**, 277 (1968).