

$n_c = 1.308$ . The "liquid" may be assumed to behave like other normal unassociated substances whose molecular refraction,  $M(n^2 - 1)/\rho(n^2 + 2)$ , is the same in the vapor and in the liquid state. For water vapor this has<sup>12c</sup> the value of 3.7660 which gives  $n_l = 1.369$ . These two values however give an average refractive index of 1.338 significantly higher than the experimental 1.334. In order to obtain a conservative value of turbidity we can assume the above estimate of  $n_c$  to be correct and take  $n_l = 1.360$  to make it consistent with  $n$ . This gives  $1.52 \times 10^{-2}$  for  $\bar{\eta}^2/\epsilon^2$ .

Combining these values gives  $1.2 \times 10^{-5}$  for the excess turbidity of this model which is only slightly lower than the total observed turbidity of water and several times higher than the experimental excess turbidity estimated above.

If the  $n_l$  based on molar refraction is taken as a basis the calculated excess turbidity rises to  $2.1 \times 10^{-5}$  which is still higher.

**Turbidity of the Network-with-Vacancies Model.**—The specific model considered, is that of Danford and Levy.<sup>4</sup> Among other features it is characterized by a large volume fraction (*ca.*  $1/9$ ) of vacancies large enough to hold a water molecule: one-half of all the cavities within a network of tetrabonded molecules is vacant whereas the other half is occupied by unbonded molecules. The optical effect of these missing molecules is the same as that of fictitious molecules having the size and mass of water molecules and a refractive index of 1 (or 1.668), *i.e.*, a refractive increment,  $\partial n/\partial c$ , equal to that of pure water. An ideal 11% solution of such fictitious molecules would have a turbidity of about  $2.5 \times 10^{-3}$   $\text{cm.}^{-1}$  in excess of that determined by compressibility. The fact that the vacancies are not random but occur only in the cavities of the network can be accounted for, in part at least, by considering them as hard spheres whose radii should be somewhere within the range of distances between the real interstitial water molecules and the

lattice ones, *i.e.*, between 3 and 4 Å., according to the Danford and Levy model. This reduces<sup>19</sup> the excess turbidity by 30 to 60%, making it comparable but still some four to eight times larger than the observed excess. A still less random spacing of these vacancies could of course bring the excess turbidities still lower but it is difficult to visualize any long range forces which could have this effect.

Vacancies postulated by Frank and Quist<sup>5</sup> in the Pauling model are considerably fewer than proposed by Danford and Levy. They correspond to only one-thirtieth of the total and should be more regularly spaced since they occur only in all the dodecahedra. Hence their contribution to the excess scattering should be smaller and close to the experimental values.

**Conclusion.**—Thus it appears that light scattering can provide some information about water structure. The rather small excess of experimental values over the turbidity due to pressure fluctuations seems to leave little room for structures involving either discrete and compact icebergs of many water molecules or any large proportion of randomly distributed holes of molecular dimensions. On the other hand, more refined experimental measurements, especially those concerning the effect of temperature, should indicate whether the observed excess is attributable to a structural inhomogeneity and should place more definite limits upon possible models.

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## Scattering of Optical Harmonics by Macromolecules

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Accompanying the light scattered by a solution of macromolecules is a feeble overtone whose intensity is proportional to the square of the incident intensity. It is a result of the fluctuation in the derivative with respect to electric field of the polarizability just as the ordinary scattered light results from the fluctuation in the polarizability. This second harmonic Rayleigh scattering is in principle observable with the use of powerful pulsed lasers.

It was Debye<sup>1</sup> who first proposed the idea of defining the shape of a macromolecule by measuring the angular dependence of the light scattered by a solution. An extensive development ensued<sup>2</sup> and light scattering has become a classic technique in the study of solutions of macromolecules. As a curious footnote to this development we note that the realization of lasers has made possible the observation of harmonic scattering of light<sup>3</sup> by solutions albeit at very low intensity.

(1) P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).

(2) C. P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

An elementary light scattering process consists of the generation by a molecule of secondary waves with the same frequency as the incident light wave albeit shifted in phase. If the macromolecule consists of  $N$  segments whose charges are approximately isolated from each other, the total scattering amplitude is

$$\sum_{\alpha} f_{\alpha}^{(1)} e^{i\vec{k} \cdot \vec{R}_{\alpha}} \quad (1)$$

(3) P. Franken and J. F. Ward, *Rev. Mod. Phys.*, **35**, 23 (1963).

where

$$\vec{\mathbf{K}} = \vec{\mathbf{k}}_1 - \vec{\mathbf{k}}_1' = \frac{2\pi}{\lambda_1} n_1(\hat{\mathbf{e}}_1 - \hat{\mathbf{e}}_1') \quad (2)$$

$\hbar\vec{\mathbf{K}}$  is the momentum change of the light quantum,  $n_1$  is the index of refraction of the medium, and  $\lambda_1$  is the wave length *in vacuo* of the incident light. The unit vectors  $\hat{\mathbf{e}}_1$  and  $\hat{\mathbf{e}}_1'$  are in the direction of the incident and scattered light, respectively.  $\vec{\mathbf{R}}_\alpha$  is a vector extending from an arbitrary origin to a fixed point in the segment  $\alpha$ . The amplitude  $f_\alpha$  is proportional to the electric dipole polarizability of the segment  $\alpha$ . The summation over  $\alpha$  depends on the structure of the macromolecule and if the wave length  $\lambda_1$  is comparable to the length of an intramolecular vector  $\vec{\mathbf{R}}_\alpha - \vec{\mathbf{R}}_{\alpha'}$ , a characteristic interference will result.

If the incident intensity is very great as with a laser source, there is a possibility of cooperative effects of two quanta. The molecular charges are caused to oscillate with a frequency of twice the incident frequency and the scattered wave has twice the frequency and energy of the incident wave. (As the optical electric field strength becomes comparable to the natural atomic field strengths even higher harmonics are, in principle, observable.) One wonders whether this new phenomenon (proportional to the *square* of the incident intensity) can provide additional information concerning the structure of a macromolecule.

If the electrons which scatter the radiation were free to move over the entire molecule or over segments whose size was comparable to the optical wave length, then one could visualize a quantum  $h\nu$  interacting with the electron at one point,  $\vec{r}$ , a second quantum  $h\nu$  interacting with the electron at another point  $\vec{r}'$ , and the quantum  $h(2\nu)$  being radiated at a third point  $\vec{r}''$ . But in almost all molecules the electron's path is limited and the three points  $\vec{r}$ ,  $\vec{r}'$ , and  $\vec{r}''$  will all lie within a region or segment very small compared to a wave length of light. This means that the total harmonic wave scattered by a molecule can be represented as a sum over the contributions of individual segments

$$\sum_{\alpha=1}^N f_\alpha^{(2)} e^{i\vec{\mathbf{K}} \cdot \vec{\mathbf{R}}_\alpha} \quad (3)$$

As usual  $\hbar\vec{\mathbf{K}}$  is the net momentum change of the light quanta so

$$\begin{aligned} \vec{\mathbf{K}} &= 2\vec{\mathbf{k}}_1 - \vec{\mathbf{k}}_2' = 2 \cdot \frac{2\pi}{\lambda_1} n_1 \hat{\mathbf{e}}_1 - \frac{2\pi}{\lambda_2} n_2 \hat{\mathbf{e}}_2' \\ &= \frac{4\pi}{\lambda_1} (n_1 \hat{\mathbf{e}}_1 - n_2 \hat{\mathbf{e}}_2') \end{aligned} \quad (4)$$

If we write for the induced dipole moment of the segment  $\alpha$  the expansion

$$\vec{P}_\alpha = \overset{\equiv}{\alpha}_\alpha \cdot \mathcal{E} + \overset{\equiv}{\beta}_\alpha : \mathcal{E}\mathcal{E} + \dots, \quad (5)$$

then the scattering amplitude  $f_\alpha^{(2)}$  will be proportional to the polarizability derivative  $\beta_\alpha$ .

The sum over  $\alpha$  (often transformed into an integral) is a function of the variable  $\vec{\mathbf{K}}R$  where  $R$  is a character-

istic dimension of the molecule. For single quantum scattering

$$|\vec{\mathbf{K}}| = \frac{4\pi}{\lambda_1} n_1 \sin \theta/2 \quad (6)$$

For double quantum scattering

$$|\vec{\mathbf{K}}| = \frac{4\pi}{\lambda_2} \frac{1}{2} (n_1 + n_2) (\sin^2 \theta/2 + \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2 \cos^2 \theta/2)^{1/2} \quad (7)$$

This equation has several consequences. If the medium is nondispersive ( $n_1 = n_2$ ), the angular distribution of the scattering is precisely the same as it would be if the incident light had the frequency  $\nu_2 = 2\nu_1$ . For most solvents and typical wave lengths  $(n_1 - n_2)(n_1 + n_2)^{-1} \sim 0.01$  or less. In general the square root in eq. 7 spans the range  $(n_1 - n_2)^{1/2}(n_1 + n_2)^{-1/2}$  to 1 instead of 0 to 1 as does  $\sin \theta/2$ . That is,  $|\vec{\mathbf{K}}|$  has a minimum observable value. The plot of scattering intensity *vs.*  $|\vec{\mathbf{K}}|R$  is precisely the same as for single scattering so that the classic work of Bueche, Debye, and Cashin<sup>4</sup> on spheres, rods, and random coils is applicable without modification. The experimental plot of intensity *vs.* scattering angle,  $\theta$ , would not be precisely the same because of the dispersion of the solution.

The amplitudes of X-ray scattering are proportional to the transform of the charge densities of the scattering entities, the amplitudes of single quantum light scattering are proportional to the dipole polarizabilities, and the amplitudes of harmonic scattering are proportional to the derivatives with respect to field of the dipole polarizabilities. One can show that

$$f_\alpha^{(1)} \propto \sum_m \left\{ \frac{(\rho_\lambda^\alpha)_{om}(\rho_\lambda^\alpha)_{mo}}{\epsilon_m - \epsilon_0 - h\nu} + \frac{(\rho_\lambda^\alpha)_{om}(\rho_\lambda^\alpha)_{mo}}{\epsilon_m - \epsilon_0 + h\nu} \right\} \quad (8)$$

and<sup>5</sup> that

$$\begin{aligned} f_\alpha^{(2)} \propto \sum_m \sum_{n \neq m} \left\{ \frac{(\rho_\lambda^\alpha)_{om}(\rho_\lambda^\alpha)_{mn}(\rho_\lambda^\alpha)_{no}}{(\epsilon_0 - \epsilon_m + h\nu)(\epsilon_0 - \epsilon_n + 2h\nu)} + \right. \\ \left. \frac{(\rho_\lambda^\alpha)_{om}(\rho_\lambda^\alpha)_{mn}(\rho_\lambda^\alpha)_{no}}{(\epsilon_0 - \epsilon_m + h\nu)(\epsilon_0 - \epsilon_n - h\nu)} + \right. \\ \left. \frac{(\rho_\lambda^\alpha)_{om}(\rho_\lambda^\alpha)_{mn}(\rho_\lambda^\alpha)_{po}}{(\epsilon_0 - \epsilon_m - 2h\nu)(\epsilon_0 - \epsilon_n - h\nu)} \right\} \quad (9) \end{aligned}$$

In the above equations  $\rho_\lambda^\alpha$  and  $\rho_{\lambda'}^\alpha$  are components of the momentum operator of the electrons of segment  $\alpha$  in the direction of polarization of the incident and scattered light, respectively. The intermediate states  $\epsilon_m$  and  $\epsilon_n$  are excited electronic states of the segment  $\alpha$ .

The principal virtue of harmonic scattering is clearly that it reveals this new molecular property, the derivative of the polarizability. Insofar as the determinations of the shapes of macromolecules are concerned, the new method appears to add little to previous methods. One exception may be noted. Inasmuch as the harmonic  $2\nu_1$  may be clearly differentiated from the incident quantum  $\nu_1$  by selective absorbers and dif-

<sup>(4)</sup> F. Bueche, P. Debye, and W. M. Cashin, *J. Chem. Phys.*, **19**, 803 (1951).

<sup>(5)</sup> J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan *Phys. Rev.*, **127**, 1918 (1962).

fraction gratings, one may observe scattering at arbitrarily small angles or even at zero angle which is, of course, impossible for ordinary scattering.

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## Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons<sup>1</sup>

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A partition function is formulated for chain molecule liquids using a model consisting of a linear sequence of segments endowed with hard sphere type repulsive potentials and soft attractions of unspecified character. The intermolecular energy is represented as varying inversely with the volume over the comparatively small range of volume of the liquid. Account is taken of intermolecular constraints on the segments by expressing the number of external degrees of freedom per segment as  $3c$  where  $c$  ( $<1$ ) enters as a parameter. In this respect the formulation follows recent treatments based on the cell model, use of which is avoided. A reduced equation of state  $\bar{p} = \bar{p}(\bar{T}, \bar{v})$  is derived, with reduced variables defined by three primary parameters, namely, a segment net volume  $v^*$ , a quantity  $s\eta$  characterizing the interaction per segment, and  $c$ . These can be evaluated from the volume, thermal expansion coefficient, and compressibility, for example. Data for the  $n$ -paraffin hydrocarbons from  $C_6$  to  $C_{20}$  are very well represented in this manner. The values of the parameters are slightly dependent, however, on the temperatures to which the experimental data refer.

### Introduction

Initiation of the investigations reported in this series of papers was motivated by the need for a basis on which to interpret and correlate the properties of macromolecular liquids and their solutions. Comprehension of the connection between molecular characteristics and thermodynamic properties of such liquids is an obvious prerequisite for interpretation of melting and glass transitions, for example. It has long been apparent also that the major discrepancies between theory and experiment on macromolecular solutions can only be resolved by treating these systems in some more satisfactory fashion than is possible within the strictures of the lattice model. By its disregard of changes in volume and local disorder with composition, this model fails to reflect changes in liquid structure, account of which is necessary for realizing an adequate grasp of solution properties.

Treatment of liquids consisting of nonspherical polyatomic molecules by methods which join rigor with tractability of result is an objective for which there is as yet small hope of fulfillment. In this paper we sacrifice rigor in favor of simplicity by resorting to a low order of approximation in formulating a partition function for chain liquids. While the level of refinement may leave much to be desired, the relationships derived are manageable, and the correlation with experiment is not altogether disappointing.

The subject is by no means new. Prigogine and co-workers<sup>2-4</sup> have adapted the cell model to chain molecule liquids. Equations of state thus derived have proved of little value.<sup>2,5,6</sup> The difficulty unquestionably is related to the unsatisfactory representation of the intermolecular energy and its dependence

on volume afforded by the cell model. As Hildebrand and Scott<sup>7</sup> have emphasized, this model, by fixing nearest neighbors of a given molecule (or segment) exactly at their mean positions, suppresses the randomness which is a foremost characteristic of the liquid state. Irregularity in the distribution of molecules about one another, as expressed by the radial distribution function for a liquid, is artificially suppressed by the assumed quasi-crystalline order. The intermolecular energy for a molecule moving in a cage provided by neighbors fixed in regular array may readily be seen to be unrepresentative of the energy for a molecule surrounded by molecules irregularly placed.

Prigogine and co-workers in later papers<sup>2,4</sup> formulated a law of corresponding states for chain molecules, and this has met with noteworthy success. Demonstration of a law of corresponding states embracing virtually the entire range of  $n$ -paraffin hydrocarbons<sup>2,4,8</sup> encourages the search for a partition function for chain liquids by means of which to rationalize an extensive body of experimental results. An analytical expression for the partition function and the equation of state derived from it are much to be preferred over the graphical-empirical methods of application of a law of corresponding states.

Our partition function is patterned after that introduced for simple liquids by Eyring and Hirschfelder<sup>9,10</sup> a number of years ago. With them, we assume the intermolecular energy to depend only on the volume, and a hard sphere repulsive potential is adopted for segments of the chain. The number of external degrees of freedom is introduced as a parameter on the premise that the corresponding modes can be separated unambiguously from the internal degrees of freedom of the molecule. In this respect we follow the procedure elaborated by Prigogine and co-workers.<sup>2-4</sup>

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