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The Lorentz-Lorenz Function of the Solidified Rare Gases

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A theory of the deviation of the Lorentz-Lorenz function, $(n^2 - 1)/(n^2 + 2)\rho$, for the solid rare gases from its gas phase value is given. A tight binding exciton model for the excitations in the solid and the mathematical formalisms of second quantization and quantum mechanical Green's functions are used. The results are in reasonable agreement with experiment. Limitations of the model are discussed, and a physical explanation of the results is given in terms of virtual excitations of excited free atom states in the many body ground state of the crystal.

I. Introduction

The noble gases consist of spherical nonpolar molecules which crystallize in a face-centered cubic structure (except for helium). Therefore, the refractive indices (dielectric constants) of crystals of these elements ought to obey the Lorentz-Lorenz (Clausius-Mosotti) law. It is found experimentally, however, that these laws are not strictly obeyed.^{2,3} The deviation is small, of the order of a per cent or so, yet it is outside the experimental error. This paper is devoted to a theoretical discussion of this deviation.

One may perhaps ask why it is desirable to perform a lengthy and fairly sophisticated calculation of such a small effect. There are several answers to this question. In the first place, it is very annoying to have unexplained observations in the literature, especially in a field as thoroughly explored as this one. But more important than this, the explanation of the phenomenon in question may have some important bearing on the problem of intermolecular forces in dense media. There is inconclusive, but suggestive, evidence from the calculation of equilibrium and transport properties of liquids^{4,5} that the intermolecular forces in dense phases differ from those inferred from the study of gas phase properties. One need only recall the approximate London formula, $V(R) = -3\alpha^2 h\nu_0/4R^6$, for the dispersion force between atoms; here α is the polarizability, and ν_0 is a characteristic frequency. The relevance of optical studies of α should be clear.

The theory presented here uses the formalism of thermodynamic Green's functions, and second quantization. For the excitations in the crystal we have used the model of tightly bound, or Frenkel-type, excitons. The radiation field is not quantized, but is treated as a classical external field.

II. Theory

The Model.—The Hamiltonian for N atoms of atomic number Z is, in dipole approximation⁶

$$H_0 = \sum_{L=1}^N \left[\sum_{i=1}^Z \frac{p_{iL}^2}{2m} - \frac{Ze^2}{|r_{iL}|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_{iL} - r_{jL}|} \right] + \frac{1}{2} \sum_{L \neq L'=1}^N \mathbf{P}_L \cdot \mathbf{T}_{LL'} \cdot \mathbf{P}_{L'} \quad (1)$$

(1) Alfred P. Sloan Foundation Fellow. This work also supported in part by the National Science Foundation (GP 1951).

(2) (a) G. O. Jones and B. L. Smith, *Phil. Mag.*, **5**, 355 (1960); (b) B. L. Smith, *ibid.*, **6**, 939 (1961).

(3) R. L. Amey and R. H. Cole, *J. Chem. Phys.*, **40**, 146 (1964).

(4) W. B. Brown and J. S. Rowlinson, *Mol. Phys.*, **3**, 35 (1960).

(5) L. D. Ikenberry and S. A. Rice, *J. Chem. Phys.*, **39**, 1561 (1963).

(6) J. J. Hopfield, *Phys. Rev.*, **112**, 1555 (1958).

where

$$\mathbf{P}_L = e \sum_{i=1}^Z \mathbf{r}_{iL}$$

and

$$\mathbf{T}_{LL'} = \mathbf{R}_{LL'}^{-3} [1 - 3(\mathbf{R}_{LL'} \cdot \mathbf{R}_{LL'} / \mathbf{R}_{LL'}^2)]$$

Here \mathbf{r}_{iL} is the vector distance of electron i from nucleus L and $\mathbf{R}_{LL'}$ is the vector distance between nuclei L and L' . The first term of H_0 is the Hamiltonian for N isolated atoms; the second is the Coulomb interaction between atoms in dipole approximation.

We take as the atomic model a two-state atom, with a ground state $|0\rangle_L$ and an excited state $|1\rangle_L$, where the subscript indicates that the atom is located at \mathbf{R}_L . Furthermore, we introduce raising and lowering operators, b_L^+ and b_L , for each atom, with the properties

$$\begin{aligned} b_L^+ |0\rangle_L &= |1\rangle_L; & b_L^+ |1\rangle_L &= 0 \\ b_L |0\rangle_L &= 0; & b_L |1\rangle_L &= |0\rangle_L \end{aligned} \quad (2)$$

and an additional set of operators b_L^0 with the property

$$b_L^0 |0\rangle_L = -|0\rangle_L; \quad b_L^0 |1\rangle_L = |1\rangle_L \quad (3)$$

These operators obey the commutation relations⁷

$$[b_L^+, b_{L'}] = \delta_{LL'} b_L^0 \quad (4a)$$

$$[b_L^0, b_{L'}] = -2\delta_{LL'} b_L \quad (4b)$$

$$[b_L^0, b_{L'}^+] = 2\delta_{LL'} b_L^+ \quad (4c)$$

In a second quantized representation, these operators permit writing the dipole moment operator \mathbf{P}_L as

$$\mathbf{P}_L = \mathbf{X}(b_L^+ + b_L) \quad (5)$$

$$\mathbf{X} = \langle 0 | e \sum_{i=1}^Z \mathbf{r}_{iL} | 1 \rangle$$

and the Hamiltonian, (1), in the form⁸

$$\begin{aligned} H_0 &= \frac{E_0}{2} \sum_{L=1}^N b_L^0 + \frac{1}{2} \sum_{L \neq L'} \phi(L - L') [b_L^+ b_{L'}^+ + \\ &\quad b_L b_{L'} + b_L^+ b_{L'} + b_L b_{L'}^+] \quad (6) \\ \phi(L - L') &= \mathbf{X} \cdot \mathbf{T}_{LL'} \cdot \mathbf{X} \end{aligned}$$

Here E_0 is the energy difference between the excited and ground states of a free atom. The form (6) for the Hamiltonian implies that we have taken the zero of energy half-way between the ground and excited

(7) R. Hoffmann, *Rad. Rev.*, **20**, 140 (1963). Discusses these commutation rules in detail, and gives references to the Russian literature. We do not make the approximation, discussed by Hoffmann, of setting $b_L^0 = -1$.

states. This is the most convenient form for our purposes and merely amounts to adding a constant to the Hamiltonian (1).

To discuss the optical properties of our model we must add to H_0 a term accounting for the interaction of the system with radiation. This is most conveniently done by describing the radiation field by its vector potential, \mathbf{A} , in Coulomb gauge. In dipole approximation the interaction Hamiltonian can be written in the second quantized form

$$H_1 = -\frac{i\omega_0}{c} \sum_L \mathbf{X} \cdot \mathbf{A}_L (b_L^+ - b_L) \quad (7)$$

Here $\omega_0 = E_0/\hbar$, and \mathbf{A}_L is the value of the vector potential at \mathbf{R}_L . \mathbf{A} is, of course, time dependent. We emphasize that \mathbf{A} is the vector potential of the macroscopic field, not the local field.

In what follows, we shall indicate by brackets, (\dots) , the expectation value of the operator which stands in the brackets, thermally averaged over the states of the system. The fundamental quantity which we wish to compute is the expectation value of the dipole moment of atom L , $\langle \mathbf{P}_L(t) \rangle$, to first order in the interaction, H_1 . Since $\mathbf{P}_L(t)$ satisfies the Heisenberg equation of motion

$$i\hbar \dot{\mathbf{P}}_L = [\mathbf{P}_L(t), H_0 + H_1(t)] \quad (8)$$

we can write, to first order in H_1

$$\langle \mathbf{P}_L(t) \rangle = i/\hbar \int_{-\infty}^t dt' \langle [H_1(t'), \mathbf{P}_L(t)] \rangle \quad (9)$$

Omitted here is the zeroth order term ($\mathbf{A} = 0$), which vanishes because our atoms are nonpolar. In (9), $\mathbf{P}_L(t)$ is the Heisenberg operator

$$\mathbf{P}_L(t) = e^{i/\hbar H_0 t} \mathbf{P}_L e^{-i/\hbar H_0 t} \quad (10)$$

for the system in the absence of radiation. Similarly the dependence of $H_1(t')$ on t' comes partly from $\mathbf{A}(t')$ and partly from the time dependence of b_L^+ and b_L , as Heisenberg operators.

Introducing the definitions (5) and (7), we can write (9) in the form

$$\langle \mathbf{P}_L(t) \rangle = \sum_M \left(\frac{-i\omega_0}{\hbar c} \right) \mathbf{X} \cdot \int_{-\infty}^{\infty} dt' \mathbf{A}_M(t') G_{ML}^+(t, t') \quad (11)$$

where

$$G_{ML}^+(t, t') = i\theta(t - t') \langle [b_M^+(t') - b_M(t'), b_L^+(t) + b_L(t)] \rangle \quad (12)$$

$\theta(x)$ is zero for $x < 0$, unity for $x > 0$. It is the insertion of the θ function which enables the upper limit of the integral in (11) to be extended to infinity.

The Green's Functions.— $G_{ML}^+(t, t')$ is called a retarded Green's function.⁸ The main property of such a function which we shall need is its equation of motion, which is⁸

$$i\hbar \frac{d}{dt} G_{ML}^+(t - t') = -\hbar\delta(t - t') \langle [b_M^+ - b_M, b_L^+ + b_L] \rangle + i\theta(t - t') \langle [b_M^+(t') - b_M(t'), [b_L^+(t) + b_L(t), H_0]] \rangle \quad (13)$$

(8) Properties of Green's functions may be found summarized in "Fluctuations, Relaxation, and Resonance in Magnetic Systems," D. ter Haar, Ed., Oliver and Boyd, Edinburgh, 1962, p. 119 *et seq.*; V. L. Bonch-Bruевич and S. V. Tyablikov, "The Green Function Method in Statistical Mechanics," North Holland Publishing Co., Amsterdam, 1962.

In the first term on the right, both factors in the commutator can be taken at the same time, because of the δ -function. By the commutation rules (4) the expectation value can be written

$$\langle [b_M^+ - b_M, b_L^+ + b_L] \rangle = 2\delta_{ML} \langle b_L^0 \rangle \quad (14)$$

To evaluate the second term on the right, we compute the commutator

$$[b_L^+ + b_L, H_0] = [b_L^+ + b_L, \frac{E_0}{2} \sum_M b_M^0] = \frac{E_0}{2} [b_L^+ + b_L, b_L^0] = -E_0(b_L^+ - b_L) \quad (15)$$

The dipole interaction term of H_0 commutes with the dipole moment operator, and hence gives no contribution. If we write

$$G_{ML}^- = i\theta(t - t') \langle [b_M^+(t') - b_M(t'), b_L^+(t) - b_L(t)] \rangle \quad (16)$$

then

$$i\hbar \dot{G}_{ML}^- = -\hbar\delta(t - t') \delta_{ML} \langle b^0 \rangle - E_0 G_{ML}^- \quad (17)$$

We have dropped the index in $\langle b^0 \rangle$ since, by translational invariance, this is independent of L .

We must now find a differential equation for G_{ML}^- . This is of the same form as (13) except that $(b_L^+ + b_L)$ is everywhere replaced by $(b_L^+ - b_L)$. This motivated the choice of the \pm superscripts which distinguish the two Green's functions. Thus

$$i\hbar \dot{G}_{ML}^- = i\theta(t - t') \langle [b_M^+(t') - b_M(t'), [b_L^+(t) - b_L(t), H_0]] \rangle \quad (18)$$

Evaluating the commutator in the same manner as above, we find

$$i\hbar \dot{G}_{ML}^- = -E_0 G_{ML}^- + 2 \sum_{K \neq L} \phi(K - L) i\theta(t - t') \times \langle [b_M^+(t') - b_M(t'), (b_K^+(t) + b_K(t)) b_L^0(t)] \rangle \quad (19)$$

At this point we see a typical feature of Green's functions; the equations of motion involve Green's functions of higher order. An approximation is therefore necessary, and we make a "decoupling" approximation which has proved reasonably successful in the theory of ferromagnetism.⁹ To wit, we factor b_L^0 out of the commutator in (19).

$$i\theta(t - t') \langle [b_M^+(t') - b_M(t'), (b_K^+(t) + b_K(t)) b_L^0(t)] \rangle \cong G_{MK}^+ \langle b^0 \rangle \quad (20)$$

The justification of this approximation will be discussed later.

With the approximation (20), (19) becomes

$$i\hbar \dot{G}_{ML}^- = -E_0 G_{ML}^- + 2\langle b^0 \rangle \sum_{K \neq L} \phi(K - L) G_{MK}^+ \quad (21)$$

Equations 17 and 21 thus form a set of linear coupled differential equations, which can be solved by Fourier techniques. If we introduce the temporal Fourier transforms, $G_{ML}^\pm(\omega)$, by

$$G_{ML}^\pm(t - t') = \int_{-\infty}^{\infty} G_{ML}^\pm(\omega) e^{-i\omega(t - t')} d\omega \quad (22)$$

(9) See the review by D. N. Zubarev, *Usp. Fiz. Nauk*, **71**, 71 (1960); *Soviet Phys.-Usp.*, **3**, 320 (1960).

then (19) and (21) become

$$\omega \mathfrak{G}_{ML}^+ = -\frac{1}{\pi} \langle b^0 \rangle \delta_{ML} - \omega_0 \mathfrak{G}_{ML}^- \quad (23)$$

$$\omega \mathfrak{G}_{ML}^- = -\omega_0 \mathfrak{G}_{ML}^+ + 2 \langle b^0 \rangle \sum_{K \neq L} \phi(K-L) \mathfrak{G}_{MK}^+ \quad (24)$$

Introduce the spatial Fourier transforms $g_{\mathbf{q}}^{\pm}$, $\varphi(\mathbf{q})$

$$\mathfrak{G}_{ML}^{\pm} = \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{R}_M - \mathbf{R}_L)} g_{\mathbf{q}}^{\pm} \quad (25)$$

$$\delta_{ML} = \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{R}_M - \mathbf{R}_L)} \quad (26)$$

$$\phi(K-L) = \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{R}_K - \mathbf{R}_L)} \varphi(\mathbf{q}) \quad (27)$$

where the sums are over the first Brillouin zone of the reciprocal lattice. Then (23) and (24) are transformed into

$$\omega g_{\mathbf{q}}^+ = -\frac{1}{\pi} \langle b^0 \rangle - \omega_0 g_{\mathbf{q}}^- \quad (28)$$

$$\omega g_{\mathbf{q}}^- = -\omega_0 g_{\mathbf{q}}^+ + 2 \langle b^0 \rangle \varphi(\mathbf{q}) g_{\mathbf{q}}^+ \quad (29)$$

These equations are trivial to solve for $g_{\mathbf{q}}^+$

$$g_{\mathbf{q}}^+ = -\frac{\omega \langle b^0 \rangle}{\pi} \left(\omega^2 - \omega_0^2 + 2 \frac{\langle b^0 \rangle}{\hbar} \omega_0 \varphi(\mathbf{q}) \right)^{-1} \quad (30)$$

It may look as though we must now perform the inverse Fourier transforms on (30), but this is not the case. In the first place, we are more interested in the frequency dependence of the observed moment than its time dependence. Hence, by the convolution theorem for Fourier transforms, (9) is equivalent to

$$\langle \mathbf{P}_L(\omega) \rangle = 2\pi \left(\frac{-i\omega_0}{\hbar c} \right) \mathbf{X} \cdot \sum_M \mathbf{A}_M(\omega) \mathfrak{G}_{ML}^+(\omega) \quad (31)$$

Secondly, we are going to assume that \mathbf{A} is a transverse field (corresponding to radiation) of wave length long compared to a lattice spacing. This is the usual optical situation. This means the spatial Fourier components of \mathbf{A} , $\mathbf{A}(\mathbf{k})$, are appreciable only for $\mathbf{k} \approx 0$, and hence only $g_0^+(\omega)$ is involved in (31)

$$\langle \mathbf{P}_L(\omega) \rangle = 2\pi \left(\frac{-i\omega_0}{\hbar c} \right) \mathbf{X} \cdot \mathbf{A}_L g_0^+(\omega) \quad (32)$$

However, $\varphi(\mathbf{q})$, being a dipole sum, is not uniformly convergent near $\mathbf{q} = 0$,¹⁰ so that it looks as though g_0 is not well defined. This is not so. We note that since \mathbf{A} is transverse, the only component of the dipole moment \mathbf{X} which is operative is that component parallel to \mathbf{A} . Hence, only the transverse part of the Fourier transform of the tensor $\mathbf{T}_{LL'}$ enters into $\varphi(\mathbf{q})$, and $\varphi(0)$ is given by^{10,11}

$$\varphi(0) = -\frac{4\pi}{3} \rho \frac{|X|^2}{3} \quad (33)$$

The $|X|^2/3$ comes from the assumption that the square of the component of the dipole moment interacting with

(10) M. H. Cohen and F. Keffer, *Phys. Rev.*, **99**, 1128 (1955).

(11) P. W. Anderson, "Concepts in Solids," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 144.

a transverse field of given polarization is $1/3$ of the total dipole moment squared. We make this assumption because we want our model to simulate the behavior of the rare gases, whose lowest excited states are P states. Hence, they are triply degenerate, though only one component of the degenerate triplet will interact with radiation of a given polarization.

The vector potential, $\mathbf{A}(t)$, is related to the electric field, \mathbf{E} , by $\mathbf{E} = -(1/c)\dot{\mathbf{A}}$. Hence

$$\mathbf{E}_L(\omega) = -\frac{i\omega}{c} \mathbf{A}_L(\omega) \quad (34)$$

and, from (32)

$$\langle \mathbf{P}_L(\omega) \rangle = -\frac{2\omega_0}{\hbar} \mathbf{E}_L(\omega) \frac{|X|^2 \langle b^0 \rangle}{3(\omega_0^2 - \omega^2)} \left(1 + \frac{2\omega_0 \langle b^0 \rangle}{\hbar(\omega_0^2 - \omega^2)} \frac{4\pi}{3} \rho \frac{|X|^2}{3} \right)^{-1} \quad (35)$$

where we have replaced $\mathbf{X}\mathbf{X}$ by $(|X|^2/3)\mathbf{1}$ in accordance with the discussion of the last paragraph.

Now the polarizability of a free atom in its ground state is

$$\alpha = \frac{2\omega_0}{3\hbar} \frac{|X|^2}{\omega_0^2 - \omega^2} \quad (36)$$

so that we finally have

$$\langle \mathbf{P}_L \rangle = -\frac{\langle b^0 \rangle \alpha \mathbf{E}_L}{1 + 4\pi \rho \alpha \langle b^0 \rangle / 3} \quad (37)$$

$\langle \mathbf{P}_L \rangle$ is the dipole moment of the atom at L . Thus, $\rho \langle \mathbf{P}_L \rangle$ is the polarization of the solid at L , so that

$$\rho \langle \mathbf{P}_L \rangle = \frac{n^2 - 1}{4\pi} \mathbf{E}_L \quad (38)$$

where n is the index of refraction. Substitution of (38) in (37) leads immediately to

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = -\langle b^0 \rangle \frac{4\pi}{3} \alpha \quad (39)$$

The physical significance of $\langle b^0 \rangle$ is that

$$\langle b^0 \rangle = 2f - 1 \quad (40)$$

where f is the probability that a given atom is excited in the true many body ground state of the system.

Evaluation of f .—To evaluate f , we consider the following Green's functions

$$U_{ML} = i\theta(t-t') \langle [b_M^+(t'), b_L(t)] \rangle \quad (41a)$$

$$V_{ML} = i\theta(t-t') \langle [b_M^+(t'), b_L^+(t)] \rangle \quad (41b)$$

The Green's functions U and V satisfy the equations

$$i\hbar \dot{V}_{ML} = -\hbar \langle b^0 \rangle \delta_{ML} \delta(t-t') + E_0 U_{ML} - \langle b^0 \rangle \sum_{K \neq L} \phi(L-K) (U_{MK} + V_{MK}) \quad (42)$$

$$i\hbar \dot{U}_{ML} = -E_0 V_{ML} + \langle b^0 \rangle \sum_{K \neq L} \phi(L-K) (U_{MK} + V_{MK}) \quad (43)$$

These equations are derived in exactly the same way as were eq. 17 and 21, and are also approximate since the factorization used in (19) has been used here also. By introduction of the space-time Fourier transforms

$u_q(\omega)$, $v_q(\omega)$ of U and V , just as above, we can easily solve (42) and (43). If we set, for compactness of notation

$$\mu_q^2 = \omega_0^2 - 2 \frac{\omega_0 \langle b^0 \rangle}{\hbar} \varphi(\mathbf{q}) \quad (44)$$

the solution is

$$u_q = -\frac{\langle b^0 \rangle}{4\pi} \left\{ \left(\frac{\mu_q}{2\omega_0} + \frac{\omega_0}{2\mu_q} + 1 \right) \frac{1}{\omega - \mu_q} - \left(\frac{\mu_q}{2\omega_0} + \frac{\omega_0}{2\mu_q} - 1 \right) \frac{1}{\omega + \mu_q} \right\} \quad (45)$$

The relevance of this formula is the following. Consider the correlation function $\langle b_M^+(t') b_L(t) \rangle$. This will have a Fourier transform, $J_{ML}(\omega)$

$$\langle b_M^+(t') b_L(t) \rangle = \int_{-\infty}^{\infty} J_{ML}(\omega) e^{-i\omega(t-t')} d\omega \quad (46)$$

The quantity f which we are trying to calculate is

$$f = \lim_{t \rightarrow t'} \langle b_M^+(t') b_M(t) \rangle = \frac{1}{N} \sum_{\mathbf{q}} \int_{-\infty}^{\infty} J_{\mathbf{q}}(\omega) d\omega \quad (47)$$

where $J_{\mathbf{q}}(\omega)$ is the spatial Fourier transform of $J_{MN}(\omega)$.

It is shown in the theory of Green's functions⁸ that

$$J_{\mathbf{q}}(\omega) = \lim_{\epsilon \rightarrow 0} \frac{i}{e^{\beta\omega} - 1} [u_{\mathbf{q}}(\omega + i\epsilon) - u_{\mathbf{q}}(\omega - i\epsilon)] \quad (48)$$

where $\beta = (kT)^{-1}$. From (48) and (45)

$$J_{\mathbf{q}}(\omega) = -\frac{\langle b^0 \rangle}{2} \frac{1}{e^{\beta\omega} - 1} \left\{ \left(\frac{\mu_q}{2\omega_0} + \frac{\omega_0}{2\mu_q} + 1 \right) \delta(\omega - \mu_q) - \left(\frac{\mu_q}{2\omega_0} + \frac{\omega_0}{2\mu_q} - 1 \right) \delta(\omega + \mu_q) \right\} \quad (49)$$

We need only consider the limit $|\beta\omega| \gg 1$ since $\hbar\omega_0 \gg kT$ for any reasonable temperature. In this limit

$$\frac{2f}{1 - 2f} = \frac{1}{N} \sum_{\mathbf{q}} \left[\frac{\mu_q}{2\omega_0} + \frac{\omega_0}{2\mu_q} - 1 \right] \quad (50)$$

The summand in (50) can be expanded in a series in $\varphi(\mathbf{q})/\hbar\omega_0$, using the definition (44): To more than sufficient accuracy we then have

$$\frac{2f}{(1 - 2f)^3} = \frac{1}{2N} \sum_{\mathbf{q}} \frac{\varphi^2(\mathbf{q})}{\hbar^2 \omega_0^2} \quad (51)$$

The summation over \mathbf{q} can be expressed in terms of nonoptical quantities by noticing that¹¹

$$\frac{1}{2N} \sum_{\mathbf{q}} \frac{\varphi^2(\mathbf{q})}{\hbar\omega_0} = \Delta E \quad (52)$$

where ΔE is the negative of the contribution to the binding energy of the crystal due to the attractive London forces, per particle. Hence

$$\frac{2f}{(1 - 2f)^3} = \Delta E/E_0 \quad (53)$$

Numerical Evaluation.— ΔE can be most easily approximated by summing the attractive part of the Lennard-Jones interaction, $-4\epsilon(\sigma/R)^6$, over the sites

of a face-centered cubic crystal. The result of such a summation is¹²

$$\Delta E = 2\epsilon \left(\frac{\sigma}{d_0} \right)^6 \times 14.454 \quad (54)$$

where ϵ and σ are the Lennard-Jones parameters and d_0 is the nearest-neighbor spacing. For argon we have used $\epsilon/k = 120^\circ\text{K}$., $\sigma = 3.41 \text{ \AA}$., and $d_0 = 3.83 \text{ \AA}$.,¹² from which $\Delta E = 0.149 \text{ e.v.}$ For argon, the lowest excitation energy is $E_0 = 11.6 \text{ e.v.}$ Hence, from (53)

$$2f = 0.0123 \quad (55)$$

and the Lorentz-Lorenz function $(n^2 - 1)/(n^2 + 2)\rho$ is 1.23% lower in the solid than in the dilute gas.

Amey and Cole³ have measured the Clausius-Mosotti function $(\epsilon - 1)/(\epsilon + 2)\rho$, and find a decrease of $(0.84 \pm 0.12)\%$ in going from the gas to the solid. The work of Jones and Smith shows a 1.7% decrease. This difference can probably be accounted for by dispersion. Our result is clearly of the right order of magnitude, although the simple model we have taken gives no dispersion for the quantity f .

For krypton, the static data of Amey and Cole³ show a decrease of the Clausius-Mosotti function of $(0.64 \pm 0.24)\%$. Our estimation yields 2.45%. We are unable to make any valid comparison with the measurements of Smith² since his data combined with the value¹³ 1.000427 for the index of refraction of krypton at STP yield a decrease of some 12%. This suggests that there may be something wrong with the data. Smith, in a private communication, has agreed with this comment and has said that he plans to redo the experiment at an early date.

III. Discussion

The theory presented here contains two important approximations. The first is the model used. The second is the linearization of the equations of motion of the Green's functions, exemplified by eq. 20.

Regarding the latter, we note that some such linearization, or truncation, is a practical necessity when using Green's function methods. The equation of motion of an n th order Green's function always involves a higher order Green's function (except for the trivial case of noninteracting particles). Problems of excitation in molecular crystals have sometimes been treated by approximating the b^+ and b operators by boson operators, *i.e.*, setting $[b_L^+, b_{L'}] = -\delta_{LL'}$.⁷ This is tantamount to setting $f = 0$, and would lead to a null result in our case. The approximation we have used is the next most complicated approximation; it is analogous to the procedure in self-consistent field theories, and leads to a nontrivial result.

The model used is, of course, oversimplified. Rare gas atoms have more than one excited state. However, in argon the first excitation has a large oscillator strength, so that we believe the model is certainly qualitatively valid. In the basic Hamiltonian (6), we have assumed that the excitations are tight-binding, or Frenkel-type, excitons. However, Knox¹⁴ has

(12) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 1040.

(13) Quoted in "Argon, Helium and the Rare Gases," Vol. 1, G. H. Cook, Ed., Interscience Publishers, New York, N. Y., 1961, p. 239.

(14) R. S. Knox, *Rad. Res.*, **20**, 77 (1963).

argued that the excitations are more like weak binding, or Wannier-type, excitons. We do not believe that this upsets the qualitative validity of the model.

We have also neglected overlap and lattice vibrations. The former would be expected to be of some importance in the solid, especially when the density is increased. This is reflected in our result; f increases with increasing density, whereas experimentally the Lorentz-Lorenz function increases with increasing density after the initial drop when the solid is formed.¹⁵

We therefore conclude that we have described correctly the main qualitative features of the physical situation. A considerably more complicated model would be necessary to handle all the secondary effects which are also operative.

(15) However, recent unpublished results of G. O. Jones and A. Eatwell, Queen Mary College, London, show a short rise in the Lorentz-Lorenz function from about 910 to 925 amagats, followed by a marked decrease extending to about 990 amagats.

The theory may certainly be classed as semiempirical, in that we have used experimental data on nonoptical properties to evaluate parameters in the final result. However, there are no adjustable parameters in the theory.

We conclude with a brief physical discussion of why the main result, eq. 39, is very reasonable. In the true ground state of the crystal, each atom has a certain amplitude for being excited. These virtual excitations are, in fact, the mechanism for producing the London forces which bind the crystal together, when looked at from the point of view of perturbation theory. Now an atom in an excited state has a negative polarizability, which is equal and opposite to the polarizability of an atom in its (unperturbed) ground state in our model. Since there are, on the average, Nf atoms in excited states, $N(1 - f)$ atoms in their ground states, the effective polarizability of an atom should be $(1 - 2f)\alpha$, which is exactly what occurs in eq. 39.

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Microwave Absorption and Molecular Structure in Liquids. LV. Intramolecular Structural Effects in the Dielectric Relaxation of Six Aromatic Compounds^{1,2}

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The dielectric constants and losses, at wave lengths of 1.3, 3.2, 10, and 25 cm. and 575 m. and temperatures of 20, 40, and 60° have been measured for anisole, *p*-dimethoxybenzene, phenylacetonitrile, *p*-xylylene cyanide, 1-(chloromethyl)naphthalene, and 1-naphthaleneacetonitrile in dilute benzene solution. The data have been used to calculate the dielectric relaxation times of the molecules. *p*-Dimethoxybenzene and *p*-xylylene cyanide relax by the rotation of the methoxy and acetonitrile groups, respectively, about their bonds to the ring. The results for anisole have been interpreted in terms of a molecular and an intramolecular relaxation process, while, although more than one relaxation process is evident in the case of phenylacetonitrile, no resolution could be effected. 1-(Chloromethyl)naphthalene and 1-naphthaleneacetonitrile show no evidence of intramolecular group rotation, confirming the steric blocking of group rotation by the hydrogen in the 8-position indicated by molecular models.

Many molecules have been observed to possess short dielectric relaxation times because of the existence of internal modes of relaxation, which are somewhat shielded from the external molecular environment. The present paper presents measurements in the kilomegacycle region on six aromatic compounds containing the CH₂Cl, CH₂CN, and the OCH₃ groups as a means of investigating the intramolecular rotational freedom of polar groups and the effects of steric repulsion.

Experimental

Apparatus.—The apparatus and various methods of measurement have been described in previous papers.³⁻⁵

Purification of Materials.—Anisole, purchased from Eastman Kodak Co., was fractionally distilled under atmospheric pressure. The fraction condensing at 154° gave an index of refraction, n_D^{20} , of 1.5179, which compares with a literature value⁶ of 1.5179.

1-(Chloromethyl)naphthalene, purchased from Eastman Kodak Co., was fractionally distilled under a reduced pressure of 10 mm. The fraction condensing between 146 and 147° was collected. 1-Naphthaleneacetonitrile, obtained from Eastman Kodak Co., was fractionally distilled under a reduced pressure of 13 mm. The fraction collected between 182 and 183° gave an index of refraction, n_D^{20} , of 1.6205. Phenylacetonitrile, purchased from Eastman Kodak Co., was fractionally distilled under reduced pressure. The distillate gave an index of refraction, n_D^{20} , of 1.5206, which compares with a literature value⁷ of 1.5211. *p*-Xylylene cyanide, obtained from Aldrich Chemical Co., was recrystallized once from ether and twice from benzene and dried in an Abderhalden pistol. The purified material gave a melting point of 98°, which compares with a literature value of 98°. *p*-Dimethoxybenzene, purchased from Eastman Kodak Co., was recrystallized four times from benzene and dried under vacuum in an Abderhalden pistol. The purified material gave a melting point of 56.2°, which compares with a literature value⁸ of 56°. Benzene, purchased from the Allied Chemical Corp., was of reagent grade, thiophene-free quality. It was dried over Drierite and used without further purification.

Results

The experimental results obtained from measurements in benzene solution were treated in the manner previously described.⁹ The dielectric constant and

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(2) This paper represents part of the work submitted by E. Forest to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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