

Rotational Relaxation of Solute Molecules in Dense Noble Gases and the Relation with Local Anisotropy Fluctuations

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Many molecular relaxation processes in fluids are sensitive to the time-dependence of local, anisotropic density fluctuations. The role played by anisotropic density fluctuations in the rotational relaxation of a linear, quantized rotor will be discussed in some detail. An expression for the dipole-correlation function of a probe molecule, dissolved in a simple fluid, will be derived along these lines. This expression will be shown to account for the experimentally observed density-dependence of the rotational linewidths of HCl in argon. Some simple models for anisotropic density fluctuations or, more precisely, for the four-point density-correlation functions, will be discussed.

Many different techniques can be used for the investigation of molecular relaxation processes. All these techniques provide us with macroscopic measurements; hence the information which one may obtain from such measurements, although commonly interpreted in terms of microscopic motions in the fluid, is statistically averaged. Which statistically averaged property of the fluid one thus may obtain depends on the specific type of experiment. For instance, inelastic neutron-scattering in simple fluids yields information on the dynamic pair-correlation function of the fluid, whereas a phenomenon like collision-induced light-scattering probes the much more complicated time-dependent four-point density correlation function. In fact, any microscopic process that is sensitive to the local, anisotropic density fluctuations in the fluid is related to this latter correlation function. In particular, the rotational relaxation of a probe molecule in a simple fluid depends on a density-correlation function of this type. A common feature in the description of these relaxation processes is that, at a certain stage, one needs to know the correlation function of a dynamical variable in terms of its dependence on the separation between two particles; for instance the collision-induced dipole in collision-induced dipolar absorption, or the anisotropic potential acting on a probe molecule in the rotational relaxation process to be described below. Assuming this dynamical variable to be pairwise additive, it is possible to relate the time dependent four-point density correlation function, $f(r_1, r_2; r_3, r_4; t)$ with the process under consideration. The experimental data depend only functionally on $f(r_1, r_2; r_3, r_4; t)$, and this latter function cannot be obtained uniquely from the data. However, different experiments often do yield complementary information about the four-point density correlation function. In particular, depending on the type of experiment, parts of $f(r_1, r_2; r_3, r_4; t)$ with different irreducible tensorial character may be probed.

One may, therefore, construct models for the four-point density correlation function which, if satisfactory, should give good agreement with a number of experiments at a time. Although simple models for $f(r_1, r_2; r_3, r_4; t)$ (and related correlation functions) have been constructed,^{1,2} no attempt has been made, at least to

our knowledge, to combine information from different experiments in order to discriminate between different models. Such tests are badly needed, as our knowledge of time-dependent higher-order density correlation functions is very limited, to say the least. Even molecular dynamics calculations have been of little help, mainly because tabulating, let alone displaying, a four-point correlation function is hardly feasible.

In the following section we will investigate in some detail the rotational relaxation of a quantized, linear rotor as an illustration of the role of higher order distribution functions in phenomena that are sensitive to the local anisotropy in the fluid. The discussion of other phenomena that depend on local anisotropy in fluids is quite similar.

THEORETICAL DESCRIPTION

In this section we will indicate how the shape of the far-infrared absorption spectrum of a linear probe molecule in a simple fluid may be related to the anisotropic density fluctuations in the host fluid around the probe.

The interaction energy between a linear probe molecule and a perturbing atom at a distance r , may quite generally be written as,

$$V(I_\mu) = \sum_{l=0}^{\infty} v_l(r) P_l(I_r \cdot I_\mu) \quad (1)$$

where $v_l(r)$ gives the r -dependence of that part of the molecule perturber potential that transforms as the l -th Legendre polynomial; I_r is the unit vector in the direction of the line joining the centres of mass of the molecule and the perturber; I_μ is the unit vector along the molecular axis. If more than one atom at a time is perturbing the molecule, the total interaction energy may (using the spherical harmonics addition theorem)³ be written as,

$$V(I_\mu) = \sum_{i=1}^N \sum_{l=0}^{\infty} v_l(r_i) [4\pi/(2l+1)] \sum_{m=-l}^l Y_{lm}^*(I_{r_i}) Y_{lm}(I_\mu) \quad (2)$$

where the pairwise additivity of intermolecular interactions has been assumed. In eqn (2), r_i denotes the coordinate of the i -th perturbing atom; the origin of the coordinate system is fixed on the centre of mass of the probe molecule. Writing the number density at a distance r from the probe as $\rho(r) = \sum_{i=1}^N \delta(r - r_i)$ the above equation may be re-written as,

$$V(I_\mu) = \sum_{l=0}^{\infty} (4\pi/[2l+1]) \sum_{m=-l}^l Y_{lm}(I_\mu) \int dr \rho(r) v_l(r) Y_{lm}^*(I_r). \quad (3)$$

Now, if one assumes that the translational motions in the fluid are not sensitive to the orientation of the dissolved molecule, the perturbation acting on the probe molecule has the character of a time-dependent, external perturbation:

$$V(I_\mu; t) = \sum_{l=0}^{\infty} [4\pi/(2l+1)] \sum_{m=-l}^l a_{lm}(t) Y_{lm}(I_\mu) \quad (4)$$

where $a_{lm}(t)$ is defined by:

$$a_{lm}(t) = \int dr \rho(r; t) v_l(r) Y_{lm}^*(I_r). \quad (5)$$

The time-dependence of the perturbation is obviously determined by the local density fluctuations around the probe; the symmetry and range of the intermolecular potential determines which type of density fluctuation couples most effectively with the rotational motion. Clearly, as the molecule is assumed to be subject to an external, time dependent perturbation, the transitions induced in the probe through coupling with the density fluctuations will not obey detailed balance; in particular, the perturbation tends to heat the probe. In calculating the dipole correlation function of the probe molecule, we will simply neglect this undesirable effect on the density matrix, by assuming that the density matrix is still equal to the density matrix of the unperturbed rotor. Depending on the physical situation, other approaches may be, and in fact have been taken.⁴

The dipole correlation function $\langle \mu(0) \cdot \mu(t) \rangle = \text{Tr}[\rho \mu \cdot U^+(t) \mu U(t)]$ may be approximated by an expansion and partial resummation of the expression for the averaged operator product. The explicit expression for the dipole correlation function of the probe molecule then becomes:

$$\langle \mu(0) \cdot \mu(t) \rangle = \sum_{J_i, J_f} P_{J_i} \langle J_i || \mu || J_f \rangle \exp(i\omega_{J_f J_i} t) \exp[-\gamma_{J_f J_i}(t)] \quad (6)$$

where P_{J_i} is the probability of finding a molecule with total angular momentum J_i , $\langle J_i || \mu || J_f \rangle$ is the reduced matrix element of the dipole-moment operator between states with total angular momentum J_i and J_f ,⁵ and $\gamma_{J_f J_i}(t)$ is a function that depends on the correlation function of the perturbation acting on the probe molecule:

$$\begin{aligned} \gamma_{J_f J_i}(t) = & \hbar^{-2} \sum_{l=0}^{\infty} (2l+1)^{-1} \int_0^t \int_0^{t''} g_l(t' - t'') \left[\begin{pmatrix} J_f & l & J_f \\ 0 & 0 & 0 \end{pmatrix}^2 (2j_f + 1) + \right. \\ & \left. \begin{pmatrix} J_i & l & J_i \\ 0 & 0 & 0 \end{pmatrix}^2 (2j_i + 1) + 2 \begin{Bmatrix} J_i & J_f & l \\ J_f & J_i & l \end{Bmatrix} \begin{pmatrix} J_i & l & J_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J_f & l & J_f \\ 0 & 0 & 0 \end{pmatrix} (2j_i + 1)(2j_f + 1) \right] dt' dt'' + \quad (7) \\ & \hbar^{-2} \sum_{l=0}^{\infty} (2l+1)^{-1} \int_0^t \int_0^{t''} g_l(t' - t'') \left[\sum_{J' \neq J_f} e^{i\omega_{J' J_f}(t' - t'')} (2j_f + 1) \begin{pmatrix} J_f & l & J_f \\ 0 & 0 & 0 \end{pmatrix}^2 + \right. \\ & \left. \sum_{J' \neq J_i} e^{i\omega_{J' J_i}(t' - t'')} (2j_i + 1) \begin{pmatrix} J_i & l & J_i \\ 0 & 0 & 0 \end{pmatrix}^2 \right] dt' dt''. \end{aligned}$$

Apart from the 3- and 6- J symbols³ appearing in this expression, $\gamma_{J_f J_i}(t)$ is only determined by the correlation functions $g_l(t)$, defined by:

$$\begin{aligned} g_l(t) = & [4\pi/(2l+1)] \sum_{m=-l}^l \langle a_{lm}(0) a_{lm}(t) \rangle \quad (8) \\ = & \iint d\mathbf{r} d\mathbf{r}' \langle \rho(\mathbf{r}, 0) \rho(\mathbf{r}'; t) \rangle v_l(\mathbf{r}) v_l(\mathbf{r}') P_l(\mathbf{I}_r \cdot \mathbf{I}_{r'}). \end{aligned}$$

The central quantity appearing in this expression is the density correlation function $\langle \rho(\mathbf{r}; 0) \rho(\mathbf{r}'; t) \rangle$. As this latter function is determined by the probability of finding a particle at distance r from the probe at time 0 and a particle at distance r' at time t , it is determined by the four-point density correlation function $f(\mathbf{r}_p, \mathbf{r}_p + \mathbf{r}; \mathbf{r}'_p, \mathbf{r}'_p + \mathbf{r}'; t)$ where \mathbf{r}_p and \mathbf{r}'_p denote the coordinates of the probe at time 0 and t respectively. Integrating over \mathbf{r}_p and \mathbf{r}'_p in the four-point correlation function, yields the function $\langle \rho(\mathbf{r}; 0) \rho(\mathbf{r}'; t) \rangle$ used above. The Legendre polynomials $P_l(\mathbf{I}_r \cdot \mathbf{I}_{r'})$ determine which symmetry components of the density fluctuations around the probe contribute to the rotational relaxation. The distance over which anisotropic density fluctuations

are felt by the probe molecule, depends on the range of $v_l(r)$. For long times $\exp[-\gamma_{J_f J_i}(t)]$ reduces to $\exp(-\Gamma_{J_f J_i} t)$ with

$$\begin{aligned} \Gamma_{J_f J_i} = & h^{-2} \sum_{l=0}^{\infty} (2l+1)^{-1} G_l(0) \left[\begin{pmatrix} J_f & l & J_f \\ 0 & 0 & 0 \end{pmatrix}^2 (2J_f+1) + \begin{pmatrix} J_i & l & J_i \\ 0 & 0 & 0 \end{pmatrix}^2 (2J_i+1) \right. \\ & \left. + 2 \begin{pmatrix} J_i & J_f & l \\ J_f & J_i & l \end{pmatrix} \begin{pmatrix} J_i & l & J_i \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J_f & l & J_f \\ 0 & 0 & 0 \end{pmatrix} (2J_i+1)(2J_f+1) \right] \\ & + h^{-2} \sum_{l=0}^{\infty} (2l+1)^{-1} \left[\sum_{J' \neq J_f} G_l(\omega_{J_f J'}) (2J'+1) \begin{pmatrix} J_f & l & J' \\ 0 & 0 & 0 \end{pmatrix}^2 + \sum_{J' \neq J_i} G_l(\omega_{J_i J'}) (2J'+1) \right. \\ & \left. \begin{pmatrix} J_i & l & J' \\ 0 & 0 & 0 \end{pmatrix}^2 \right] \end{aligned} \quad (9)$$

where $G_l(\omega)$ is the Fourier-Laplace transform of $g_l(t)$

$$G_l(\omega) = \int_0^{\infty} e^{-i\omega t} g_l(t) dt. \quad (10)$$

If all $g_l(t)$ are rapidly decaying functions of time (compared with the decay time of the dipole correlation function), one may replace $\exp[-\gamma_{J_f J_i}(t)]$ by $\exp(-\Gamma_{J_f J_i} t)$ for all times. The power spectrum of the molecular dipole moment then reduces to a sum of Lorentzians with width $\Delta\nu_{\pm} = \text{Re} \Gamma_{J_f J_i}$ and shift $\Delta\nu_{\pm} = \text{Im} \Gamma_{J_f J_i}$. Eqn (9) indicates that there is a linear relation between the width and shift of all rotational lines and the Fourier-Laplace transform of the correlation function of the perturbing potential acting on the probe molecule.

The widths and shifts only depend on the value of $G_l(\omega)$ calculated at frequencies corresponding to level spacings in the unperturbed rotor (including $\omega = 0$). Intuitively this relation may be understood by noting that $\text{Re} G_l(\omega)$ is the power spectrum of the l -th perturbing potential. Simple first order perturbation theory would predict that the rate at which transitions occur from states J to J' is proportional to $G_l(\omega_{J J'})$. If only the first one or two terms in the Legendre polynomial expansion of the molecule-perturber potential contribute to the rotational relaxation, it is possible to obtain the corresponding frequency components, $G_l(\omega)$, directly by inverting the set of linear eqn (9). The most interesting dynamical information may be obtained by using a probe molecule having rotational transitions throughout the frequency region characteristic for molecular motions.

Rotational Raman line broadening may be analyzed in much the same way; comparison of the data obtained from far-infrared- and Raman-rotational line broadening of the same system would constitute a nice check on the method.

At this stage it is useful to give the relation between local density fluctuations and a number of other relaxation processes, as it shows how different experiments probe the density fluctuations over a different range. For collision-induced dipolar absorption of a dilute solution of one noble gas in another, the dipole correlation function may be written as

$$\langle \mu(0) \cdot \mu(t) \rangle = \int \int d\mathbf{r} d\mathbf{r}' \langle \rho(\mathbf{r}; 0) \rho(\mathbf{r}'; t) \rangle \mu(\mathbf{r}) \mu(\mathbf{r}') P_1(I_r \cdot I_{r'}) \quad (11)$$

where $\rho(\mathbf{r}; t)$ denotes the density at distance \mathbf{r} from the dissolved atom; implicit is the assumption that collision-induced dipoles are pairwise additive. Collision-induced dipolar absorption gives information about the very short range density fluctuations, as the collision-induced dipole decays to a good approximation exponen-

tially, with a characteristic length that is typically 0.1 times the Lennard-Jones diameter.

Collision-induced depolarized light scattering occurs even in a pure fluid. The density correlation function that governs collision-induced light scattering is related to that four-point density correlation function which gives the probability of finding a pair of particles at r_0 and $r_0 + r$ at time 0 and a pair (possibly the same) at r'_0 and $r'_0 + r'$ at time t , $f'(r_0; r_0 + r; r'_0; r'_0 + r'; t)$. Averaging over r_0 and r'_0 gives the density correlation function $\langle \rho'(r; 0) \rho'(r'; t) \rangle$ which, in contrast to the one defined before does not only contain information on the time-correlation of density fluctuations around a given particle, but also on the correlation of fluctuations around different particles. The relevant correlation function for collision-induced light-scattering is:

$$\int \int dr dr' \langle \rho'(r; 0) \rho'(r'; t) \rangle f(r) f(r') P_2(I_r \cdot I_{r'})$$

where $f(r)$ describes the r -dependence of the collision-induced anisotropic polarizability. For not-too-short distances this r -dependence is of course simply r^{-3} . Clearly this is a much slower r -dependence than the one which determines collision-induced dipolar absorption. The long range part of the anisotropic potential between a linear molecule and a solvent atom is typically dominated by an r^{-6} or r^{-7} term. Rotational relaxation measurements, therefore, probe density fluctuations over a range intermediate between the cases just mentioned. Very similar, be it static, information is contained in the r -dependence of $g(r)$ through the relation⁶

$$-\rho kT \frac{\partial}{\partial r} g(r) = \rho g(r) \frac{\partial v_0(r)}{\partial r} + \int \frac{\partial v_0(r)}{\partial r} \langle \rho(r; 0) \rho(r; 0) \rangle P_1(I_r \cdot I_r) dr. \quad (12)$$

Finally, the isothermal pressure derivative of the van Hove self-correlation function, that may be obtained from inelastic neutron scattering, may also be expressed in terms of the four-point density correlation function.⁷

RESULTS AND DISCUSSION

Having indicated in what way rotational relaxation measurements are related to the local fluctuations in a fluid, we now show how the description outlined above may be used to give a qualitative explanation of the density dependence of the width and shift of the far-infrared rotational lines of HCl, dissolved as a probe molecule in argon. The far-infrared spectrum of HCl in Ar has been measured by Frenkel *et al.*⁸ for argon densities between 100 and 480 Amagat at $T = 162.5$ K. It is observed that, although the spectrum may be described by a sum of Lorentzians up to the highest density, the density dependence of the different linewidths is distinctly non-linear and, moreover, different for different lines. This effect is in striking contrast with what is usually observed in dilute gas systems. It demonstrates the need for an approach that takes fully into account the dynamic particulars of higher density systems.

To compute the rotational line-widths, one needs to know the correlation functions of the different irreducible parts of the perturbing potential, $g_l(t)$. These correlation functions depend on the shape of $v_l(r)$ and, of course, on the dynamics of the medium. As there hardly exists any *a priori* knowledge of the correlation functions $g_l(t)$, we undertook a molecular dynamics (M.D.) study to compute $g_l(t)$ for $l = 1$ and $l = 2$.⁹ The M.D. calculations were done, using the Lennard-Jones parameters $\epsilon/k = 119.5$ K

and $\sigma = 3.405 \text{ \AA}$ for argon. As the mass of HCl and the Lennard-Jones σ of the HCl-Ar potential are rather close to the corresponding argon values, HCl was replaced in the computation by argon, in order to improve the statistics of the M.D. calculation. For simplicity $v_1(r)$ and $v_2(r)$ were assumed to have the same r -dependence as $v_0(r)$; the strength of the anisotropic potential was used as an adjustable parameter. Fig. 1 to 4 show the correlation functions $g_1(t)$ and $g_2(t)$ and their Fourier transforms at

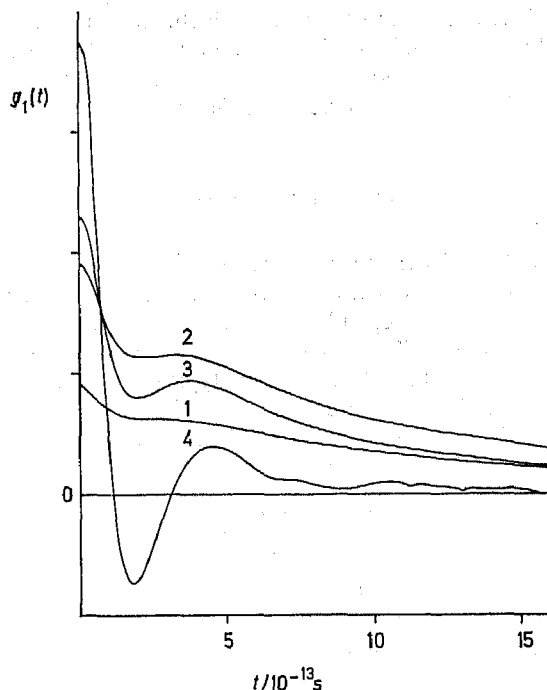


FIG. 1.—The correlation function of the part of the anisotropic perturbation that transforms as an irreducible tensor of rank one. The correlation functions were computed for argon densities of 100(1), 300(2), 500(3) and 784(4) Amagat at $T = 160 \text{ K}$. All functions are drawn to the same, arbitrary scale.

densities between 100 and 784 Amagat. From these data the linewidths of a number of rotational lines of HCl in argon were calculated. In table 1 these computed widths are compared with the experimental values. The computed linewidths clearly reproduce the non-linear density dependence that is observed experimentally. The consideration of the simultaneous perturbation by many particles seems, therefore, to be a fruitful approach. Unfortunately, the method is restricted to systems of which information about the many-particle dynamics is known, inferred from M.D. calculations or otherwise.

It is of course of considerable interest to compare the dynamics of local density fluctuations in different fluid systems. One simple way to extrapolate the results of the M.D. calculations to other fluids would be to scale the results of the computations to the mass and L.J. parameters of the fluid under consideration. Such an extrapolation would, however, also require the mass and L.J. parameters of the probe to be scaled in the same ratio, which is physically quite unrealistic. Indeed, simple scaling of the argon results to krypton and xenon does not seem to reproduce the experimentally observed increase in rotational structure of the dissolved HCl with

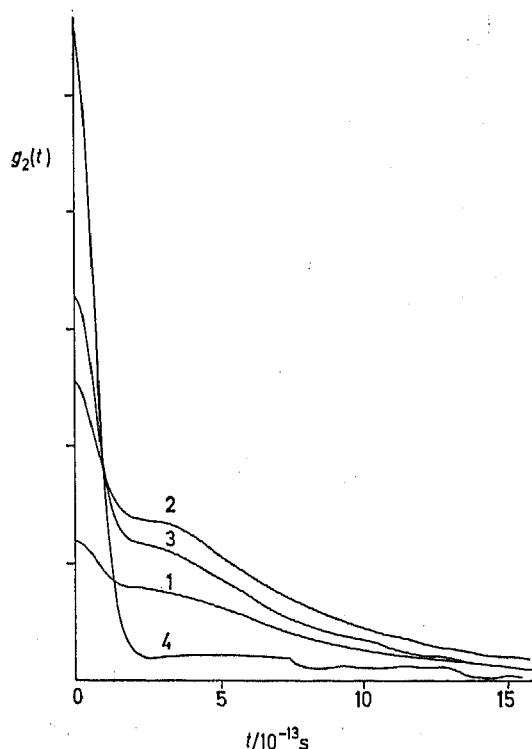


FIG. 2.—The correlation function of the part of the anisotropic perturbation that transforms as an irreducible tensor of rank two. The correlation functions were computed for argon densities of 100(1), 300(2), 500(3) and 784(4) Amagat at $T = 160$ K. All functions are drawn to the same, arbitrary scale.

the mass of the solvent noble gas atoms.¹⁰ This indicates, not surprisingly, that the ratios of mass and size of the probe to the mass and size of the solvent atoms plays an important role in determining the dynamics of the solvent around the probe. A second important point to note is that, if one is studying molecular fluids, it is not just the translational motion but also the internal motion (rotation) of the solvent molecules that modulates local density fluctuations. For instance, the L-J parameters and mass of SF_6 and CCl_4 are quite close, yet HCl dissolved in the former liquid does show rotational fine structure in the far-infrared absorption spectrum¹¹ whereas dissolved in the latter, surrounded by clearly less spherical molecules, it does not.¹²

To get some physical insight into the factors which determine local density fluctuations in simple fluids, we now discuss a few simple models that describe limiting cases of the microscopic dynamics of the fluid. Simplest is of course the very dilute gas. In the dilute gas, only binary encounters contribute to the local density fluctuations. The correlation functions $g_i(t)$ are, therefore, only dependent on the dynamics of a pair of particles during an encounter. In lowest order, increasing the density only increases the number of encounters, thereby affecting the magnitude of $g_i(t)$ but not its shape. As can be seen from fig. 1 and 2, increasing the "argon" density in the M.D. experiment from 100 to 300 Amagat, clearly changes the shape of $g_1(t)$ and $g_2(t)$, thus indicating that ternary and higher order encounters

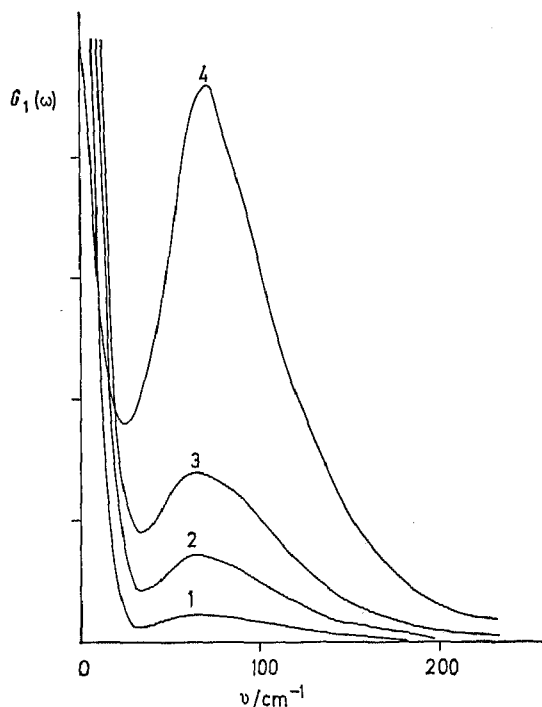


FIG. 3.—The Fourier transform of $g_i(t)$ at $T = 160$ K as a function of the argon density. The functions $G_i(\omega)$, for 100(1), 300(2), 500(3) and 784(4) Amagat, are all drawn to the same, arbitrary scale.

become important. (A correlation in density fluctuations during successive encounters is actually present even in the dilute gas, giving rise to the well-known intercollisional interference dip in collision-induced dipolar absorption,¹³ but this effect only adds a small, be it slowly decaying, part to the relevant correlation functions). A suitable model, for the high density limit, is the ideal, harmonic solid. Density fluctuations around a given point in a solid may be analysed in terms of phonons. For simplicity, we assume the solid to be an elastic continuum. Although the probe molecule takes part in the collective motions of the solid, we neglect this aspect of the problem and assume the probe to be fixed. Using the expansion of a plane wave in spherical waves,³ it may be shown that the Fourier-transform of $g_i(t)$ is proportional to $D(\omega)V_i^2(\omega)$ where $D(\omega)$ is the density of states of longitudinal phonons, and $V_i^2(\omega)$ is defined by:

$$V_i^2(\omega) = \int V_i^2(k)\delta[\omega - \omega(k)] dk / \int \delta[\omega - \omega(k)] dk \quad (13)$$

where

$$V_i(k) = \int_a^\infty v_i(r)j_i(kr)4\pi r^2 dr. \quad (14)$$

$j_i(kr)$ is the i -th spherical Bessel function, $v_i(r)$ is the r -dependent part of the anisotropic potential and a is the radius of the probe molecule. It is important to note that this (oversimplified) model indicates that the power spectrum of the anisotropic

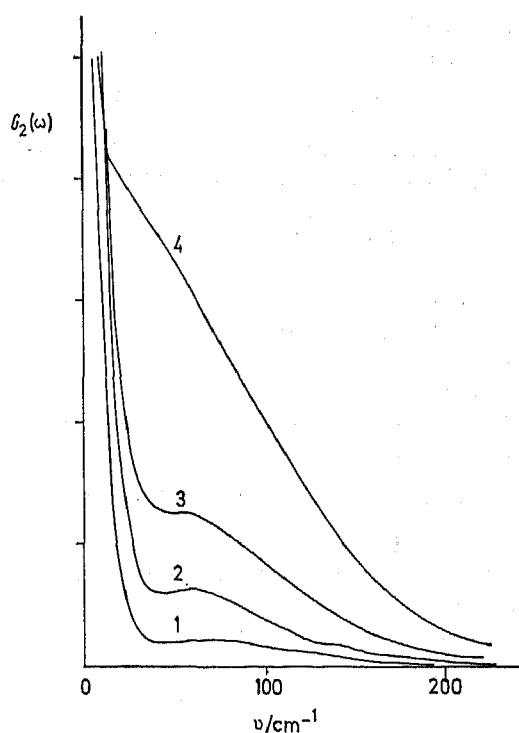


FIG. 4.—The Fourier transform of $g_2(t)$ at $T = 160$ K as a function of the argon density. The functions $G_2(\omega)$, for 100(1), 300(2), 500(3) and 784(4) Amagat, are all drawn to the same, arbitrary scale.

TABLE 1.—DENSITY DEPENDENCE OF ROTATIONAL LINEWIDTHS OF HCl IN ARGON

initial J	$\Delta\nu_{1/2}/\text{cm}^{-1}$					
	$\rho = 100$ Amagat		$\rho = 300$ Amagat		$\rho = 480$ Amagat	
	exp.	calc.	exp.	calc.	exp.	calc.
$J = 4$	2.66 ± 0.1	3.31	7.51 ± 0.24	7.51	12.0 ± 1.8	12.01
$J = 5$	2.09 ± 0.22	2.28	5.67 ± 0.37	5.20	8.01 ± 0.24	7.81
$J = 6$	1.65 ± 0.16	1.54	3.91 ± 0.24	3.66	5.58 ± 0.3	5.04
$J = 7$	1.21 ± 0.19	1.09	2.46 ± 0.36	2.41	3.23 ± 0.16	3.36
$J = 8$	0.87 ± 0.06	0.76	1.54 ± 0.32	1.55	1.88 ± 0.17	2.36

potential is proportional to the frequency-distribution of the solvent. It is tempting to consider the strong increase with density of $g_1(\omega)$ in the frequency range between 30 and 100 cm^{-1} as a reflection of the fact that, in the dense fluid, propagating modes in this frequency range start to appear. If the fluid were an elastic continuum $D(\omega)$ and therefore $g_1(\omega)$ would be zero at $\omega = 0$; the fact that the computed $g_1(\omega)$ are clearly distinct from zero at $\omega = 0$ is an indication that the collective excitations that are responsible for local density fluctuations, have a finite lifetime.

The picture given above may be extended in such a way that it does take the decay of density fluctuations into account. Instead of assuming that the auto-

correlation function of a density fluctuation with wave-vector \mathbf{k} is simply $\exp[-i\omega(\mathbf{k})t]$, one may get a more realistic picture by putting

$$N^{-1} \langle \rho_{-\mathbf{k}}(0) \rho_{\mathbf{k}}(t) \rangle = I(\mathbf{k}, t) \quad (15)$$

where $I(\mathbf{k}, t)$ is the intermediate scattering function; this latter function may be obtained experimentally from inelastic neutron scattering. One then obtains:

$$g_i(\omega) \sim \int S(\mathbf{k}, \omega) V_i^2(\mathbf{k}) k^2 d\mathbf{k}. \quad (16)$$

Although the simple models described above give a qualitative insight into the factors that influence local density fluctuations in a fluid, they are very crude and only suitable to make order-of-magnitude estimates. More sophisticated models are needed to describe local anisotropy in a fluid in a realistic way. One interesting possibility would be to make an approximation for the four-point correlation function similar to the superposition approximation for g_3

$$f(\mathbf{r}_P; \mathbf{r}_P + \mathbf{r}; \mathbf{r}'_P; \mathbf{r}'_P + \mathbf{r}'; t) = \rho g(\mathbf{r}) g(\mathbf{r}') G_s(\mathbf{r}'_P - \mathbf{r}_P; t) G(\mathbf{r}' - \mathbf{r}; t). \quad (17)$$

Such an approximation may be tested directly through a molecular dynamics simulation. The attractive feature of this approximation is that it yields expressions for all the relevant correlation functions described above, without adjustable parameters. For instance, in this approximation $g_i(t)$ may be written as,

$$g_i(t) = \rho \int v_i^2(\mathbf{k}) I_s(\mathbf{k}, t) I(\mathbf{k}, t) 4\pi k^2 d\mathbf{k} \quad (18)$$

where

$$v_i(\mathbf{k}) = \int_0^\infty g(\mathbf{r}) v_i(\mathbf{r}) j_i(kr) 4\pi r^2 d\mathbf{r}; \quad (19)$$

where $I_s(\mathbf{k}, t)$ is the self-part of the intermediate scattering function. In the correlation functions for collision induced light scattering $I_s(\mathbf{k}, t)$ is replaced by $I(\mathbf{k}, t)$. The correlation function for collision induced light scattering should always be positive in this approximation, as the integrand is always positive. M.D. calculations by Alder, Strauss and Weiss do indeed show this behaviour.¹⁴

However, possible deviations from this approximation are in fact most interesting, as they would indicate that the study of time-dependent anisotropic density fluctuations does yield new information that is not contained in the dynamic pair correlation functions.

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⁵ The reduced matrix element $\langle J|T(k)|J' \rangle$ used in the text, is defined by $\langle Jm|T(kq)|J'm' \rangle =$

$$(-1)^{J-m} \begin{pmatrix} J & k & J' \\ -m & q & m' \end{pmatrix} \langle J||T(k)||J' \rangle (2J+1)^{\frac{1}{2}}.$$

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