was found not to be fulfilled except in the limit of elastic collisions. A relation connecting the bulk viscosity with the self-diffusion coefficient and the shear viscosity was presented.

The applicability of the proposed model as a model for planar molecules was analyzed by numerical calculations on models for C_2H_4, C_6H_6, and SO_2. No final conclusions could be drawn due to the lack of experimental data. Qualitatively the predicted results seem reasonable.

Note added in proof: The theory of nonspherical molecules of Curtiss *et al.*[1–3] has been rederived in a later paper by Curtiss and Dahler.[19] A difference from the original theory[1–3] appeared in the general form of the Boltzmann-type equation. Equivalence with the original theory was established for the SPHCL model. For the C–P model used here the question of equivalence has not been analyzed. Certain corrections to the Chapman–Enskog-solution method used in Refs. 1–3 are given in the papers.[4–6] They may be of importance especially for the heat-conductivity coefficient, but are not included in this paper. The author thanks Professor J. S. Dahler for a discussion of these points.

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Optical Model Calculation of the Electronic States of Mixed Disordered Systems*

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This paper reports a study of the normal modes of simple disordered systems using a dispersion oscillator model with dipolar coupling for the unperturbed electronic states. An equation is derived for the normal-mode frequencies and for the excitation amplitudes of the system. This equation displays the local structure of the fluid in an explicit way. The nature of the resonance and localized impurity modes is discussed in the particular case of an isotopically disordered uniform system. Finally, the contribution of the thermal motion of the atoms to the damping of the normal modes is discussed. The significance of the results and the relationship to other formal studies of disordered systems is briefly considered.

I. INTRODUCTION

The structure of the energy spectrum of a disordered system has been extensively investigated in recent years. We regard one of the most remarkable achievements of these investigations to be the construction of formal methods which permit analysis of the phonon spectrum of a substitutionally disordered crystal; similar methods can be used to describe electronic excitations in a disordered crystal.[1–3] However, the success of these formal methods is limited by technical difficulties to the discussion of planewavelike electronic states, and in mixed crystals to the range of low concentration of impurity atoms. Moreover, the analyses published usually fail to take into account the contribution of the lattice vibrations to the shift and the damping of the electronic excitation waves.

A theory of the electronic states of mixed molecular crystals, including the influence of the lattice vibrations on the electronic states in the weak coupling limit, has been constructed by Sommer and Jortner using the one-particle Green's function method.[4] One important generalization of the Sommer–Jortner analysis with respect to the previous theories[1–3] is the discussion of bound electronic states, such as the electronic states of organic molecular crystals, which can be adequately described in terms of the Frenkel excitation model.[5] All of the extant theories predict an impurity-induced splitting of the unperturbed electronic states of the completely ordered crystal and the appearance, under certain conditions, of new localized impurity states. The usual proofs use an expansion in powers of the concentration or neglect simultaneous interactions involving more than two impurity atoms. Because of the use of these approximations, doubts have been expressed concerning both the structure and the existence of localized modes, as well as about other of the properties of the spectrum of heavily doped systems. For the low-density approximation cannot be used to de-

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* This paper belongs to the recent series of studies on the theory of excitons in liquids and other disordered systems by the authors and J. Popielawski.

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scribe the impurity subsystem when the concentration is large. The reason that the low-density approximation has not yet been substantially improved is related to the great mathematical complexity involved in the use of the Green's function method for systems of arbitrary structure. In particular, the absence of obvious parameters of smallness prohibits the application of perturbation theoretic techniques to the description of dense disordered systems.

Now, one might expect that the use of simplified models, representing only the essential properties of the system under consideration, will permit a more complete mathematical treatment of the problem and lead to results which will be valid over a wide range of values of the parameters involved. Such simplified models (in the main restricted to one-dimensional systems) have been extensively investigated in the past, both for the lattice-vibration problem[6,7] and in studies of the structure of the electronic spectrum.[8–10]

Among the more realistic three-dimensional models we mention a generalization of Fano's model of a cubic lattice of dispersion oscillators[11] to liquids or, more generally, to systems in which the thermal motion of the atoms cannot be neglected. This generalization, which has been described in a recent series of papers,[12,13] has provided a convenient starting point for the discussion of the structure of localized excited electronic states in liquids. An essential feature of the original model, as well as of its generalization, is the existence of resonance coupling between the dispersion electrons (oscillators), which coupling is treated in the dipole approximation. We believe that this approximation accurately represents the behavior of the system under the influence of perturbations of long wavelength. Since the typical electromagnetic excitations in the visible or ultraviolet region have wavelengths which are large relative to the near-neighbor separation, it may be concluded that the model should give a satisfactory description of the optical properties of the system.

The purpose of the present paper is to discuss the properties of the electronic states of a disordered mixed system using the optical model described above. In Sec. II we set up the equations of motion for the excitation amplitudes of the dispersion electrons of a two-component system, assuming that for each isolated component a generalized Fano model provides a satisfactory description. In Sec. III we consider the properties resulting from a completely random distribution of the two components of the system. The equations found are relatively simple and yield a dispersion relation for the excitation frequencies (normal modes) which takes full account of the local structure and which contains contributions from arbitrary orders in the concentrations of the two components. This dispersion relation is fully analyzed in a particular case, and the existence of local modes is established for arbitrary values of the concentrations. Section IV is devoted to the discussion of the influence of the thermal motion of the atoms on the frequencies of the electronic excitations. In a final section, V, we discuss a number of possible generalizations of the analysis of Sec. IV along with some comments on the significance of the results derived in the previous sections.

II. EQUATIONS OF MOTION

We consider a system consisting of two isotropic components enclosed in a volume V. The N_1 atoms of mass M_1 of component 1 occupy the positions $\mathbf{r}_{i_1}$ (which may depend on time) and the N_2 impurity atoms of mass M_2 occupy the positions $\mathbf{r}_{i_2}$. We allow the number densities $c_i=(N_i/V)$ to be arbitrarily large. At each atom there are a number of electrons of mass m, represented by dispersion oscillators. Let the charges, the amplitudes, and the natural dispersion frequencies of these oscillators be $ef_n^{1/2}$, a_n, ω_n $(n=1, \cdots, s_1)$ and $e\rho_\nu^{1/2}$, b_ν, ϕ_ν $(\nu=1, \cdots, s_2)$ for components 1 and 2, respectively. As usual, the coefficients $f_n^{1/2}$, $\rho_\nu^{1/2}$ are the oscillator strengths for the corresponding electronic transitions. In the following only the dipole transitions will be considered to be important. Thus, the interatomic coupling within each component is given by[11–13]:

$$V_{11}=\sum_{ni_1<n'j_1} f_{ni_1}{}^{1/2} f_{n'j_1}{}^{1/2} a_{ni_1} a_{n'j_1} u_{11}(\mathbf{r}_{i_1j_1}, \boldsymbol{\lambda}, \mathbf{p}) \qquad (2.1)$$

$$V_{22}=\sum_{\nu i_2<\nu' j_2} \rho_{\nu' i_2}{}^{1/2} \rho_{\nu' j_2}{}^{1/2} b_{\nu i_2} b_{\nu' j_2} u_{22}(\mathbf{r}_{i_2j_2}, \boldsymbol{\lambda}, \mathbf{p}). \qquad (2.2)$$

Here $u_{ii}=\mathcal{O}(e^2)$ is the spatial part of the resonance dipole–dipole interaction, which depends on the distance $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, on a polarization vector $\mathbf{p}$, and on a vector $\boldsymbol{\lambda}$ characterizing the wavelength of the transitions.

In general, the interatomic coupling between the two components will not be represented by a resonance interaction. At the present stage of our analysis it suffices to express this intercomponent interaction in the form

$$V_{12}=V_{21}=\sum_{ni_1,\nu j_2} U_{12}(\mathbf{r}_{i_1j_2}, a_n, b_\nu). \qquad (2.3)$$

In addition to the energies V_{ij} $(i, j=1, 2)$ the system is characterized by the "unperturbed" Hamiltonian

$$H_0=H_{\mathrm{vib}}+H_k+H_h, \qquad (2.4)$$

where H_{vib} is the kinetic energy of thermal motion of the atoms, H_k is the kinetic energy of the dispersion

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electrons,

$$H_k=\sum_{ni_1}\tfrac{1}{2}(m\dot{a}_{ni_1}{}^2)+\sum_{\nu i_2}\tfrac{1}{2}(m\dot{b}_{\nu i_2}{}^2), \tag{2.5}$$

and H_h is the harmonic energy of interaction of the dispersion electrons with their own nuclei:

$$H_h=\sum_{ni1}\tfrac{1}{2}(m\omega_n{}^2a_{ni_1}{}^2)+\sum_{\nu i2}\tfrac{1}{2}(m\phi_\nu{}^2b_{\nu i}{}^2). \tag{2.6}$$

The total energy of the system is, of course,

$$H=H_0+V=H_0+V_{11}+V_{22}+V_{21}. \tag{2.7}$$

From Eqs. (2.1)–(2.7) we deduce the following set of classical equations of motion for the dispersion-oscillator amplitudes:

$$\ddot{a}_{ni_1}=-\omega_n{}^2a_{ni_1}-(f_n{}^{1/2}/m)\sum_{i_1\neq j_1}\sum_m f_m{}^{1/2}a_{mj_1}u_{11}(\mathbf{r}_{i_1,j_1})-(f_n{}^{1/2}/m)\sum_{j_2}\sum_\mu(\partial U_{12}/\partial a_{ni_1}), \tag{2.8}$$

$$b_{\nu i_2}=-\phi_\nu{}^2b_{\nu i_2}-(\rho_\nu{}^{1/2}/m)\sum_{j_1}\sum_m(\partial U_{19}/\partial b_{\nu i_2})-(\rho_\nu{}^{1/2}/m)\sum_{i_2\neq j_2}\sum_\mu\rho_\mu{}^{1/2}b_{\mu j_2}u_{22}(\mathbf{r}_{i_2j_2}). \tag{2.9}$$

It is convenient to express Eqs. (2.8) and (2.9) in terms of the microscopic configurational distribution functions, $w_{ij}{}^{(2)}$. The result is

$$\frac{m}{f_n{}^{1/2}}(\ddot{a}_{ni_1}+\omega_n{}^2a_{ni_1})=-\sum_m f_m{}^{1/2}\int d\mathbf{r}_{j_1}a_{mj_1}u_{11}w_{11}{}^{(2)}-\sum_\mu\int d\mathbf{r}_{j_2}\frac{\partial U_{12}}{\partial a_{ni_1}}w_{12}{}^{(2)}, \tag{2.10}$$

$$\frac{m}{\rho_\nu{}^{1/2}}(b_{\nu i_2}+\phi_\nu{}^2b_{\nu i_2})=-\sum_m\int d\mathbf{r}_{j_1}\frac{\partial U_{12}}{\partial b_{\nu i_2}}w_{12}{}^{(2)}-\sum_\mu\rho_\mu{}^{1/2}\int d\mathbf{r}_{j_2}b_{\mu j_2}u_{22}w_{22}{}^{(2)}. \tag{2.11}$$

The structure of this system of equations simplifies considerably in the case that the intercomponent interaction term V_{12} may be represented as a dipole interaction. In particular, this covers the physically most interesting case of an isotopic mixture of two components. Alternatively, one might express V_{12} in the following form:

$$V_{12}=V_{12}{}^d+v_{12}, \tag{2.12}$$

where $V_{12}{}^d$ is a dipole–dipole interaction and v_{12} is at least cubic in the oscillator amplitudes $\{a\}$ and $\{b\}$. Since we are interested primarily in the normal mode structure of our system we may use the part $V_{12}{}^d$ of V_{12} as a starting point in our calculation and introduce later the additional term v_{12} which will contribute to a phase mixing of the normal modes derived from the equations with $V_{12}{}^d$ alone. Here we use the part $V_{12}{}^d$ only and refer the reader to Sec. V and to Ref. 13 for further comments on the role of the additional term v_{12}.

When V_{12} is replaced by $V_{12}{}^d$, Eqs. (2.10) and (2.11) become linear in the amplitudes. We may, therefore, seek solutions of the form

$$a_{ni}=\exp(-i\Omega_\theta t)\sum_k\tilde{a}_{nk}\exp(i\mathbf{k}\cdot\mathbf{r}_i),$$
$$b_{\nu j}=\exp(-\Omega_\theta t)\sum_k\tilde{b}_{\nu k}\exp(i\mathbf{k}\cdot\mathbf{r}_j), \tag{2.13}$$

where θ stands for the set of parameters $\{\lambda, \mathbf{p}\}$ of the resonance interaction[14] and Ω_θ is an average response frequency. Substituting (2.13) into Eqs. (2.10) and (2.11) and passing to relative and center-of-mass coordinates, we finally obtain the system of equations

$$\frac{m}{f_n{}^{1/2}}(-\Omega_\theta{}^2+\omega_n{}^2)\tilde{a}_{nk}=-\frac{\mathcal{V}}{8\pi^3}\int d\mathbf{k}'d\mathbf{k}''\int d\mathbf{R}d\mathbf{r}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}]\exp[i(\mathbf{k}'-2\mathbf{k}''+\mathbf{k})\cdot\tfrac{1}{2}\mathbf{r}]S_{k'k''}{}^{11,2},$$

$$S_{k'k''}{}^{11,2}=\sum_m f_m{}^{1/2}\tilde{a}_{mk'}\tilde{u}_{11}(\mathbf{k}'',\theta)w_{11}{}^{(2)}(\mathbf{R},\mathbf{r})+\sum_\mu\rho_\mu{}^{1/2}\tilde{b}_{\mu k'}\tilde{u}_{12}(\mathbf{k}'',\theta)w_{12}{}^{(2)}(\mathbf{R},\mathbf{r}), \tag{2.14}$$

$$\frac{m}{\rho_\nu{}^{1/2}}(-\Omega_\theta{}^2+\phi_\nu{}^2)\tilde{b}_{\nu k}=-\frac{\mathcal{V}}{8\pi^3}\int d\mathbf{k}'d\mathbf{k}''\int d\mathbf{R}d\mathbf{r}\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}]\exp[i(\mathbf{k}'-2\mathbf{k}''+\mathbf{k})\tfrac{1}{2}\mathbf{r}]S_{k'k''}{}^{22,1},$$

$$S_{k'k''}{}^{22,1}=\sum_m f_m{}^{1/2}\tilde{a}_{mk'}\tilde{u}_{12}(\mathbf{k}'',\theta)w_{12}{}^{(2)}(\mathbf{R},\mathbf{r})+\sum_\mu\rho_\mu{}^{1/2}\tilde{b}_{\mu k'}\tilde{u}_{22}(\mathbf{k}'',\theta)w_{22}{}^{(2)}(\mathbf{R},\mathbf{r}), \tag{2.15}$$

where we have defined

$$\tilde{u}_{ij}(\mathbf{k})=(2\pi)^{-3/2}\int d\mathbf{r}\exp(i\mathbf{k}\cdot\mathbf{r})u_{ij}(\mathbf{r}). \tag{2.16}$$

In the next section this system of equations is analyzed for the interesting case of a uniform distribution of components.

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[14] In the case of disordered systems, such as those formed from the mixing of two components, the translational symmetry is destroyed. For this reason, a superposition of plane waves of the form (2.13) becomes necessary to describe the amplitudes. In the particular case of a superlattice, a form of translational symmetry is restored and a single term in the **k** sum is sufficient in Eq. (2.13).

III. THE DISPERSION RELATION IN THE LIMIT OF A UNIFORM DISTRIBUTION OF COMPONENTS

We assume that the two components are distributed completely randomly, so that the distribution functions $w_{ij}^{(2)}$ are independent of the center-of-mass coordinate **R**. In this case the **R** and **k′** integrations in Eqs. (2.14) and (2.15) can be performed immediately. After integration these integral equations become a set of algebraic equations:

$$\frac{m}{f_n^{1/2}}(-\Omega_\theta^2+\omega_n^2)\tilde{a}_{nk}=-\sum_m f_m^{1/2}\tilde{a}_{mk}\int d\mathbf{k}'\tilde{w}_{11}^{(2)}(\mathbf{k}'-\mathbf{k})\tilde{u}_{11}(\mathbf{k}')-\sum_\mu \rho_\mu^{1/2}\tilde{b}_{\mu k}\int d\mathbf{k}'\tilde{w}_{12}^{(2)}(\mathbf{k}'-\mathbf{k})\tilde{u}_{12}(\mathbf{k}'), \quad (3.1)$$

$$\frac{m}{\rho_\nu^{1/2}}(-\Omega_\theta^2+\phi_\nu^2)\tilde{b}_{\nu k}=-\sum_m f_m^{1/2}\tilde{a}_{mk}\int d\mathbf{k}'\tilde{w}_{12}^{(2)}(\mathbf{k}'-\mathbf{k})\tilde{u}_{12}(\mathbf{k}')-\sum_\mu \rho_\mu^{1/2}\tilde{b}_{\mu k}\int d\mathbf{k}'\tilde{w}_{22}^{(2)}(\mathbf{k}'-\mathbf{k})\tilde{u}_{22}(\mathbf{k}'), \quad (3.2)$$

where

$$\tilde{w}_{ij}^{(2)}(\mathbf{k})=(8\pi^3)^{-1}\int d\mathbf{r}\exp(i\mathbf{k}\cdot\mathbf{r})w_{ij}^{(2)}(\mathbf{r}). \quad (3.3)$$

In order to obtain the frequency Ω_θ from the above equations it is convenient to use the set of auxiliary variables

$$X=\sum_n f_n^{1/2}\tilde{a}_{nk}, \quad (3.4)$$

$$Y=\sum_\nu \rho_\nu^{1/2}\tilde{b}_{\nu k}. \quad (3.5)$$

We first define the quantities γ_i and C_{ij} by the following relationships:

$$\gamma_1(\Omega_\theta)=m^{-1}\sum_n[f_n/(\omega_n^2-\Omega_\theta^2)],$$

$$\gamma_2(\Omega_\theta)=m^{-1}\sum_\nu[\rho_\nu/(\phi_\nu^2-\Omega_\theta^2)], \quad (3.6)$$

$$C_{ij}(\mathbf{k},\theta)=\int d\mathbf{k}'\tilde{w}_{ij}^{(2)}(\mathbf{k}'-\mathbf{k})\tilde{u}_{ij}(\mathbf{k},\theta). \quad (3.7)$$

The quantities X and Y may be shown to satisfy the following algebraic equations in terms of γ_1, γ_2, and C_{ij}:

$$X=-\gamma_1C_{11}X-\gamma_1C_{12}Y, \quad (3.8)$$

$$Y=-\gamma_2C_1X-\gamma_2C_{22}Y, \quad (3.9)$$

and the secular equation of this system provides a dispersion relation from which the normal frequencies Ω_θ of the electronic excitations may be determined:

$$(1+\gamma_1C_{11})(1+\gamma_2C_{22})-\gamma_1\gamma_2C_{12}^2=0. \quad (3.10)$$

Equation (3.10) is of considerable generality. In fact, aside from the limitations introduced by the optical model the only additional assumption has been the neglect of the term v_{12} in the decomposition (2.12) of the interaction V_{12}. Thus, Eq. (3.10) is exact as regards the concentration dependence, contains the effects of the local structure of the fluid explicitly (via the coefficients C_{ij}), and also describes those effects of the thermal motion of the atoms which appear implicitly through the influence of $w_{ij}^{(2)}$ in C_{ij} and through the values of the frequencies ω_n and ϕ_ν upon which γ_1 and γ_2 depend. In order to simplify the discussion we now make the additional assumption that the two components forming the disordered system are isotopes of one another. In this case we expect that

$$\{f_n\}\equiv\{\rho_\nu\}. \quad (3.11)$$

Upon substituting these relations into Eq. (3.10) and taking definition (3.6) into account we obtain

$$\sum_{n=1}^{s}\frac{f_n}{m}\left(\frac{C_{11}}{\omega_n^2-\Omega_\theta^2}+\frac{C_{22}}{\phi_n^2-\Omega_\theta^2}+(C_{11}C_{22}-C_{12}^2)\sum_{m=1}^{s}\frac{f_m}{m}[(\omega_n^2-\Omega_\theta^2)(\phi_m^2-\Omega_\theta^2)]^{-1}\right)+1=0. \quad (3.12)$$

It is essential to remember that the structure coefficients C_{ij} depend on the polarization properties of the system. Using the definition (3.7) and the fact that u_{ij} is a dipole–dipole interaction, it is inferred that these coefficients are either purely longitudinal, C_l, or purely transverse, C_t.

Equation (3.13) is to be compared with the dispersion relation found in Ref. 11–13:

$$\sum_{n=1}^{s}\frac{f_n}{m}(\omega_n^2-\Omega_\theta^2)^{-1}=-[B_{11}(\theta)]^{-1},\text{ etc.,} \quad (3.13)$$

where the B_{ii} are the counterparts of the C_{ii} in the case of pure substances. It is seen that the presence of the two components leads to the existence of additional solutions of the dispersion relation. Alternatively, each of the "unperturbed" excitation modes of the single component may be said to split into two modes as a result of the presence of the impurities.[5,15] The important point to note is that Eq. (3.13) provides a value for this splitting in terms of the local structure and the properties of thermal excitations of the system, and is independent of any assumption of low-impurity density. It is instructive to give a detailed analysis of Eq. (3.13) in the neighborhood of a single resonance. We obtain,

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then,

$$\frac{\bar{C}_{11}}{\omega_n^2-\Omega_\theta^2}+\frac{\bar{C}_{22}}{\phi_n^2-\Omega_\theta^2}+\frac{(\bar{C}_{11}\bar{C}_{22}-\bar{C}_{12}^2)}{(\omega_n^2-\Omega_\theta^2)(\phi_n^2-\Omega_\theta^2)}+1=0, \tag{3.14}$$

where

$$\bar{C}_{ij}=(f_n/m)C_{ij}. \tag{3.15}$$

We first express Eq. (3.14) in terms of the unperturbed excitation frequencies Ω_0, Z_0, of each of the two components in the absence of the other. Using Eq. (3.13) we obtain

$$2\Omega_\theta^2=[\Omega_0^2+Z_0^2+\Delta_{11}+\Delta_{22}]$$
$$\pm[4\bar{C}_{12}^2+(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})^2]^{1/2}, \tag{3.16}$$

where we have defined

$$\Delta_{ii}=\bar{C}_{ii}-\bar{B}_{ii},$$
$$\bar{B}_{ii}=(f_n/m)B_{ii}. \tag{3.17}$$

Obviously the quantities Δ_{ii} depend on the differences in structure of the configurational distribution functions of components 1 and 2 in the binary mixture and in the pure substance.

Let $\Omega_{\theta+}^2$, $\Omega_{\theta-}^2$ be the two values of Ω_θ^2 given by Eq. (3.16). ($\theta\pm$ refer to the longitudinal and transverse modes.) The following sum rule is immediately deduced:

$$\Omega_{\theta+}^2+\Omega_{\theta-}^2=\Omega_0^2+Z_0^2+(\Delta_{11}+\Delta_{22}). \tag{3.18}$$

It is important to investigate the positions of $\Omega_{\theta\pm}$ relative to the frequencies in the unperturbed system, Ω_0 and Z_0. It is found that the relationship between the perturbed and unperturbed frequencies depends on the importance of the interaction term $\bar{C}_{12}$, as well as on the differences in spatial distribution of the two components in the mixture and in the pure substance. In Eq. (3.16) these differences are accounted for by the quantities Δ_{ii}. To illustrate the interplay between these different factors we consider the form of Eq. (3.16) in certain specific cases.

(a) We assume that the two components are regularly distributed to form a rigid superlattice and that their concentrations are equal. It follows that $\Delta_{11}=\Delta_{22}$ (see Ref. 11 and 12). It also follows that $\bar{C}_{11}=\bar{C}_{22}=\frac{1}{2}\bar{B}=\bar{C}_{12}$. Equation (3.16) becomes, in this case,

$$2\Omega_\theta^2=\Omega_0^2+Z_0^2-\bar{B}\pm[\bar{B}^2+(\Omega_0^2-Z_0^2)]^{1/2}. \tag{3.19}$$

It is easy to find upper and lower bounds for the quantities $\Omega_{\theta+}^2$ and $\Omega_{\theta-}^2$, respectively. Using the convention $\Omega_0^2>Z_0^2$ we obtain

$$\Omega_{\theta+}^2\leq\Omega_0^2-\tfrac{1}{2}\bar{B}+\tfrac{1}{2}|\bar{B}|, \tag{3.20}$$

$$\Omega_{\theta-}^2\geq Z_0^2-\tfrac{1}{2}\bar{B}-\tfrac{1}{2}|\bar{B}|. \tag{3.21}$$

For longitudinal excitations one has $\bar{B}>0$, whereas for transverse excitations $\bar{B}<0$.[11,12] We have thus shown that, both in the longitudinal and in the transverse cases, the normal modes of the unperturbed system are split into two components.[16,17] In the longitudinal case one of these modes may lie below the "plasmon band" of the unperturbed system but presumably within the "exciton band" since $\Omega_{0l}^2>\Omega_{0t}^2$. The other longitudinal mode and the two transverse modes all lie within the exciton band or the plasmon band and eventually decay into the quasicontinuum of states belonging to these bands. We conclude that in the case of an isotopically disordered rigid superlattice there cannot appear any localized modes as a result of an impurity substitution.

(b) The example of a rigid superlattice discussed above shows the importance of the influence of the thermal motion of the atoms upon the nature of the modes arising as a result of an impurity splitting. Thus, whenever the system is not rigid one always has $\omega_n^2\neq\phi_n^2$. Moreover, the simple relationships between $\bar{B}$, $\bar{C}$, and Δ used above do not hold and the distribution of normal frequencies may be markedly different. In the next section we present a systematic discussion of the influence of the thermal motion on the electronic spectrum. Here we wish to comment on a particular circumstance which may arise when nonrigid isotopically disordered lattices or two-component liquids are considered. Consider a case where the interaction term $|\bar{C}_{12}|$ is much larger than the terms $|\bar{B}_{ii}|$,$|\bar{C}_{ii}|$, $|\Omega_0^2-Z_0^2|$. Equation (3.16) may then be expanded in the smallness parameter $(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})/2\bar{C}_{12}$. The first-order result is

$$\Omega_{\theta+}^2=\tfrac{1}{2}(\Omega_0^2+Z_0^2)+\tfrac{1}{2}(\Delta_{11}+\Delta_{22}+2|\bar{C}_{12}|)$$
$$-[(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})/8|\bar{C}_{12}|], \tag{3.22}$$

$$\Omega_{\theta-}^2=\tfrac{1}{2}(\Omega_0^2+Z_0^2)+\tfrac{1}{2}(\Delta_{11}+\Delta_{22}-2|\bar{C}_{12}|)$$
$$-[(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})/8|\bar{C}_{12}|]. \tag{3.23}$$

Since the separation between Ω_0^2 and Z_0^2 depends on $\bar{B}_{ii}$ only, and since $|\bar{C}_{12}|$ is much larger than these terms, we conclude that

$$\Omega_{\theta-}^2<Z_0^2. \tag{3.24}$$

There exists, therefore, a transverse mode lying below the "exciton band" of the unperturbed systems, in addition to a second transverse mode $\Omega_{\theta+}^2$ lying above or within the band of excited states. The former may thus be described as a localized mode and the latter as a resonance mode. In Eqs. (3.22) and (3.23) the band structure and the density dependence of both kinds of modes is exhibited in the factors Δ_{ii} and $\bar{C}_{12}$ which have

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[16] In the special case $\omega_n^2=\phi_n^2$ one also has $\Omega_0^2=Z_0^2$ and Eq. (3.19) yields a single solution:

$$\Omega_t^2=\Omega_{0t}^2-\tfrac{1}{2}\bar{B}-\tfrac{1}{2}|\bar{B}|,$$
$$\Omega_l^2=\Omega_{0l}^2-\tfrac{1}{2}\bar{B}+\tfrac{1}{2}|\bar{B}|.$$

In the particular example of the rigid superlattice this yields $\Omega_t^2=\Omega_{0t}^2$, $\Omega_l^2=\Omega_{0l}^2$, i.e., the modes are not split as a result of the isotopic substitution.

[17] We recall that the existence of this mode has been established here under the condition that the system is in the neighborhood of a resonance.

been defined previously. It should be emphasized that, apart from the assumption of large $|\bar{C}_{12}|$, no additional approximation has been made in deducing this result. In particular, no restrictions have been imposed on the range of the impurity density.

In the opposite limit, when $|\bar{C}_{12}|$ is small compared to $|\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22}|$, we obtain the following result:

$$\Omega_{\theta+}^2=\Omega_0^2+\Delta_{11}+(|\bar{C}_{12}|^2/|\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22}|), \quad (3.25)$$

$$\Omega_{\theta-}^2=Z_0^2+\Delta_{22}-(|\bar{C}_{12}|^2/|\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22}|). \quad (3.26)$$

For the transverse modes it can be shown from Refs. 11 and 12 that $\Delta_{11}\geq 0$, $\Delta_{22}\geq 0$. It follows that the two split transverse modes lie within or above the "exciton band." However, in the particular case of vanishingly small-impurity concentration one has $\Delta_{11}\cong 0$, i.e., the normal mode that may lie above the band at finite concentrations is now pushed into the "exciton band." As for the longitudinal modes, for which $\Delta_{ii}\leq 0$, one can see that both lie within or below the "plasmon band," but again not below the exciton band.

From the above discussion we see that in a nonrigid lattice the existence of localized modes depends on the strength of the coupling term $|\bar{C}_{12}|$ as well as on the impurity concentration. The interplay between these two factors becomes more subtle in the case of small $|\bar{C}_{12}|$, whereas for large $|\bar{C}_{12}|$ the structure of the spectrum does not depend very critically on the magnitude of the concentration.

IV. SCATTERING BY THERMAL EXCITATIONS

Thus far our analysis has been concerned with the derivation of the dispersion relation (3.16) for a mixed disordered system, and with the properties arising from the multicomponent nature of the system. In performing this calculation we have neglected the influence of the interaction between an excited dispersion electron and the surrounding atoms. [This is obvious from the equations of motion (2.10) and (2.11) for the electron excitation amplitudes.] As a result of this approximation we have derived expressions which describe the excitation frequency Ω_θ as a real quantity. Or, using Eq. (2.13), it may be said that we have neglected the damping of the collective electronic excitations arising from the scattering between an excited electron and the neighboring atoms undergoing thermal motion.[18]

In Ref. 13 we have presented systematic approaches to the calculation of the shift and the damping of excitation waves arising from the thermal motion in a liquid. Because of their generality the methods developed therein can also be applied to the problem discussed in this paper. In order to keep the formalism in as simple a form as possible, we prefer to present here still another approach. The new approach, which has considerable intrinsic interest, is suggested naturally by the very use of the optical model (see also the comment in Ref. 12). Thus, instead of describing the free-atom electrons as undamped dispersion oscillators, we introduce a damping and then couple the damped oscillators through the dipole field considered in Sec. 11. The damping coefficient will then be appropriately related to the local structure of the system. We expect that this phenomenological approach, which is closely related to the idea underlying the polariton model, will permit a straightforward and simple estimate to be made of the damping of the collective excitations described in Sec. III. It will not be found necessary to introduce concepts and methods not already used in the discussion of the first parts of this paper.

When the free-atom electrons are described as damped oscillators the equations of motion (3.1) and (3.2) are modified.[19] The new system of equations reads

$$\frac{m}{f_n^{1/2}}(-\Omega_\theta^2+\omega_n^2+i\Omega_\theta\gamma_n)\tilde{a}_{nk}=-\sum_m f_m^{1/2}\tilde{a}_{mk}\int d\mathbf{k}'\tilde{w}_{11}^{(2)}(\mathbf{k}'-\mathbf{k})\tilde{u}_{11}(\mathbf{k}')-\sum_\mu \rho_\mu^{1/2}\tilde{b}_{\mu k}\int d\mathbf{k}'\tilde{w}_{12}(\mathbf{k}'-\mathbf{k})u_{12}(\mathbf{k}'), \quad (4.1)$$

$$\frac{m}{\rho_\nu^{1/2}}(-\Omega_\theta^2+\phi_\nu^2-i\Omega_\theta\delta_\nu)\tilde{b}_{\nu k}=-\sum_m f_m^{1/2}\tilde{a}_{mk}\int d\mathbf{k}'\tilde{w}_{12}^{(2)}(\mathbf{k}'-\mathbf{k})\tilde{u}_{12}(\mathbf{k}')-\sum_\mu \rho_\mu^{1/2}\tilde{b}_{\mu k}\int d\mathbf{k}'\tilde{w}_{22}^{(2)}(\mathbf{k}'-\mathbf{k})\tilde{u}_{22}(\mathbf{k}'), \quad (4.2)$$

where γ_n, δ_ν are the damping coefficients for the dispersion electrons of the free atoms of species 1 and 2, respectively. These coefficients can easily be related to observable quantities by using the expression for the dielectric constant of a system of noninteracting atoms[20]

$$\begin{aligned}\epsilon(\omega)&=1+\omega_p^2\sum_n[f_n/(\omega_n^2-i\omega\gamma_n-\omega^2)]\\&=\epsilon_1(\omega)+i\epsilon_2(\omega),\end{aligned} \quad (4.3)$$

where we have defined

$$\omega_p^2=4\pi\rho^{(1)}e^2/m \quad (4.4)$$

and $\rho^{(1)}$ is the fluid-number density.

Since we are constructing a first-order theory, we expand Eq. (4.3) in powers of $\omega\gamma_n/\omega_n^2$ and retain only the first nontrivial term. Moreover, we introduce an average damping coefficient γ which is the same for

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[18] The influence of the thermal motion of the atoms also appears indirectly in the coefficients Δ_{ii} and $\bar{C}_{12}$ of Eq. (3.16). This, however, cannot lead to a damping of the electronic excitations but only yields a shift of the frequency Ω_θ from its value in the absence of thermal motion (as in the example of a rigid superlattice discussed in Sec. III).

[19] The incorporation of the damping in the representation of the Hamiltonian presents problems which require further consideration. Within the framework of our quasiphenomenological approach, it suffices to introduce the damping directly in the equations of motion.

[20] See, e.g., W. Panofsky and M. Phillips, *Classical Electricity and Magnetism* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1956).

all the dispersion electrons. From Eq. (4.3) we obtain

$$\gamma=\epsilon_2/\omega\epsilon_1', \tag{4.5}$$

where

$$\epsilon_1'=(d/d\omega^2)\epsilon_1(\omega). \tag{4.6}$$

Using Eq. (4.5) and the stability conditions for the dielectric function[21] we obtain the general result

$$\gamma>0. \tag{4.7}$$

Proceeding in the same fashion we obtain

$$\delta=e_2/\omega e_1'>0, \tag{4.8}$$

where now $e=e_1+ie_2$ is the dielectric function of species 2.

It is now straightforward to generalize the dispersion relation obtained in Sec. III to the case of a system of damped oscillators. Considering again the case of isotopically related species in the neighborhood of a resonance, we obtain

$$2\Omega_\theta^2=(\Omega_0^2+Z_0^2+\Delta_{11}+\Delta_{22})\pm[4\bar{C}_{12}^2(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})^2]^{1/2} \\ -i\left[\left(\frac{\epsilon_2}{\epsilon_1'}+\frac{e_2}{e_1'}\right)\pm\left(\frac{\epsilon_2}{\epsilon_1'}-\frac{e_2}{e_1'}\right)\frac{(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})}{[4\bar{C}_{12}^2+(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})^2]^{1/2}}\right]. \tag{4.9}$$

In deriving this expression we have considered terms up to first order in the damping coefficient. Furthermore, the real and imaginary parts of the dielectric function are now taken at frequencies satisfying the dispersion relations in the absence of coupling between the two species. The remaining symbols have exactly the same interpretation as in Sec. III. In particular, Ω_0 and Z_0 are the exciton frequencies of species 1 and 2 in the absence of damping.

From Eq. (4.9) we obtain, again to first order in the damping coefficient,

$$\Omega_\theta=\Omega_{1\theta}+i\Omega_{2\theta}, \tag{4.10}$$

$$\Omega_{1\theta}=2^{-\frac{1}{2}}\{(\Omega_0^2+Z_0^2+\Delta_{11}+\Delta_{22})\pm[4\bar{C}_{12}^2+(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{12})^2]^{1/2}\}^{1/2}, \tag{4.11}$$

$$\Omega_{2\theta}=-(2^{3/2}\Omega_{1\theta})^{-1}\left[\left(\frac{\epsilon_2}{\epsilon_1'}+\frac{e_2}{e_1'}\right)\pm\left(\frac{\epsilon_2}{\epsilon_1'}+\frac{e_2}{e_1'}\right)\frac{(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})}{[4\bar{C}_{12}^2+(\Omega_0^2-Z_0^2+\Delta_{11}-\Delta_{22})^2]^{1/2}}\right]. \tag{4.12}$$

Combining Eq. (4.12) with Eqs. (2.13), (4.7), and (4.8) we conclude that $\Omega_{2\theta}<0$, i.e., that the collective electronic excitations are damped. The rate of damping is seen to be proportional to a combination of the ratios

$$\epsilon_2/\epsilon_1'\Omega_{1\theta} \quad \text{and} \quad \epsilon_2/\epsilon_1'\Omega_{1\theta}, \tag{4.13}$$

where $\Omega_{1\theta}$ is the real part of the frequency of the normal modes. As a result of the isotopic mixing the damping coefficient $\Omega_{2\theta}$ assumes two different values, corresponding to the two values of the real part $\Omega_{1\theta}$ which have been analyzed in Sec. III. In the case of the localized mode lying below the exciton band [cf. Eq. (3.24)], the frequency $\Omega_{1\theta}$ is small relative to the frequencies of the other modes, whereas the term of Eq. (4.12) proportional to $[(\epsilon_2/\epsilon_1')+(e_2/e_1')]$ is negligible.

We therefore conclude that whenever a localized mode exists, it is damped more rapidly than are the other modes.

A more satisfactory theory of the damping of the normal modes, again using the equations of motion as a starting point,[22] could be constructed as follows. It is known that the set of equations of motion (3.1) and (3.2) is equivalent to the Liouville equation

$$da/dt=-i\mathbf{L}a, \tag{4.14}$$

where $\mathbf{L}$ is the Liouville operator descriptive of the electrons. It has been shown recently[23] that a mechanical equation of this form may be transformed to a stochastic equation of the form

$$\frac{du}{dt}=\int_0^t dt'\psi(t-t')u(t')+R(t), \tag{4.15}$$

where u is an appropriate projection of a, and the kernel $\psi(t-t')$ is defined in terms of the Liouville operator $\mathbf{L}$ acting on the projection space. Finally, the inhomogeneous term R plays the role of a stochastic (Langevin) interaction. Clearly the solution of Eq. (4.15) will yield a dispersion relation which will describe the damping of the electronic excitations as a result of the many-body interactions. However, unless drastic approximations are made from the beginning of the analysis, finding the solution of Eq. (4.15) reduces to exactly the same problem as the one encountered in solving a kinetic equation in nonequilibrium statistical mechanics. An approximate treatment of this problem was given in Ref. 13. In this paper we

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[21] V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons* (Interscience Publishers, Inc., New York, 1966).

[22] As contrasted to the kinetic equation approach which was adopted in Ref. 13b.

[23] H. Mori, Progr. Theoret. Phys. (Kyoto) **33**, 423 (1965).

have followed a more phenomenological path in which the damping is introduced by anticipating the results one would expect to derive from a consistent statistical mechanical treatment of the problem. As a result, we have been able to derive explicit expressions for the damping rate in terms of the local structure of the fluid and the impurity concentration. These expressions are very simple and permit a number of qualitative predictions of interest to be made.

V. DISCUSSION

Aside from the limitations arising from the use of the optical model, which have been discussed in previous papers,[11–13] the main additional approximation which has been introduced in this paper is the use of damped oscillators to describe the damping of the collective electronic excitations. This representation of the damping mechanism has certain obvious disadvantages. From a purely conceptual point of view it is unsatisfactory because it anticipates the existence of damping instead of deducing it as a many-body effect from a general statistical mechanical treatment. From a more practical standpoint, it is clear that the use of individually damped dispersion electrons neglects the effects arising from the fluctuations of the instantaneous force acting on the electron. In other words, the approach described accounts only for the average field effects, which are described here self-consistently. At present it cannot be conjectured with any degree of certainty whether the formalism based on the neglect of fluctuations about the average force leads to a realistic representation of the dynamics of the bound electronic states.[24] It is likely that this formalism will be most useful in the limiting case in which there is small overlap between atomic states.

The principal motivation for using the damped oscillator model lies in the simplicity of the formalism. As we have shown in Sec. IV, one can easily derive expressions for the damping coefficient in which the local properties of the fluid and the influence of the impurity concentration are displayed explicitly and to all orders of the concentration. In addition, such explicit expressions make possible certain interesting predictions concerning the rates of damping of different impurity-induced modes. Even if the model neglects certain effects, as discussed earlier in this section, we anticipate that our qualitative predictions will not be completely altered by more refined descriptions of the damping. Finally, it is useful to recall that, aside from the approximate treatment outlined in Ref. 13a, the formal study of the damping of excitons in disordered systems other than molecular crystals has not yet led to formulas which can be simply applied to experimental data.[13b] In view of this situation, it is our openion that a reasonable model, such as the one introduced herein, will provide desirable insights into the nature of the damping of excitons arising from thermal motion in a disordered system.

In addition to the questions concerning the damped oscillator model, we wish to note again that the analysis presented in this paper has been restricted to the case of a uniform spatial distribution of both components. If the distribution of one of the species is nonuniform, the equations of motion are no longer algebraic, but become instead coupled linear integral equations with nondegenerate kernels. A Hilbert–Schmidt analysis of these equations reveals the existence of a whole spectrum of modes induced by the inhomogeneities. We do not present the details of this analysis here since we believe that the case of a uniform distribution describes correctly all physically interesting disordered systems.

Within the framework of the assumptions described above, there are two main points of interest in the analysis presented herein. First, the manner in which the disordered system is described is very general and is equally applicable to crystals and to liquids, depending only on the specific expressions we assign to the coefficients Δ_{ii}, $\bar{C}_{12}$, ϵ, and e appearing in Eqs. (3.16) and (4.12). Second, the real part of the normal mode frequency and the damping coefficient are both exact to all orders in the impurity concentration. In particular, the existence of localized modes is established here without the use of perturbation expansions.

When compared to previous general analyses of the electronic structure of disordered systems,[1–4] our analysis appears simpler and more restrictive from the point of view of the formal description of the spectrum. It is, however, more general in some other respects, since it avoids the use of perturbation theory and also deals with the damping of the collective excitations. A first-order theory of disordered systems, including electronic vibrational coupling in the absence of damping, has been constructed by Sommer and Jortner.[4] It is our opinion that the work presented herein also serves to illustrate some of the conjectures made in the Sommer–Jortner analysis. At the same time, it provides a bridge between the theory of excitons in liquids, developed in earlier papers of this series, and some phenomena specific to the electronic structure of mixed disordered systems which, until now, have been investigated only from the standpoint of solid-state theory.

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[24] The reader should note that in many other problems (plasma physics, equilibrium theory of fluids, etc.) average field theories have met with considerable success.