mechanism in which otherwise unspecified defects cause complete loss of correlation whenever one reaches a molecular site. By assuming that the motion of these defects has the nature of one-dimensional diffusion with time constant τ_d, Glarum[18] showed, for suitable values of the ratio τ_d/τ_r, this model to predict relaxation functions closely resembling the empirical skewed-arc function for β in the range $0.5 < \beta < 1$. In particular, his result gives exactly the function $(1 + i\omega\tau_0)^{-1/2}$ for $\beta = 0.5$ if the reorientation and diffusion times are the same, $\tau_d = \tau_r = \tau_0$, and the Debye function $(1 + i\omega\tau_0)^{-1}$ for $\tau_r = \tau_0 \ll \tau_d$.

Although Glarum's model is admittedly crude and highly simplified, it has two important features: first, the observed behavior can be reproduced without invoking distributions of exponential decay functions, the deviations from the simple Debye behavior arising from the fact that the diffusive or random-walk mechanism of cooperative interactions has a nonexponential time dependence; and, second, a limiting low-temperature behavior with $\beta = 0.50$ corresponds to equal time of the assumed local molecular reorientations and cooperative loss of correlation. A proper molecular interpretation of the significance of the second result obviously requires a more fundamental justification of the model from molecular dynamics of liquids.

Anderson and Ullman[28] have recently developed a modified treatment of molecular relaxation in the spirit of Glarum's approach, in which the probability of molecular reorientations is assumed to vary with fluctuations in the environment and to satisfy an Ornstein–Smoluchowski equation[29] for Brownian motion of a bound particle as a function of a fluctuation variable. This variable is called a free volume without implying that this description or connotation is to be taken too literally. As for Glarum's result, their development leads, for appropriate values of somewhat similar parameters, to predictions of relaxation functions resembling the skewed arc function; for details, their interesting paper should be consulted.

From the discussion above, characteristic features of the observed relaxation in isoamyl bromide have intriguing and suggestive similarities to recent theories which have the common feature that they invoke cooperative interaction effects. These theories are still far from explaining both temperature and frequency dependence of the observed relaxation effects within a single framework having a reasonably direct connection with molecular dynamics, but they suggest viewpoints and directions of attack for further developments of theory. The fact that the present results are broadly similar to those for other "cold" liquids of quite different molecular composition suggests the need for a quite general form of explanation.

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The Quadrupole Moments of Some Simple Molecules

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Abstract: The birefringence induced in a number of simple gases by an electric field gradient has been measured. In general, this birefringence is composed of two terms, a temperature-dependent one due to the orientation of quadrupolar molecules, and a small temperature-independent term B. Values are derived for the quadrupole moments of carbon dioxide, nitrogen, oxygen, ethane, and ethylene by neglecting contributions from B. For isotropically polarizable molecules, only B contributes to the birefringence; it has been measured for methane, argon, and sulfur hexafluoride. The importance of contributions from B to the induced birefringence in anisotropic molecules is considered, and an experimental value of B is obtained for H_2. Values are recorded for the effective quadrupole moments of the dipolar molecules COS, CO, and N_2O. These values are compared with center-of-mass quadrupole moments calculated from rotational g factors and magnetic susceptibility anisotropies. The differences between these quadrupole moments yield values for some new polarizabilities describing the behavior of molecules in electromagnetic fields.

In one of his classic early papers,[2] Debye showed how measurements of the static dielectric constant ϵ of a gas at low pressure lead to molecular dipole moments μ

$$\epsilon - 1 = 4\pi N[\alpha + \mu^2/(3kT)] \qquad (1)$$

where N is the number of molecules in unit volume and α is the mean molecular polarizability. The polarizability contribution represents distortion of the electronic and nuclear arrangement by the applied electric field, and the term in $\mu^2(kT)^{-1}$ describes the effect of dipolar orientation (*i.e.*, distortion of the molecular rotation).

The dipole is the first moment of the electric charge

$$\mu = \sum_i e_i z_i \qquad (2)$$

where z_i is the average distance of the ith charge e_i along the z axis fixed in the molecule. Molecular dipole moments have the magnitude of the Debye unit (1 D =

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[2] P. Debye, *Physik. Z.*, **13**, 97 (1912).

10^{-18} esu). The electric quadrupole Θ is the second moment of the charge

$$\Theta = {}^{1}\!/_{2}\sum_i e_i(3z_i^2 - r_i^2) \tag{3}$$

where $r_i^2 = x_i^2 + y_i^2 + z_i^2$; Θ is of the order of magnitude 10^{-26} esu. If the z axis is an axis of threefold or higher rotational symmetry, the molecule possesses just one independent dipole and one quadrupole; the quadrupole moment is independent of the choice of origin only if μ is zero. The energy of a molecule in a non-uniform electrostatic field is

$$u = -\mu F_z - {}^{1}\!/_{2}\Theta F'_{zz} - \dots \tag{4}$$

where F_z and F'_{zz} are the components of the field and field gradient along the molecular axis. At a distance of 4 Å from a proton, $F_z \sim 3 \times 10^5$ esu and $F'_{zz} \sim -1.5 \times 10^{13}$ esu, and the quadrupolar interaction energy may be comparable to the dipolar. Hence a knowledge of Θ is important for an understanding of intermolecular forces, as well as molecular structure. In the laboratory it is easy to obtain $F_z \sim 10^2$ esu and $F'_{zz} \sim 10^3$ esu; in this case the quadrupolar energy is only $\sim 10^{-7}$ of the dipolar, so Θ has been difficult to measure. In 1921, in discussing the origin of intermolecular forces, Debye[3] suggested that it may be possible to measure Θ by looking for the birefringence induced by a laboratory field gradient. In 1959, the theory of an appropriate experiment was developed.[4] In the field gradient $F'_{xx} = -F'_{yy}$, the difference in the refractive indexes for light traveling along the z axis and polarized in the x and y directions is

$$n_x - n_y = 2\pi N F'_{xx}\left[B + \frac{2\Theta(\alpha_{||} - \alpha_\perp)}{15kT}\right] \tag{5}$$

where $\alpha_{||} - \alpha_\perp$ is the anisotropy in the molecular polarizability; B describes the change in the effective polarizability induced by the field gradient. Equation 5 is analogous to the Debye equation (1) and to the formula describing the Kerr effect in which the anisotropy in the refractive index is induced by a uniform electric field. In the Kerr effect, $n_x - n_y$ is proportional to $\mu^2(\alpha_{||} - \alpha_\perp)(kT)^{-2}$ and is *quadratic* in the electric field F_x, in contrast to the linear dependence on F'_{xx} in (5). Both dielectric studies and the Kerr effect give only the magnitude of μ, whereas measurements of the field gradient induced anisotropy are capable of yielding both the magnitude and sign of Θ through (5). The first direct measurement of the quadrupole moment of CO_2 was reported to the American Chemical Society Meeting in honor of Debye;[5] the published value was -4.1×10^{-26} esu.[6] This figure requires each oxygen atom in a point charge model of CO_2 to carry a charge of 0.32 electron.

In the derivations of eq 1 and 5, the rotational motion of the molecules is assumed to be classical. If quantization is considered, (5) must be replaced by[7]

$$n_x - n_y = 2\pi N F'_{xx}\left[B' + \frac{2\Theta(\alpha_{||} - \alpha_\perp)}{15kT}\,\mathrm{f}(T)\right] \tag{6}$$

where B' differs slightly from B because of centrifugal distortion; for a linear molecule

$$\mathrm{f}(T) = 1 - \sigma + \frac{8}{15}\sigma^2 - \dots \tag{7}$$

where $\sigma = hcB_0/(kT)$ and B_0 is the rotational constant. For H_2 at room temperature, f(T) is 0.75, and for CO_2 0.998.

For dipolar molecules, the origin of Θ in (5) is a point called the "effective quadrupole center"[8] at which $A_{||} + 2A_\perp + 10c\omega^{-1}G$ is zero. The higher polarizabilities **A** and **G** describe the electric dipole induced by the field gradient and time-dependent magnetic field associated with the electromagnetic wave

$$\boldsymbol{\mu}_{\text{induced}} = \boldsymbol{\alpha}\cdot\mathbf{F} + \frac{1}{3}\mathbf{A}:\mathbf{F}' + \mathbf{G}\cdot\mathbf{H}\,\omega^{-1} + \dots \tag{8}$$

The effective quadrupole center varies to some extent with the angular frequency ω of the radiation used to measure $n_x - n_y$, but to a high degree of accuracy is independent of the nuclear masses; it is the center in a centrosymmetric molecule, for at this point $\mathbf{A} = \mathbf{G} = 0$. If the molecule is considered to comprise i noninteracting atoms at positions Z_i, each with polarizabilities $\alpha_{||}^{(i)}$ and $\alpha_\perp^{(i)}$ along and at right angles to the axis

$$\begin{aligned} A_{||} &= 2\sum_i \alpha_{||}^{(i)} Z_i \\ A_\perp &= \frac{3}{2}\sum_i \alpha_\perp^{(i)} Z_i \\ G &= -\frac{\omega}{2c}\sum_i \alpha_\perp^{(i)} Z_i = -\frac{\omega}{3c}A_\perp \end{aligned} \tag{9}$$

and

$$\left(A_{||} + 2A_\perp + \frac{10c}{\omega}G\right) = 2\sum_i(\alpha_{||}^{(i)} - \alpha_\perp^{(i)})Z_i \tag{10}$$

Thus the effective quadrupole center may be regarded as the point at which the first moment of the polarizability anisotropy vanishes. If the center of mass is distant Z from the effective quadrupole center in the direction of the electric dipole moment (from − to +), and if primes are used to denote quantities referred to the center of mass as origin

$$\begin{aligned} \Theta' &= \Theta - 2\mu Z \\ A_{||}' &= A_{||} - 2\alpha_{||}Z \\ A_\perp' &= A_\perp - \frac{3}{2}\alpha_\perp Z \\ G' &= G + \frac{\omega}{2c}\alpha_\perp Z \\ \left(A_{||}' + 2A_\perp' + \frac{10c}{\omega}G'\right) &= -2(\alpha_{||} - \alpha_\perp)Z \end{aligned} \tag{11}$$

Hence measurements of Θ and Θ' give Z and therefore $(A_{||}' + 2A_\perp' + 10c\omega^{-1}G')(\alpha_{||} - \alpha_\perp)^{-1}$.

The temperature-independent distortion contribution to $n_x - n_y$ in (5) is related[8] to higher polarizabilities describing the effect of a field gradient on $\boldsymbol{\alpha}$ and a field on **A** and **G**. For a hydrogen atom, B has been calcu-

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Table I. The Induced Birefringence at 24°, Polarizability Anisotropies, and Derived Quadrupole Moments of Nondipolar Gases

Gas	$10^{36}(n_z - n_y)/NF'_{zz}$,[a] esu	$10^{24}(\alpha_{\parallel} - \alpha_{\perp})$,[a] cm^3	$10^{26}\Theta$, esu	$10^{38}\cdot 2\Theta(\alpha_{\parallel} - \alpha_{\perp})/15kT$, esu
Carbon dioxide	−1.83 ± 0.08	2.10	−4.3 ± 0.2	−29
Nitrogen	−0.20 ± 0.02	0.696	−1.4 ± 0.1	−3.2
Oxygen	−0.08 ± 0.02	1.10	−0.4 ± 0.1	−1.3
Hydrogen	+0.018 ± 0.003	0.314	+0.651[b]	+0.50[c]
Ethane	−0.13 ± 0.02	0.77	−0.8 ± 0.1[d]	−2.1[e]
Ethylene[e]	+0.75 ± 0.05	1.81	+2.0 ± 0.15	+12

[a] At 6328 Å. [b] See text. [c] Allowing for a 25% quantum correction. [d] This value is considerably reduced if allowance is made for the contribution of the higher polarizability B (see text). [e] It has been assumed that the polarizabilities perpendicular to the double bond are equal; Θ is the quadrupole moment along this bond.

lated[8] to be -0.242×10^{-38} esu in the limit of zero frequency. B is independent of origin and a function of frequency.

Experimental Section

The apparatus used to measure quadrupole moments has been described in an earlier paper.[6] An improved detection system and the use of a high-power helium–neon gas laser as light source have resulted in a gain in signal:noise of a factor of 10. The wavelength of the light used in these experiments was 6328 Å.

Measurements of birefringence are made relative to the Kerr constant of a liquid. In the earlier experiments this was nitrobenzene, but carbon disulfide is now used. Carbon disulfide cells do not "age;" they retain a low conductivity indefinitely, unlike nitrobenzene whose conductivity and Kerr constant are a function of sample life. The carbon disulfide Kerr cell has been calibrated, so a knowledge of the geometry and end corrections of the cell, and Kerr constant of the liquid, is unnecessary.

The quantity $n_z - n_y$ was measured for each gas at a series of field gradients (up to 500 esu) and gas pressures (up to 80 atm in some cases). Gas densities were calculated from the measured pressures and temperatures using published virial coefficients. No departure from a linear dependence of birefringence on gas density was observed, so molecular interactions are unimportant except in so far as they influence the gas density.

Results and Discussion

Table I shows values of $(n_z - n_y)/NF'_{zz}$ for some simple nonpolar gases. Neglecting contributions from the higher polarizabilities B, and using values for $\alpha_{\parallel} - \alpha_{\perp}$ obtained from light-scattering measurements,[9] the molecular quadrupole moments in Table I may be obtained through eq 5.

For isotropically polarizable molecules, $(n_z - n_y)/NF'_{zz}$ is directly proportional to B, and Table II lists measured values for methane, argon, and sulfur hexafluoride. In molecules with small quadrupole moments, contributions from B to the induced birefringence may be important. The quadrupole moment of hydrogen is accurately known to be $+0.651 \times 10^{-26}$ esu;[10] making allowance for the quantum correction this contributes 170% of the observed birefringence. Thus B is responsible for −70% of the measured effect (see Table II). Methane has a larger $|B|$ than either argon or sulfur hexafluoride. A crude estimate of B for ethane may be made from the bond additivity approximation

$$B_{\text{ethane}} = 2B_{\text{methane}} - B_{H_2}$$

This gives $B_{\text{ethane}} = -2.2 \pm 0.7 \times 10^{-38}$ esu and hence $\Theta_{\text{ethane}} = +0.1 \pm 0.5 \times 10^{-26}$ esu. For oxygen and nitrogen the contribution of B to the induced birefringence may be less important. Values of B for a few simple molecules and the hydrogen atom are given in Table II. The importance of the B contribution to the induced birefringence may be ascertained by comparing it with $2\Theta(\alpha_{\parallel} - \alpha_{\perp})/15kT$; this quantity is also listed in Tables I and II.

Table II. The Higher Polarizability B

Gas	$10^{38}B$, esu	$10^{38}\cdot 2\Theta(\alpha_{\parallel} - \alpha_{\perp})/15kT$, esu
Hydrogen atom	−0.242 (calcd)	0
Hydrogen	−0.21 ± 0.07	+0.50[a]
Methane	−1.2 ± 0.3	0
Ethane	−2.2 (estd)	+0.2
Argon	0 ± 0.5	0
Sulfur hexafluoride	0 ± 0.5	0

[a] Allowing for a 25% quantum correction.

The effective quadrupole moments of three dipolar gases have been measured, neglecting contributions of B to the birefringence, and are given in Table III. From a knowledge of the magnetic susceptibility anisotropy $\chi_{\parallel} - \chi_{\perp}$ and rotational g factor, it is possible to derive a value for the center-of-mass quadrupole moment (providing nuclear vibrations are neglected)[11]

$$\Theta' = e\left(\frac{Ig}{M}\right) - \frac{4mc^2}{e}(\chi_{\parallel} - \chi_{\perp}) \tag{12}$$

where e and M are the charge and mass of a proton, m the mass of an electron, I the molecular moment of inertia, and c the velocity of light. Values of Θ′ also appear in Table III. The distance Z of the center of mass from the effective quadrupole center, and hence $(A_{\parallel}' + 2A_{\perp}' + 10c\omega^{-1}G')$ at the center of mass, may be obtained through eq 11, and these values are included in Table III. The center-of-mass quadrupole moments of nitrous oxide and carbon monoxide are unreliable because of uncertainties in $\chi_{\parallel} - \chi_{\perp}$. We have used $\chi_{\parallel} - \chi_{\perp}$ obtained from the Cotton–Mouton constants of these gases,[12] neglecting any higher polarizability contributions. A 10% error in $\chi_{\parallel} - \chi_{\perp}$ leads to uncertainties in Θ′ of $\sim 1 \times 10^{-26}$ esu. The values of Z and $(A_{\parallel}' + 2A_{\perp}' + 10c\omega^{-1}G')$ for these gases may be subject to large errors, and we do not take the CO value seriously, except in so far as it implies an error in the quoted value of $\chi_{\parallel} - \chi_{\perp}$. The magnitude and sign of Z provide information about the distribution of the polarizability anisotropy and the sense of the dipole moment.

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Table III. Comparison of Effective Quadrupole Moments Θ with Center-of-Mass Quadrupole Moments Θ′

Gas	Dipole moment, D	$10^{26}\Theta$, esu	g,[a] nuclear magneton	$10^{30}(\chi_{\parallel} - \chi_{\perp})$, emu	$10^{26}\Theta'$, esu	Z, Å	$10^{32}(A_{\parallel}' + 2A_{\perp}' + 10c\omega^{-1}G')$, esu
Carbonyl sulfide	0.712	−0.3 ± 0.1[b]	−0.02889[d]	−13.9[g]	−2.0	+1.2	−13
Nitrous oxide	0.167	−3.5 ± 0.3[c]	−0.086[e]	−18	−4.2	+2.1	−12
Carbon monoxide	0.112	−2.5 ± 0.3[c]	−0.2689[f]	−17	+0.4	−13	+14

[a] The sign of g for N_2O is not known; we have assumed it to be negative. [b] Using $\alpha_{\parallel} - \alpha_{\perp} = 5.34 \times 10^{-24}$ cm³, as measured for static fields: L. H. Scharpen, J. S. Muenter, and V. W. Laurie, *J. Chem. Phys.*, **46**, 2431 (1967). [c] Using values for $\alpha_{\parallel} - \alpha_{\perp}$ from ref 9. [d] J. W. Cederberg, C. H. Anderson, and N. F. Ramsey, *Phys. Rev.*, **136**, A960 (1964). [e] C. K. Jen, *ibid.*, **81**, 197 (1951). [f] I. Ozier, P. Yi, A. Khosla, and N. F. Ramsey, *J. Chem. Phys.*, **46**, 1530 (1967). [g] H. Taft and B. P. Dailey, *ibid.*, **48**, 597 (1968).

Negative charge in a plane at right angles to the molecular axis of a linear molecule contributes a positive amount to the quadrupole moment, while negative charge distributed along the molecular axis contributes negatively. Hence oxygen, with two more π electrons than nitrogen, has a less negative quadrupole moment. The positive sign of the quadrupole moment of ethylene may be attributed to the π character of the carbon–carbon double bond; acetylene is expected to have an even larger positive quadrupole moment.

Light Scattering by Crystalline Polystyrene and Polypropylene

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Abstract: The light scattering by crystallizable polymers can yield valuable information regarding the crystallization behavior and the resulting crystalline morphology if (i) quantitative measurements are carried through and (ii) these are analyzed by using a physically realistic model. It is found that isotactic polystyrene and polypropylene samples can be adequately described as containing imperfect spherulites in which a number of perfectly spherulitic and a number of "random orientation" crystallites are present. Growth rates, sizes, and the number of spherulites follow easily from the scattering data. The internal structure of the imperfect spherulites can be characterized by the birefringence of the perfectly spherulitic crystallites plus a density correlation distance, two orientation correlation distances, and the mean polarizability and anisotropy fluctuations of the "random orientation" crystallites. It is found that in isotactic polystyrene the crystallinity of the spherulites is a decreasing function of the radius. In the case of isotactic polypropylene it could be shown that the secondary crystallization is not spherulitical, in contradistinction to the primary crystallization.

In 1949 Debye and Bueche[1] demonstrated how measurements of the light scattering by an amorphous polymer could be used to obtain a density correlation function $\gamma(r)$ describing the supermolecular order in the samples. Since that time several investigators,[2] notably Stein,[3] have extended this method of investigation to other, more complicated, polymer systems. In the present article we will demonstrate the usefulness of *quantitative* light-scattering data for studying the crystallization behavior and the resulting supermolecular order in crystalline polymers. Our samples consisted of bulk crystallized isotactic polystyrene and polypropylene which upon microscopic examination are found to contain spherulitic aggregates of crystallites.

Necessary conditions for such a quantitative study are (i) a light-scattering photometer of high resolution, capable of measuring down to very small angles, and (ii) a physically realistic model for the structure of the spherulites. The first requirement offers no serious difficulties; a convenient instrument, constructed in our laboratory, has been described previously.[4] It consists essentially of a finely collimated primary beam and a photomultiplier–detector, mounted on a swivelling arm. With this combination one can measure down to 30′ from the primary beam. The second requirement implies that maximum information can only be obtained if some previous knowledge of the morphology is available through other experimental techniques. This requirement derives from the fact that there is little use introducing a set of correlation functions which formally describe the structure. In the first place the physical interpretation of such a set of functions remains dubious, and, secondly, the experimental results do not always allow reliable Fourier inversions which are needed to yield the functions.

In the recent past, two main models have been described in the literature. In one[5,6] the spherulite is considered to be perfect; *i.e.*, all crystallites are con-

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