Delocalization of Vibrational Modes Caused by Electric Dipole Interaction

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The electric dipole interaction of vibrational modes destroys their localization. Real-space renormalization is constructed for the process of delocalization. The renormalization-group equation for the distribution of dipole parameters is similar to the Boltzmann kinetic equation. Conservation laws are found and an H theorem is proven. Stationary distributions form a six-parameter manifold of fixed points. The two-point dynamical correlation function has the form $t^{-1}F(t^{-1/3}\mathbf{r})$, where $F(\mathbf{x})$ is a universal function.

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Vibrational modes in a periodic crystal are propagating waves. If any disorder is introduced in the structure then some of the modes become localized. Localized states constitute a part of the spectrum near its upper bound. The number of localized states is small when the randomness is weak and it grows when the amount of defects increases. These results are well established for many models with short-range interaction.[1] Here we study the effect of the long-range electric dipole interaction on localized states. Only dielectric materials are considered since in metals this interaction is absent due to screening. It is known[2] that in systems of dimension d with $\mathbf{r}^{-\alpha}$ interaction, localization can exist only if $\alpha > d$. For $\alpha \le d$ the diverging number of resonances destroys localized states.[3] For $\alpha = d = 3$ the divergence is logarithmic, so the effect of delocalization is *weak*. This enables one to construct a renormalization group and study the effect within its framework.

Basic model.— We are interested in the part of the spectrum consisting of states localized in the absence of a long-range interaction. The Hamiltonian can be written[3] as

$$H=\sum_i \tfrac{1}{2}(p_i^2+\omega_i^2 q_i^2)+\sum_{i<j} q_i q_j D_{ij}\,, \tag{1}$$

$$D_{ij}=\frac{\mathbf{a}_i\cdot\mathbf{a}_j-3\mathbf{a}_i\cdot\mathbf{n}_{ij}\,\mathbf{a}_j\cdot\mathbf{n}_{ij}}{|\mathbf{r}_i-\mathbf{r}_j|^3}\,, \tag{2}$$

where $\mathbf{n}_{ij}=(\mathbf{r}_i-\mathbf{r}_j)/|\mathbf{r}_i-\mathbf{r}_j|$. The first sum stands for localized normal modes, while their long-range electric dipole interaction is given by the second term. The positions $\mathbf{r}_i$ of localized modes randomly (but uniformly) fill the space (denote their concentration by n). The ambiguity of the choice of $\mathbf{r}_i$ is of the order of the localization radius of the modes—this uncertainty is not crucial since the most important contribution comes from large scales where Eq. (2) for D_{ij} is correct. The vectors $\mathbf{a}_i$ are defined by $\mathbf{d}_i=\mathbf{a}_i q_i$, where $\mathbf{d}_i$ is the electric dipole caused by the displacement q_i of the ith oscillator. Random numbers ω_i^2 are assumed to be uncorrelated, uniformly filling the interval $[\Delta_-^2,\Delta_+^2]$, so their distribution function is $\nu(\omega)=2\nu\omega$ for $\Delta_- < \omega < \Delta_+$, and 0 otherwise $[\nu=(\Delta_+^2-\Delta_-^2)^{-1}]$. We take $\mathbf{a}_i$ as random uncorrelated vectors with some distribution function $f(\mathbf{a})$: $dP=f(\mathbf{a})d^3a$. Since our plan is to treat the second term of (1) as a perturbation we impose the condition $\lambda \ll 1$ $[\lambda=\langle \mathbf{a}^2\rangle \nu n,\ \langle \mathbf{a}^2\rangle=\int \mathbf{a}^2 f(\mathbf{a})d^3a]$. The important parameter λ plays the role of a coupling constant in this problem; its smallness is systematically used below.

Now we recall the arguments[3] showing that normal modes of the problem (1) cannot be localized. Consider two oscillators having frequencies ω_i,ω_j, positions $\mathbf{r}_i,\mathbf{r}_j$, and dipole parameters $\mathbf{a}_i,\mathbf{a}_j$. They are *in resonance* if $|D_{ij}| \gtrsim |\omega_i^2-\omega_j^2|$. If this condition is true the eigenmodes of the problem

$$H=\tfrac{1}{2}(p_i^2+\omega_i^2q_i^2)+\tfrac{1}{2}(p_j^2+\omega_j^2q_j^2)+D_{ij}q_iq_j$$

are not localized on one oscillator but are essentially nonzero at both places $\mathbf{r}_i,\mathbf{r}_j$. In order to establish the absence of localization we calculate $n_i(V)$, the average number of oscillators forming resonances with the ith one and contained in a sphere of volume V centered at $\mathbf{r}_i$. We find $n_i(V)=\int nP(\mathbf{r})d^3r$, where $P(\mathbf{r})$ is the probability for two oscillators separated by a distance $|\mathbf{r}|$ to form a resonance. Estimating $P(\mathbf{r})$ as $\nu\langle a^2\rangle/|\mathbf{r}|^3$ gives[3]

$$n_i(V)\simeq\lambda\ln(V)\,. \tag{3}$$

The divergence of $n_i(V)$ indicates delocalization. The weak (logarithmic) character of the divergence and $\lambda \ll 1$ suggests that one employs renormalization-group ideas.

Renormalization equation.— First, we discuss one property of resonance oscillators that will be basic for our approach. Let two oscillators (having labels i and j) form a resonance. Consider another oscillator (having label k) which is also in resonance with either of these two. Using the result (3) one can estimate the following probability:

$$P[\tfrac{1}{2}\le\Delta_{ji}/\Delta_{ki}\le 2]\simeq\lambda\ll 1\quad(\Delta_{pq}=|\mathbf{r}_p-\mathbf{r}_q|) \tag{4}$$

(here 2 can be replaced by any other number of order of 1). In other words, if three oscillators placed at r_i,r_j,r_k

are in resonance, then one side of the triangle (say, $|r_i - r_j|$) is much shorter than the other two ($|r_i - r_k|, |r_j - r_k|$). Moreover, our estimate implies $\log_2(\min[\Delta_{ki},\Delta_{kj}]/\Delta_{ij}) \simeq \lambda^{-1} \gg 1$ (again 2 can be replaced by any reasonable number). These results have clear meaning: *Since resonances are rarely distributed in the "logarithmic space," they are mainly formed by pairs of oscillators.* Triplet resonances usually do not appear—our estimate gives the probability $\simeq\lambda^2$ for such resonance to occur. Similar arguments show that the probabilities of finding resonances of k oscillators ($k=4,5,6,\ldots$) are $\simeq\lambda^{k-1}$. This should be compared with the probability of a pair resonance, $\simeq\lambda$. We see that pair resonances occur $\simeq\lambda^{2-k}$ times more frequently than k-oscillator resonances. This gives a basis for our method. Let us truncate the $\mathbf{r}^{-3}$ interaction at some R_0: Put $D_{ij}=0$ for all pairs (i,j) such that $|\mathbf{r}_i - \mathbf{r}_j| > R_0$. Find exact normal modes for this truncated Hamiltonian (denote them R_0 modes). Then replace R_0 by R_1 such that $R_1 \gg R_0$, but $\lambda \log_2(R_1/R_0) \ll 1$. Find R_1 modes and consider them as linear combinations of R_0 modes. According to the above discussion, R_1 modes are either single R_0 modes or resonance pairs of R_0 modes (one can neglect triple and other many-oscillator resonances). Moreover, the separation of R_0 modes in resonance pairs is $\simeq R_1$, while their localization radius is $\le R_0$. This enables us to treat the interaction in such resonance pairs as the $\mathbf{r}^{-3}$ interaction of effective dipoles corresponding to R_0 modes. Consider two oscillators (R_0 modes) numbered 1 and 2. They interact according to

$$H_{12} = \tfrac{1}{2}(p_1^2 + \omega_1^2 q_1^2) + \tfrac{1}{2}(p_2^2 + \omega_2^2 q_2^2) + D_{12} q_1 q_2 .$$

Normal modes q^+, q^- are given by

$$q^+ = \cos\theta q_1 + \sin\theta q_2 ,$$
$$q^- = -\sin\theta q_1 + \cos\theta q_2 \tag{5}$$

$[\cot 2\theta = (\omega_1^2 - \omega_2^2)/2D_{12}]$. Their frequencies $\omega_\pm$ are defined by $\omega_\pm^4 - (\omega_1^2 + \omega_2^2)\omega_\pm^2 + \omega_1^2\omega_2^2 = D_{12}^2$. The total electric dipole $\mathbf{d}$ of the modes 1,2 can be expressed as $\mathbf{d} = \mathbf{a}_1 q_1 + \mathbf{a}_2 q_2 = \mathbf{a}^+ q^+ + \mathbf{a}^- q^-$, where

$$\mathbf{a}^+ = \cos\theta \mathbf{a}_1 + \sin\theta \mathbf{a}_2 ,$$
$$\mathbf{a}^- = -\sin\theta \mathbf{a}_1 + \cos\theta \mathbf{a}_2 . \tag{6}$$

This means that any mode (say, the kth one) which comes into a resonance with a $(+)$ mode or a $(-)$ mode at some next step of the renormalization interacts with them via the amplitude $D_{k\pm}$ of the form (2) containing $\mathbf{a}^\pm$ instead of $\mathbf{a}_{1,2}$.

Note that

$$|\omega_+^2 - \omega_-^2| \ge |D_{12}| \simeq \text{const} \times \langle \mathbf{a}^2 \rangle / |\mathbf{r}_1 - \mathbf{r}_2|^3 ;$$

i.e., the separation of ω_+ and ω_- is much bigger than any possible value of the interaction at all next steps. Hence, all further resonances cannot cause any coupling of the modes $(+)$ and $(-)$. Consequently, the resonances (interactions) of pairs of modes can be considered as uncorrelated [we mean correlations at different moments of the "renormalization time" $\xi = \ln(R)$].

An important analogy with the Boltzmann kinetic equation should be stressed. The derivation of the kinetic equation for rarefied gases is based on the absence of correlations of subsequent collision processes, which, in turn, is caused by the large mean free path of the molecules [similar to our condition $\lambda \ll 1$, see (4)]. Besides providing the possibility of a probabilistic approach, the largeness of the mean free path (the smallness of λ) allows one to not take into account triple and other multiple collisions (many-oscillator resonances in our problem).

Finishing the discussion, we formulate the renormalization procedure. After finding normal modes for the R_1-truncated interaction, we come to R_1 modes which can be either single R_0 modes or resonance pairs of R_0 modes. Positions and frequencies of R_1 modes remain uncorrelated and uniformly distributed, while the new distribution function $\tilde{f}(\mathbf{a})$ of the dipole parameters must be recalculated (according to the above discussion the vectors $\tilde{\mathbf{a}}_i$ for R_1 modes can be taken as uncorrelated).

We derive a recursion relation for $\tilde{f}(\mathbf{a})$ and $f(\mathbf{a})$:

$$\tilde{f}(\mathbf{a}) - f(\mathbf{a}) = \int f(\mathbf{a}_1) d^3 a_1 f(\mathbf{a}_2) d^3 a_2 n\, d^3 r\, v\, dE\, [\delta(\mathbf{a} - \mathbf{a}^+) + \delta(\mathbf{a} - \mathbf{a}^-) - \delta(\mathbf{a} - \mathbf{a}_1) - \delta(\mathbf{a} - \mathbf{a}_2)] . \tag{7}$$

Here $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, $E = |\omega_1^2 - \omega_2^2| \ge 0$, and $n, v, \mathbf{a}^+, \mathbf{a}^-$ are defined above. It is convenient to introduce a new variable τ instead of E according to $E = 2D_{12}\tau$. The variable τ defines the angle θ of the rotation transforming $\mathbf{a}_1, \mathbf{a}_2$ to $\mathbf{a}^-, \mathbf{a}^+$ (see above). The usefulness of τ becomes clear from the identity

$$d^3 r\, dE = (2|\mathbf{r}_1 - \mathbf{r}_2|^3 |D_{12}|) d(\ln|\mathbf{r}|) d\Omega\, d\tau .$$

Here $d\Omega$ is the area element of the unit sphere corresponding to the unit vector $\mathbf{n}_{12}$. Since the product $|\mathbf{r}_1 - \mathbf{r}_2|^3 |D_{12}|$ depends not on $|\mathbf{r}_1 - \mathbf{r}_2|$ but only on $\mathbf{n}_{12}$, one can integrate Eq. (7) over $|\mathbf{r}|$ and find that its right-hand side $\simeq \lambda \ln(R_1/R_0) \ll 1$. Hence Eq. (7) can be transformed into a differential form by taking $\xi = \ln(R)$ as a renormalization "time":

$$\frac{\partial}{\partial \xi} f(\mathbf{a}) = n v \int d\tau\, d^3 a_1\, d^3 a_2 f(\mathbf{a}_1) f(\mathbf{a}_2) Q(\mathbf{a}_1, \mathbf{a}_2) [\delta(\mathbf{a} - \mathbf{a}^+) + \delta(\mathbf{a} - \mathbf{a}^-) - \delta(\mathbf{a} - \mathbf{a}_1) - \delta(\mathbf{a} - \mathbf{a}_2)] , \tag{8}$$

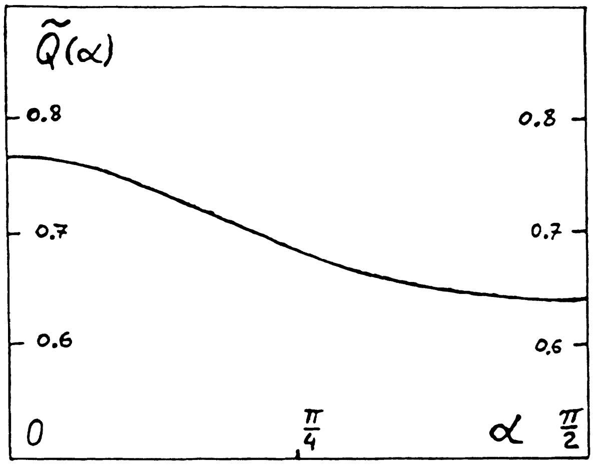

FIG. 1. Function $\tilde{Q}(\alpha)$ defined by $Q(\mathbf{a},\mathbf{b})=4\pi|\mathbf{a}||\mathbf{b}|\times\tilde{Q}(\alpha)$ (α is the angle between the vectors $\mathbf{a},\mathbf{b}$). $\tilde{Q}(\alpha)$ is shown in the interval $[0,\pi/2]$; for other α it can be found using the identities $\tilde{Q}(\alpha\pm\pi)=\tilde{Q}(\alpha)$, $\tilde{Q}(-\alpha)=\tilde{Q}(\alpha)$. Since $\max[\tilde{Q}(\alpha)]=\tilde{Q}(0)=4/3\sqrt{3}=0.7698\ldots$, $\min[\tilde{Q}(\alpha)]=\tilde{Q}(\pi/2)=2/\pi=0.6366\ldots$, the function $\tilde{Q}(\alpha)$ can be approximated by $Q^*=0.5[\tilde{Q}(0)+\tilde{Q}(\pi/2)]=0.7032\ldots$ with an accuracy of 10%: $|[\tilde{Q}(\alpha)-Q^*]/Q^*|<0.1$.

where

$$Q(\mathbf{a}_1,\mathbf{a}_2)=\int d\Omega\,|\mathbf{a}_1\cdot\mathbf{a}_2-3\mathbf{a}_1\cdot\mathbf{n}\,\mathbf{a}_2\cdot\mathbf{n}|\,.$$

One gets the following for $Q(\mathbf{a},\mathbf{b})$: $Q(\mathbf{a},\mathbf{b})=4\pi\times|\mathbf{a}|\,|\mathbf{b}|\tilde{Q}(\alpha)$, where $\tilde{Q}(\alpha)$ is a function of the angle α between the vectors $\mathbf{a},\mathbf{b}$ (Fig. 1). Note that $\tilde{Q}(\alpha)$ can be well approximated by a constant $Q^*=0.7$ with a reasonable accuracy of 10%.

Concerning Eq. (8) our main task is to find and study its solutions $f(\mathbf{a},\xi)$ such that $f(\mathbf{a},0)=f(\mathbf{a})$, the microscopic distribution of vectors $\mathbf{a}_i$. Of considerable interest is the asymptotic behavior of $f(\mathbf{a},\xi)$ at $\xi\to\infty$, related to important dynamical characteristics of the problem (see below). Our analysis of Eq. (8) will be strongly motivated by its analogy with the Boltzmann equation.

Integrals of Eq. (8).— First, we prove the conservation of $\langle\mathbf{a}^2\rangle$: $\partial\langle\mathbf{a}^2\rangle/\partial\xi=0$ or

$$\int\mathbf{a}^2 f(\mathbf{a},\xi)d^3a=\int\mathbf{a}^2 f(\mathbf{a},\xi=0)d^3a$$

for all ξ. The proof follows from the identity $\mathbf{a}^{+2}+\mathbf{a}^{-2}=\mathbf{a}_1^2+\mathbf{a}_2^2$ (see above). This result is analogous to the conservation of energy for the Boltzmann equation.

Besides $\langle\mathbf{a}^2\rangle$ there exist other invariants of Eq. (8). Consider the three components of the vector $\mathbf{a}=(a_x, a_y,a_z)$. Using the same method one easily finds that each of the six quantities $\langle a_x^2\rangle$, $\langle a_y^2\rangle$, $\langle a_z^2\rangle$, $\langle a_xa_y\rangle$, $\langle a_ya_z\rangle$, $\langle a_za_x\rangle$ is conserved when $f(\mathbf{a},\xi)$ satisfies Eq. (8).

One might suspect that the conservation of these quantities is an approximate result which fails when not only interacting pairs but also many-oscillator resonances are taken into account. Let us show that such resonances do not destroy the conservation of $\langle a_\alpha a_\beta\rangle$ ($\alpha,\beta=x,y,z$). Consider k oscillators forming a resonance system:

$$H_k=\tfrac{1}{2}\sum p_i^2+\tfrac{1}{2}\sum K_{ij}q_iq_j\quad(i,j=1,\ldots,k)\,.$$

The variables q_i are connected with normal modes q_i' by a transformation $q_i=R_{ij}q_k'$, where $\hat{R}$ is an orthogonal $k\times k$ matrix. From the expression for the electric dipole of the system $\mathbf{d}=\sum\mathbf{a}_iq_i=\sum\mathbf{a}_i'q_i'$ we find the transformation rule for $\mathbf{a}_i$: $\mathbf{a}_i=R_{ij}\mathbf{a}_k'$. We see that the vectors $\mathbf{a}_i$ are transformed exactly as the variables q_i. The orthogonality of the transformation matrix $\hat{R}$ enables one to repeat the above given calculation and check the invariance of the quantities $\langle a_\alpha a_\beta\rangle$.

Further results of Eq. (8) can be obtained only for its approximate version which we get by replacing $Q(\mathbf{a}_1,\mathbf{a}_2)\to4\pi Q^*|a_1||a_2|$ in (8) (the error introduced by this replacement is $\leq10\%$). The modified Eq. (8) [denote it Eq. (8M)] turns out to be much more treatable. It has some exact properties resembling those of the Boltzmann equation. Since the theories for Eq. (8M) and for the Boltzmann equation are completely parallel, we only quote the results (proofs will be presented elsewhere).

(I) Invariants: The quantities $\langle\mathbf{a}_\alpha\mathbf{a}_\beta\rangle$ are invariants of Eq. (8M), not only of Eq. (8).

(II) H theorem: Let $f(a,\xi)$ satisfy Eq. (8M). Define "entropy" H as

$$H[f]=-\int\ln[|\mathbf{a}|f(\mathbf{a},\xi)]f(\mathbf{a},\xi)d^3a\,.$$

The function $H(\xi)=H[f(a,\xi)]$ grows monotonously: $\partial H(\xi)/\partial\xi\geq0$.

(III) Stationary solutions of Eq. (8M): All stationary solutions of Eq. (8M) are $f_G(\mathbf{a})=A|\mathbf{a}|^{-1}\times\exp(-a_\alpha G_{\alpha\beta}a_\beta)$, where $\hat{G}$ is a positively defined symmetric 3×3 matrix [A depends on $\hat{G}$, since $f(\mathbf{a})$ is normalized: $\int f(\mathbf{a})d^3a=1$].

(IV) Maximum of entropy: The entropy $H[f]$ reaches its maximal value for the distributions $f_G(\mathbf{a})$. More precisely, consider all functions $f(\mathbf{a})$ such that $\int f(\mathbf{a})d^3a=1$, $\int a_\alpha a_\beta f(\mathbf{a})d^3a=G_{\alpha\beta}$ ($\alpha,\beta=1,2,3$). Then always $H[f]\leq H[f_G]$; $H[f]=H[f_G]$ only if $f(\mathbf{a})=f_G(\mathbf{a})$.

The stationary solutions $f_G(\mathbf{a})$ are analogous to the Maxwell distribution which is conserved by the Boltzmann equation. An important distinction is that the Maxwell distribution has only one free parameter (temperature), while the distributions $f_G(\mathbf{a})$ are characterized by six parameters $G_{\alpha\beta}$ ($\alpha,\beta=1,2,3$; $\alpha\leq\beta$). Note that the existence of the six parameters is directly connected with the conservation of the six quantities $\langle a_\alpha a_\beta\rangle$.

Thus, we see that the asymptotic properties of the solutions of Eq. (8M) are very simple: Any solution converges to one of the stationary distributions $f_G(\mathbf{a})$. The parameters $G_{\alpha\beta}$ are completely determined by second moments of the initial distribution $f(\mathbf{a},\xi=0)$.

Unfortunately, none of the results (II), (III), or (IV) can be extended to the case of Eq. (8). Nevertheless, some understanding of its asymptotic properties can be reached if we utilize the closeness of Eq. (8) and Eq. (8M). Clearly Eq. (8M) defines a dynamical system in the space of all distributions $f(\mathbf{a})$ [Eq. (8) does the same]. The analysis of Eq. (8M) presented above enables one to extract two main features of this system: (i) Six integrals of motion $\langle a_\alpha a_\beta \rangle$ decompose the phase space into a bundle of invariant surfaces labeled by six parameters. (ii) Restricted on each of the invariant surfaces the system has one attracting fixed point $f_G(\mathbf{a})$. The properties (i) and (ii) fully characterize the qualitative picture of motion guided by Eq. (8M). As for Eq. (8), it undoubtedly satisfies condition (i) and apparently possesses property (ii): According to the theory of dynamical systems the property (ii) is "rough," i.e., it cannot be destroyed by small changes of the system. For making use of this roughness we have to assume that the difference of right-hand sides of Eqs. (8) and (8M) (estimated as 10%) is sufficiently small. Of course this argument is not very convincing, so the property (ii) needs more investigation (perhaps numerical). Nevertheless, here we take it as being well established and formulate its consequences: (a) Every solution $f(\mathbf{a},\xi)$ of Eq. (8) converges to a stationary distribution as $\xi \to \infty$, (b) stationary distributions form a six-parameter set, where the parameters can be chosen as $G_{\alpha\beta}=\int a_\alpha a_\beta f(\mathbf{a},\xi=0)d^3a$. We come to the main conclusion: *The renormalization group Eq. (8) has a six-dimensional manifold of nontrivial fixed points parametrized by symmetric positively defined* 3×3 *matrices.*

Some implications of this result for the dynamics should be finally mentioned. Fixed points of our dynamical problem are stable under rescaling $(\mathbf{r},t)\to(Z\mathbf{r},Z^3t)$. Hence, all dynamical correlation functions depend essentially only on the combination $t^{-1/3}\mathbf{r}$. For example, the two-point energy-energy correlation function $\langle E(\mathbf{r},t) \times E(\mathbf{0},0)\rangle$ is given by $K(\mathbf{r},t)=t^{-1}F_G(t^{-1/3}\mathbf{r})$, where $F_G(\mathbf{x})$ is some universal function of x depending also on $G_{\alpha\beta}$ [energy is conserved, so $\int K(\mathbf{r},t)d^3r=1$]. Thus the dynamics is slower than diffusive: $R\simeq T^{1/3}$.

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[1] J. M. Ziman, *Models of Disorder* (Cambridge Univ. Press, New York, 1979); E. N. Economou, Solid State Commun. **9**, 1317 (1971).

[2] P. W. Anderson, Phys. Rev. **109**, 1492–1505 (1958).

[3] L. S. Levitov, Europhys. Lett. **9**, 83–86 (1989).