# Total dielectric function: Algebraic sign, electron-lattice response, and superconductivity

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The interaction between two test charges in a solid can be described in terms of a total dielectric function that includes electronic and lattice polarization. Crystal stability requires the eigenvalues of $\epsilon^{-1}$ to be $\leq 1$. Some implications for superconductivity are discussed. A total dielectric function for the electron-lattice system is derived in the mean-field approximation and its inverse is explicitly constructed. The low-lying poles of $\epsilon^{-1}$ give the correct phonon frequencies as determined by the usual dynamical matrix.

## I. INTRODUCTION

The effective interaction between two test charges is $\epsilon^{-1}v$ where $v=e^2/|\mathbf{r}-\mathbf{r}'|$ and $\epsilon$ is the total dielectric function including all contributions such as exchange of phonons, plasmons, or excitons. Restrictions on the sign and magnitude of $\epsilon$ place restrictions on the interaction $\epsilon^{-1}v$ which are independent of the mechanisms creating the polarization. This could have important implications for superconductivity which is favored by a net attractive interaction at zero frequency. Pines and Nozières[1] have stated that stability requires $\epsilon>0$ but, it has been shown[2,3] that the only model-independent restriction on $\epsilon$ is $\epsilon^{-1}<1$ which permits $\epsilon$ to be negative except at small wave vectors where $\epsilon>0$.[4]

Pines and Nozières argued that the energy required to generate a spontaneous charge, $\delta\rho_s$, in a solid is proportional to $\delta\rho_s^2/\epsilon$ and must be positive if the ground state is stable giving $\epsilon>0$. However, the interaction between two test charges each with charge $\delta\rho_t$ must be greater in vacuum than in the solid so that $\delta\rho_t^2>\delta\rho_t^2/\epsilon$ or $1/\epsilon<1$. The argument of Pines and Nozières that led to the condition $\epsilon>0$ is incomplete because the creation of a spontaneous charge fluctuation should include not only the Coulomb energy but quantum-mechanical effects such as the change in kinetic energy as well. This is discussed further in Sec. III.

We do not investigate the question of whether specific polarization mechanisms can result in more stringent limitations on $\epsilon$. For example, Cohen and Anderson[5] assumed that for the case that the dielectric response is due to Coulomb interactions and phonons one has $\epsilon>0$ if local fields are neglected but that no such restriction exists if they are included. This allowed them to place limits on the superconducting transition temperature $T_c$ in the former case. The present analysis does not permit us to make a definitive statement regarding the validity of Cohen and Anderson's assumptions.

It is clear from the work of Cohen and Anderson, or for example Kittel[6] on ferroelectrics, that local fields are important for questions of stability and phase transitions. Therefore, it is important to extend the arguments of Refs. 2 and 3 to the case of a nonhomogeneous medium where $\epsilon^{-1}(\mathbf{r},\mathbf{r}')$ is not just a function of $|\mathbf{r}-\mathbf{r}'|$. This was done by Car *et al.*[7] for the electronic part of the response function. In the present paper we generalize the arguments of Refs. 2, 3, and 7 to the full response function including lattice as well as electronic polarizability. In agreement with Car *et al.*,[7] we find that the eigenvalues $\lambda_i$ of the dielectric function $\epsilon(\mathbf{r},\mathbf{r}')$ [or in a periodic medium, in reciprocal space, $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$] are restricted by stability to the range $1/\lambda_i<1$. This result generalizes the statement $1/\epsilon_M(q)<1$ (Ref. 2), where $1/\epsilon_M$ is the macroscopic dielectric response [essentially $\epsilon^{-1}(\mathbf{r},\mathbf{r}')$ with $\mathbf{r}$ and $\mathbf{r}'$ averaged over a local region, a unit cell if the medium is crystalline.]

The present paper discusses the fully general case of a crystalline medium with arbitrarily strong nonlocality effects [$\epsilon(\mathbf{r},\mathbf{r}',\omega)$ can be very different from $\epsilon(\mathbf{r}-\mathbf{r}',\omega)$]. Both normal and Umklapp events are treated on the same footing, the medium may be metallic or insulating, and the electron-ion interaction is not treated in a weak-pseudopotential approximation. The arguments of Refs. 2, 3, and 7 are confirmed and generalized in Sec. II, where the definitions and general properties are discussed, and in Sec. III where the test-charge–test-charge

 

interaction and the relation to $T_c$ are discussed. In Sec. IV we introduce a simple new version of mean-field theory which allows $\epsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)$ to be expressed explicitly, including lattice polarizability effects, in a random-phase-approximation (RPA) type of theory. In Sec. V the inverse dielectric matrix $\epsilon^{-1}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)$ is found and the test-charge–test-charge interaction is shown to conform to the usual screened Coulomb plus screened electron-phonon terms, with the phonons fully renormalized by electron-phonon interactions. Section VI contains a brief summary. A surprising feature is that the bare frequencies $\Omega_0^2$ which appear in $\epsilon$ (but not $\epsilon^{-1}$) are negative and diverging to $-\infty$. The Appendix clarifies this feature.

Finally, because units and dimensions are somewhat arbitrary and confusing, it is worth mentioning the policy we have followed. All symbolic quantities like $V(r,t)$ have explicit dimensions; we have not taken refuge in the device $e=\hbar=\Omega=1$. We have decided that $\rho(r)$ should have units $\Omega^{-1}$ (where $\Omega$ is volume), not $e/\Omega$. Correspondingly, all potentials have units of energy, not work per unit charge. When Fourier transforming from $\mathbf{r}$ to $\mathbf{k}$ and vice versa, it is possible to use factors of $\Omega^{-1}$ and $\Omega$ in such a way as to prevent $f(r)$ and $f(k)$ from having different dimensions. This has always been exploited in order to make potentials (denoted by $V$ or $v$) have units of energy, and $\epsilon(Q+G,Q+G',\omega)$ be dimensionless. With these choices, the natural units for both $\epsilon(r,r't-t')$ and $\epsilon^{-1}(r,r',t-t')$ are $\Omega^{-1}t^{-1}$ which is the same as the dimensions of the unit tensor in $(\mathbf{r}t)$ space, $\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$. Susceptibilities acquire various units: $\chi(r,r',t-t')$ is $\Omega^{-2}t^{-1}$ (energy)$^{-1}$ while $\chi(r,r',\omega)$ is $\Omega^{-2}$ (energy)$^{-1}$ and $\chi^{-1}(r,r',\omega)$ is energy. Free energy $F$ and interaction energies $V_{12}$ always have units of energy. These units are usually self-evident in the equations.

## II. RESTRICTIONS ON THE DIELECTRIC FUNCTION FROM STABILITY REQUIREMENTS

The inverse longitudinal dielectric function $\epsilon_{\text{tot}}^{-1}$ is defined in terms of the total change in potential energy of a test charge at point $\mathbf{r}$ and time $t$ which arises from the presence of an infinitesimal perturbing field $\delta V_{\text{ext}}(\mathbf{r}',t')$ at other points in space and time

$$\delta V_{\text{tot}}(\mathbf{r},t)=\int_{-\infty}^{\infty}dt'\int d^3r'\epsilon_{\text{tot}}^{-1}(\mathbf{r},\mathbf{r}',t-t')\delta V_{\text{ext}}(\mathbf{r}',t') . \tag{1}$$

The dielectric function $\epsilon_{\text{tot}}$ gives the inverse relation and thus obeys

$$\int_{-\infty}^{\infty}dt''\int d^3r''\epsilon_{\text{tot}}(\mathbf{r},\mathbf{r}'',t-t'')\epsilon_{\text{tot}}^{-1}(\mathbf{r}'',\mathbf{r}',t''-t') =\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') . \tag{2}$$

The function $\epsilon^{-1}$ is causal (vanishes for $t'>t$), whereas $\epsilon$ is not;[2,4] thus $\epsilon^{-1}$ is more "fundamental." In some ways a still more fundamental response function is the density response function or susceptibility $\chi$, given as the relation between $V_{\text{ext}}$ and the induced charge density $\delta\rho_{\text{tot}}$, where the subscript "tot" is intended to emphasize that electronic *and* nuclear charge is included (but *not* any external charge which might serve as a source for $\delta V_{\text{ext}}$),

$$\delta\rho_{\text{tot}}(\mathbf{r},t)=\int_{-\infty}^{\infty}dt'\int d^3r'\chi(\mathbf{r},\mathbf{r}',t-t')\delta V_{\text{ext}}(\mathbf{r}',t') . \tag{3}$$

This $\chi$ is also causal, and is directly related to $\epsilon^{-1}$ because the total potential $\delta V_{\text{tot}}$ felt by a test charge is $\delta V_{\text{ext}}$ plus the classical Coulomb field of the screening charge $\delta\rho_{\text{tot}}$:

$$\epsilon_{\text{tot}}^{-1}(\mathbf{r},\mathbf{r}',t-t')=\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') +\int d^3r''\frac{e^2}{|r-r''|}\chi(\mathbf{r}'',\mathbf{r}',t-t') . \tag{4}$$

The screening charge $\delta\rho_{\text{tot}}$ is the change in the ensemble-average expectation value of the total charge-density operator $\hat{\rho}_{\text{tot}}(\mathbf{r})$, defined as

$$\hat{\rho}_{\text{tot}}(\mathbf{r})=Z\sum_{\mathbf{l}}\delta(\mathbf{r}-\mathbf{R}_{\mathbf{l}})-\sum_i\delta(\mathbf{r}-\mathbf{r}_i) . \tag{5}$$

It has been convenient to remove a factor of $e=|e|$ from the charge density Eq. (5), inserting it back into $e^2/|\mathbf{r}-\mathbf{r}''|$ in Eq. (4). Thus all potentials have units of energy. For simplicity, all nuclei are assumed identical, with charge $Z$ and mass $M$, located on a primitive lattice. Operators are denoted by carets; nuclear coordinates are denoted by $\mathbf{R}_{\mathbf{l}}$ where the vector index $\mathbf{l}$ also denotes the lattice site $\mathbf{l}$ such that the displacement $\mathbf{u}_{\mathbf{l}}=\mathbf{R}_{\mathbf{l}}-\mathbf{l}$ is small; $\mathbf{r}_i$ denotes electron coordinates.

It is convenient to work with the Fourier transform of the time variable; if $\delta V_{\text{ext}}(r't')$ has a time dependence $e^{-i\omega t'}$, then the relevant response functions are $\chi(\mathbf{r},\mathbf{r}',\omega)$ and $\epsilon^{-1}(\mathbf{r},\mathbf{r}',\omega)$ and the inverse $\epsilon(\mathbf{r},\mathbf{r}',\omega)$ obeys

$$\int d^3r''\epsilon(\mathbf{r},\mathbf{r}'',\omega)\epsilon^{-1}(\mathbf{r}'',\mathbf{r}',\omega)=\delta(\mathbf{r}-\mathbf{r}') . \tag{6}$$

Causality requires $\chi$ and $\epsilon^{-1}$ be analytic functions when $\omega$ is continued to the complex variables $z$ in the upper half-plane. We will later make use of the Kubo-type formula,

$$\chi(\mathbf{r},\mathbf{r}',\omega)=-\frac{i}{\hbar}\int_0^{\infty}dt\langle[\hat{\rho}_{\text{tot}}(\mathbf{r},t),\hat{\rho}_{\text{tot}}(\mathbf{r}',0)]\rangle e^{+i\omega t} . \tag{7}$$

The dc limit ($\omega=0$) of $\chi$, denoted by $\chi(\mathbf{r},\mathbf{r}')$ is real and symmetric in $(\mathbf{r},\mathbf{r}')$ and has especially convenient properties. If an arbitrary static charge disturbance $\delta\rho$ is introduced, the Helmholtz free energy $F$ of this system would be altered by the amount

$$\delta F=-\tfrac{1}{2}\int d^3r\,d^3r'\delta\rho(\mathbf{r})\chi^{-1}(\mathbf{r},\mathbf{r}')\delta\rho(\mathbf{r}') +\int d^3r\delta\rho(\mathbf{r})\delta V_{\text{ext}}(\mathbf{r}) . \tag{8}$$

The actual equilibrium charge density $\delta\rho_{\text{tot}}$ must minimize $\delta F$, and is obtained when Eq. (3) is obeyed. In Eq. (8), $\delta V_{\text{ext}}$ is time-independent (otherwise thermodynamics does not apply) and the inverse of $\chi$ is defined as in Eq. (6).

Consider next the case when $\delta V_{\text{ext}}=0$. Then the equilibrium charge satisfies $\delta\rho=0$. For this to be a stable minimum of $F$, $\chi^{-1}$ must obey, for arbitrary $\delta\rho=f(r)$,

$$\langle f|\chi^{-1}|f\rangle\equiv\int d^3r\,d^3r'f^*(\mathbf{r})\chi^{-1}(\mathbf{r},\mathbf{r}')f(\mathbf{r}')\le 0 , \tag{9}$$

i.e., $\chi^{-1}$ is a nonpositive operator. Equation (9) is the fundamental condition for crystal stability.[2] Because $\chi^{-1}$ is Hermitian, a complete set of eigenvectors $|n\rangle$ and

corresponding real, nonpositive eigenvalues $\chi_n^{-1}$ can be found and made orthonormal

$$\chi^{-1}\,|\,n\,\rangle=\chi_n^{-1}\,|\,n\,\rangle\ ,\qquad \langle\,n'\,|\,n\,\rangle=\delta_{nn'}\ . \tag{10}$$

Let us denote $\langle\,\mathbf{r}\,|\,n\,\rangle$ as $f_n(\mathbf{r})$. An arbitrary static charge fluctuation can be expanded as

$$\delta\rho(\mathbf{r})=\sum_n \delta\rho_n f_n(\mathbf{r})\ , \tag{11}$$

where the coefficient $\delta\rho_n$ is $\langle\,n\,|\,\delta\rho\,\rangle$. In the absence of an external field, the free energy (8) becomes

$$\delta F=-\tfrac{1}{2}\sum_n \chi_n^{-1}\,|\,\delta\rho_n\,|^2\ . \tag{12}$$

If a second-order structural instability occurs, this is driven by some eigenvalue, call it $\chi_s^{-1}$, going to zero

$$\chi_s^{-1}=-a(T-T_s)\ , \tag{13}$$

where $T_s$ is the mean-field approximation to the structural transition temperature. The free energy then takes the familiar Landau form

$$\delta F=\tfrac{1}{2}a(T-T_s)\delta\rho_s^2-\tfrac{1}{2}\sum_{\substack{n\\(n\neq s)}}\chi_n^{-1}\delta\rho_n^2\ , \tag{14}$$

where $\delta\rho_s$ is the order parameter. The point of this discussion is to show that eigenvalues of $\chi$ (which are reciprocals $\chi_n$ of the eigenvalues of $\chi^{-1}$) can cover a wide range of negative values, approaching $-\infty$ near a structural instability. There are also three special eigenvectors

$$\delta\rho_\alpha(r)=\nabla_\alpha\langle\hat{\rho}_{\rm tot}(r)\rangle \tag{15}$$

which correspond to infinitesimal translations of the total charge density. Since there is no restoring force for such a translation, $\delta F=\langle\,\delta\rho_\alpha\,|\,\chi^{-1}\,|\,\delta\rho_\alpha\,\rangle$ equals zero, or the set $\delta\rho_\alpha(r)$ spans a three-dimensional null space of $\chi^{-1}$. All other eigenvalues must be negative. In a crystal, $\chi(\mathbf{r},\mathbf{r}')$ is invariant under discrete translations $\chi(\mathbf{r}+\mathbf{l},\mathbf{r}'+\mathbf{l})$ so Bloch's theorem applies and eigenvectors can be chosen as simultaneous eigenvectors of the translation operator (i.e., labeled by a wave vector $\mathbf{Q}$).

The restriction to nonpositive eigenvalues for $\chi^{-1}$ and $\chi$ can be used to deduce restrictions on $\epsilon^{-1}$ and $\epsilon$. Unfortunately, the relation (4) shows that $\epsilon^{-1}$ as defined in (1) is not symmetric in $(\mathbf{r},\mathbf{r}')$ at $\omega=0$. This introduces minor complications which can be dealt with by defining a "symmetric dielectric function:"

$$\epsilon_s^{-1}(\mathbf{r},\mathbf{r}',\omega)\equiv\delta(\mathbf{r}-\mathbf{r}')+\int d^3r_1 d^3r_2 v_{1/2}(\mathbf{r}-\mathbf{r}_1)\times\chi(\mathbf{r}_1,\mathbf{r}_2,\omega)v_{1/2}(\mathbf{r}_2-\mathbf{r}')\ , \tag{16}$$

where $v_{1/2}(r-r')$ is defined as the "positive square root" of the operator $v(\mathbf{r}-\mathbf{r}')=e^2/|\,\mathbf{r}-\mathbf{r}'\,|$ and

$$\int d^3r'' v_{1/2}(\mathbf{r}-\mathbf{r}'')v_{1/2}(\mathbf{r}''-\mathbf{r}')\equiv v(\mathbf{r}-\mathbf{r}')\ . \tag{17}$$

The existence of a positive square root can be deduced as follows: $v(r-r')$ is translationally invariant, so the functions $e^{i\mathbf{Q}\cdot\mathbf{r}}$ form a complete set of eigenvectors. The corresponding eigenvalues, $4\pi e^2/Q^2$, are all positive, so $v$ is a positive operator. The operator with eigenfunctions $e^{i\mathbf{Q}\cdot\mathbf{r}}$ and eigenvalues $+(4\pi e^2/Q^2)^{1/2}$ is then the "positive square root." In $(\mathbf{r},\mathbf{r}')$ space the operator happens to be $\pi^{-3/2}e/|\,r-r'\,|^2$. It is clear from the definition Eq. (16) that when $\omega=0$, $\epsilon_s^{-1}$ is real and symmetric. It consists of a positive part, the unit operator $\delta(\mathbf{r}-\mathbf{r}')$ and a negative part, $v_{1/2}\chi v_{1/2}$. The eigenvalues, $\lambda_i$, of $\epsilon_s^{-1}$, obey

$$\epsilon_s^{-1}\,|\,i\,\rangle=\lambda_i\,|\,i\,\rangle\ ,\qquad \langle\,i\,|\,j\,\rangle=\delta_{ij}\ ,\qquad \lambda_i=\langle\,i\,|\,\epsilon_s^{-1}\,|\,i\,\rangle=1+\langle\,i\,|\,v_{1/2}\chi v_{1/2}\,|\,i\,\rangle\ . \tag{18}$$

The operator $\chi$ can be replaced by $\sum_n |\,n\,\rangle\chi_n\langle\,n\,|$, which yields for $\lambda_i$

$$\lambda_i=1+\sum_n |\,\langle\,i\,|\,v_{1/2}\,|\,n\,\rangle\,|^2\chi_n\ . \tag{19}$$

This shows the following properties of eigenvalues $\lambda_i$ of $\epsilon_s^{-1}$. (1) $\lambda_i\leq 1$ (since $\chi_n\leq 0$). (2) If an eigenvalue $\chi_s$ of $\chi$ diverges to $-\infty$ [as $-1/a(T-T_c)$, for example] then all eigenvectors $|\,i\,\rangle$ of $\epsilon^{-1}$ of the same symmetry as $|\,s\,\rangle$ have eigenvalues $\lambda_i$ which also diverge to $-\infty$. (3) For each eigenvector $|\,i\,\rangle$ of $\epsilon_s^{-1}$ with eigenvalue $\lambda_i$, a corresponding right eigenvector $v_{1/2}\,|\,i\,\rangle$ and left eigenvector $\langle\,i\,|\,v_{-1/2}$ exist for the unsymmetrized operator $\epsilon_{\rm tot}^{-1}$, and both correspond to eigenvalue $\lambda_i$. Here $v_{-1/2}$ is the inverse of $v_{1/2}$.

Finally, all of the above translate immediately into statements about the dielectric function $\epsilon_{\rm tot}$ and its eigenvalues, $1/\lambda_i$. In particular the restriction $\lambda_i\leq 1$ on eigenvalues of $\epsilon_s^{-1}$ require $1/\lambda_i\geq 1$ if $\lambda_i>0$ or $1/\lambda_i<0$ if $\lambda_i<0$. The only restriction on eigenvalues of $\epsilon_{\rm tot}$ is that the region between 0 and 1 is forbidden. The possible behavior of $\chi$, $\epsilon^{-1}$, and $\epsilon$ as a function of temperature is schematically illustrated in Fig. 1. These results reproduce the conclusions of Refs. 2 and 3, in a generalized form which applies to inhomogeneous systems. The same conclusions have already been reached by Car *et al.*[7] for the electronic response of an inhomogeneous medium. Their argument is based on causality and confirmed by explicit construction of the Lehmann representation for $\epsilon^{-1}$.

In the case of a periodic lattice the dielectric response of the solid is described by $\epsilon^{-1}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',0)$ where $\mathbf{G},\mathbf{G}'$ are reciprocal-lattice vectors. The macroscopic response is given by $\epsilon_M(\mathbf{q},\omega)=1/\epsilon^{-1}(\mathbf{q},\mathbf{q},0)$. As shown above the eigenvalues of $\epsilon^{-1}$ satisfy $\lambda_i<1$. In the case of a Hermitian matrix it is easily shown that if the eigenvalues satisfy $\lambda_i<1$ then the diagonal elements are also less than 1. This follows from the variational principle which states that no diagonal matrix element can exceed the maximum eigenvalue, which is 1. Consequently $1/\epsilon_M(\mathbf{q},0)<1$ in agreement with Ref. 2.

Previous workers[2-4] have found an additional restriction on $\epsilon_M$; $\lim_{q\to 0}\epsilon_M(\mathbf{q},0)>1$. This condition is more stringent than $\lim_{q\to 0}[1/\epsilon_M(\mathbf{q},0)]<1$ as can be seen in

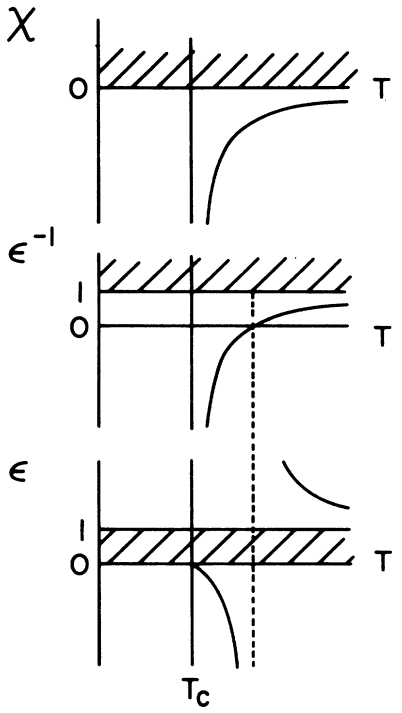


FIG. 1. Schematic behavior of $\chi$, $\epsilon^{-1}$, and $\epsilon$ as a function of temperature near a second-order instability. $\chi$ actual refers to the eigenvalue of $\chi(r,r')$ and $\epsilon^{-1}$ and $\epsilon$ are similarly defined.

Fig. 1. Thus, for a spatially uniform instability the phase transition would not occur at $T_c$ in Fig. 1 but rather at the higher temperature indicated by the dashed line. An example is the ferroelectric transition discussed by Kittel.[7]

## III. THE TEST CHARGE-TEST CHARGE INTERACTION

We now examine the interaction energy between two test charges inserted in a medium. Consider first a medium with no test charges, equilibrium charge density $\rho_0(\mathbf{r})$, and susceptibility $\chi$. Then insert a single test charge of infinitesimal charge $Q_1$ ($|Q_1| \ll e$) at point $\mathbf{r}_1$. There is a charge distortion $\delta\rho_1(\mathbf{r})$ which minimizes the energy functional

$$F_1[\delta\rho] = \int \delta^3 r \frac{Q_1 e}{|\mathbf{r}_1-\mathbf{r}|}[\rho_0(\mathbf{r})+\delta\rho_1(\mathbf{r})] - \tfrac{1}{2}\int d^3r d^3r' \delta\rho_1(\mathbf{r})\chi^{-1}(\mathbf{r},\mathbf{r}')\delta\rho_1(\mathbf{r}') . \quad (20)$$

Equation (20) is simply Eq. (8) supplemented by the background energy of the test charge in the medium with charge $\rho_0$. After minimizing, the energy is

$$F_1[\min] = \int d^3 r \frac{Q_1 e}{|\mathbf{r}_1-\mathbf{r}|}\rho_0(\mathbf{r}) + \tfrac{1}{2}\int d^3r d^3r' \frac{Q_1 e}{|\mathbf{r}_1-\mathbf{r}|}\chi(\mathbf{r},\mathbf{r}')\frac{Q_1 e}{|\mathbf{r}'-\mathbf{r}_1|} . \quad (21)$$

This is interpreted as the background energy plus a negative energy of charge relaxation around the point charge, namely the test charge interacting with its oppositely charged screening cloud. Next, insert a second test charge of charge $Q_2$ at location $\mathbf{r}_2$. The total change in energy will have a direct interaction $Q_1Q_2/|\mathbf{r}_1-\mathbf{r}_2|$ and then a term of the type of Eq. (21) except that each occurrence of $Q_1e/|\mathbf{r}_1-\mathbf{r}|$ is replaced by $[Q_1e/|\mathbf{r}_1-\mathbf{r}|+Q_2e/|\mathbf{r}_2-\mathbf{r}|]$. There are two background terms, and the term with each test charge interacting with the screening cloud of *both* charges. The total energy can now be separated into three pieces, $F_1+F_2+(Q_1Q_2/e^2)V_{12}$, where $F_1$ and $F_2$ are given by Eq. (21) and its equivalent for an isolated charge 2. The interesting piece is $V_{12}$

$$(Q_1Q_2/e^2)V_{12}(\mathbf{r}_1,\mathbf{r}_2) = \frac{Q_1Q_2}{|\mathbf{r}_1-\mathbf{r}_2|} + \int d^3r\delta^3r' \frac{Q_1e}{|\mathbf{r}_1-\mathbf{r}|}\chi(\mathbf{r},\mathbf{r}')\frac{Q_2e}{|\mathbf{r}'-\mathbf{r}_2|} \quad (22)$$

which is the total energy of interaction. This has a direct interaction and a screening part which *tends* to have opposite sign. In the limit $\mathbf{r}_2 \to \mathbf{r}_1$ the screening must have opposite sign to the direct term because of the nonpositivity of $\chi$. Equation (22) can be written in various alternate forms. In short-hand operator notation they are

$$V_{12} = v + v\chi v , \quad (23)$$

$$V_{12} = \epsilon_{\text{tot}}^{-1} v = v_{1/2}\epsilon_s^{-1}v_{1/2} . \quad (24)$$

As long as the point charges are located at distinct points in space, the restrictions on $\chi$ place no restrictions on $V_{12}$.

Equations (22)–(24) can be immediately generalized to the case where the point charges are smeared into distributed charges $\delta\rho_1$ and $\delta\rho_2$; the interaction energy is then

$$\delta U_{12} = \langle \delta\rho_1 | V_{12} | \delta\rho_2 \rangle . \quad (25)$$

In the special case where the two charge distributions $\delta\rho_1$ and $\delta\rho_2$ are the same, the interaction energy of the charge cloud $\delta\rho$ with itself is

$$\delta U_{11} = \tfrac{1}{2}\langle \delta\rho_1 | v + v\chi v | \delta\rho_1 \rangle . \quad (26)$$

We picture the charge distribution as a cloud of point charges and sum up (by integration) the pairwise energy of each piece with every other piece. Each pair should only be counted once, hence a factor of $\frac{1}{2}$ is introduced to avoid double counting. The first term of Eq. (26) is the positive energy of direct Coulomb repulsion, while the second term, representing the screening effect of the intervening medium, is negative. Thus the requirement of stability enforces the equally necessary requirement that the relaxation or screening must reduce the electrostatic interaction energy of an inserted charge distribution. It seems paradoxical that the energy in Eq. (26) can actually be negative, as is implied by the existence of negative eigenvalues of $\epsilon_s^{-1}$. The paradox seems to involve the supposition that if Eq. (26) is negative for some $\delta\rho(r)$, then

the system should be unstable relative to a spontaneous distortion of type $\delta\rho(r)$. However, Eq. (26) is not the total energy of a spontaneous distortion $\delta\rho_1(r)$, but rather $\delta\rho_1$ is an externally introduced charge. Energy was required to assemble this distribution, part of which (the direct Coulomb part) is included and part of which is omitted from Eq. (26). If $\delta\rho_1$ is actually an internal charge fluctuation, we must include the quantum kinetic energy operator, for example, in finding its energy.

Finally, let us examine the effective screened total electron interaction which appears in the theory of superconductivity. The matrix element for scattering a Cooper pair from a state $k$ to $k'$ on the Fermi surface (FS) is

$$V_{kk'}=\langle k'\uparrow,-k'\downarrow \mid V_{\rm tot} \mid k\uparrow,-k\downarrow\rangle = \int d^3r\, d^3r'[\psi^*_{k'}(\mathbf{r})\psi_k(\mathbf{r})]V_{\rm tot}(\mathbf{r},\mathbf{r}')[\psi^*_{k'}(\mathbf{r}')\psi_k(\mathbf{r}')] \,. \tag{27}$$

There are two questions: (1) what is the correct expression for $V_{\rm tot}(r,r')$, and (2) what can be said about the sign of $V_{kk'}$? The interaction $V_{kk'}$ appears in BCS theory in the form

$$-N_\uparrow(0)V_{\rm BCS}=\mu-\lambda=N_\uparrow(0)\langle V_{k,k'}\rangle_{\rm FS} \,, \tag{28}$$

where the minus sign recognizes the reversed sign convention of BCS, $\mu$ is the purely electronic interaction, including bare Coulomb interaction and screening by electron density distortions, and $-\lambda$ is the attractive electron-phonon part from screening caused by lattice distortions. Question (2) above asks whether $\mu-\lambda$ is necessarily positive. Question (1) asks whether $V_{\rm tot}$ is adequately given by $\epsilon_{\rm tot}^{-1}v$. The answer to both questions is apparently no.

The unambiguous procedure for determining $V_{\rm tot}$ is Feynman-Dyson perturbation theory as extended by Gor'kov and Eliashberg to the superconducting state. Various Feynman graphs contributing to $V_{\rm tot}(k,k')$ are shown in Fig. 2. The first 3 graphs (bare Coulomb repulsion, purely electronic screening of the Coulomb repulsion, and screened electron-phonon graphs) are all properly included in $\epsilon_{\rm tot}^{-1}v$, as will be shown explicitly in Sec. V. The remaining three are not. There are two distinct effects which are not included in $\epsilon^{-1}v$: (1) vertex corrections as in graphs 4 and 5, and (2) nonlinear effects as in graph 6. It is possible to view graph 6 as a fancy vertex correction, but other graphs exist which cannot be so classified. The physical origin of vertex corrections lies in the fact that the electron is not a test charge, it has an exchange interaction with the other electrons of the medium. The physical origin of nonlinear effects is the fact that the charge $e$ is not infinitesimal, so linear response theory is not exact.

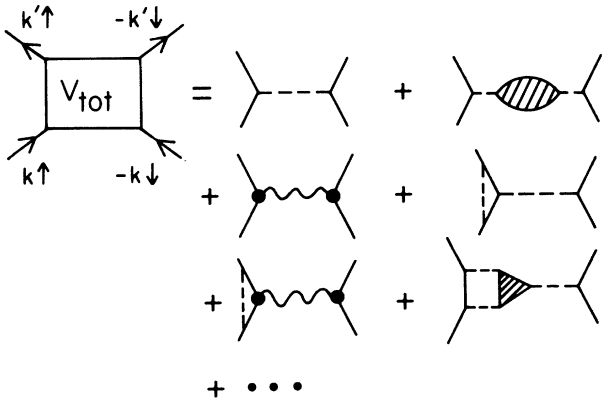


FIG. 2. Feynman graphs for the effective electron-electron interaction which binds a Cooper pair in the BCS theory.

In spite of the fact that $V_{\rm tot}$ is not $\epsilon^{-1}v$,[8] the possibility remains that either the corrections are small or they can be approximately included as a multiplicative correction. We now work out a formula for $\mu-\lambda$ in the $\epsilon^{-1}v$ approximation. First notice that time reversal symmetry tells us that $\psi^*_{-k}=\psi_k$. This enables the second set of brackets [ ] of Eq. (27) to be written as the complex conjugate of the first. If we define

$$g_{kk'}(r)=\psi_{k'}(r)\psi^*_k(r) \tag{29}$$

then Eq. (27) in $\epsilon^{-1}v$ approximation is

$$V_{kk'}=\langle g_{kk'} \mid \epsilon_{\rm tot}^{-1}v \mid g_{kk'}\rangle \,. \tag{30}$$

From Eq. (23) the first term in $\epsilon_{\rm tot}^{-1}v$, namely $v(\mathbf{r},\mathbf{r}')$, gives a purely repulsive contribution, while the second term, $v\chi v$, gives a purely attractive contribution. Stability places no restriction on the sign of the total, so $\mu-\lambda$ may be positive or negative. Little is known about the magnitude of $\mu$ except that in jellium, and by extension, simple metals, it is probably between 0.0 and 0.5, whereas $\lambda$ as determined by experiment is $\sim 0.1$ in alkali metals and 1.5–2.0 in Pb and Pb-Bi alloys. Therefore experiment strongly suggests that $\mu-\lambda$ can take either sign. This does not contradict stability arguments, both because $\epsilon^{-1}v$ can have negative eigenvalues, and because $\epsilon^{-1}v$ is an approximation to $V_{\rm tot}$. These conclusions largely restate results found in Refs. 2 and 3.

## IV. MEAN-FIELD TREATMENT

The purpose of this section is to derive an expression for $\epsilon_{\rm tot}$ in a mean-field treatment which generalizes the familiar (RPA) mean-field treatment of $\epsilon_{\rm el}$, the purely electronic dielectric screening function. To do this, we formulate a mean-field theory which approximates the crystal Hamiltonian by a solvable noninteracting one, then solve for the noninteracting response function of that system, and finally make a mean-field treatment of the fluctuations around the noninteracting system to obtain the mean-field response function. The result is simple, and in Sec. V we show that the answer embodies a large amount of physics.

The total Hamiltonian can be written in terms of the total density operator of Eq. (5), which has two pieces, $\hat\rho_{\rm tot}(r)=\hat\rho_L(\mathbf{r})+\hat\rho_{\rm el}(\mathbf{r})$, the "lattice" and electronic pieces:

$$H_{\rm tot}=\sum_i p_i^2/2m+\sum_l P_l^2/2M + \tfrac{1}{2}\int d^3r\, d^3r'\hat\rho_{\rm tot}(\mathbf{r})v(\mathbf{r}-\mathbf{r}')\hat\rho_{\rm tot}(\mathbf{r}') \,. \tag{31}$$

The mean-field treatment consists of writing the density operator as

$$\langle\rho_{\rm tot}(\mathbf{r})\rangle+[\hat{\rho}_{\rm tot}(\mathbf{r})-\langle\rho_{\rm tot}(\mathbf{r})\rangle]$$

and temporarily ignoring the part of Eq. (31) which is quadratic in the fluctuation term. A convenient way of subdividing $H_{\rm tot}$ is as follows

$$H_{\rm tot}=H_{0,\rm el}+H_{0,L}+H_{\rm int}+H_{\rm extra}\ , \tag{32}$$

where the first two pieces contain the noninteracting electronic and phonon parts. The electronic part,

$$H_{0,\rm el}=\sum_i p_i^2/2m+\int d^3r\,d^3r'\hat{\rho}_{\rm el}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')\langle\rho_{\rm tot}(\mathbf{r})\rangle \tag{33}$$

contains the Hartree interaction of each electron with the mean field of every electron, as well as the interaction of the electrons with the mean field of the nuclei. Since it is linear in $\hat{\rho}_{\rm el}$, it is the sum of $ZN$ one-electron Hamiltonians $H_{1e}$, where $Z$ is the nuclear charge and $N$ the number of nuclei:

$$H_{1e}=p^2/2m+\int d^3\mathbf{r}'v(\mathbf{r}-\mathbf{r}')[\langle\rho_{\rm el}(r')\rangle+\langle\rho_L(r')\rangle]\ . \tag{34}$$

In a crystal, this is periodic and can be solved in principle

$$H_{1e}\psi_k(r)=\epsilon_k\psi_k(r)\ , \tag{35}$$

where $k$ is short for the quantum numbers $(kn)$. This Hartree theory requires a self-consistent solution because $\langle\rho_{\rm el}(\mathbf{r}')\rangle$ is the sum of the occupied single electron charge densities $|\psi_k(\mathbf{r}')|^2$. In principle, the nuclear charge density $\langle\rho_L(\mathbf{r}')\rangle$ also could enter in a self-consistent way, but it will be sufficient to let $\langle\rho_L(\mathbf{r}')\rangle$ refer to nuclei frozen at perfect lattice positions. The Hartree treatment is of course, less accurate than modern density-functional procedures, which are no more complicated and could be included at this stage, but we omit such refinements.

The phonon term is chosen to be

$$H_{0,L}=\sum_{\rm l} P_{\rm l}^2/2M+\int d^3r\,d^3r'[\hat{\rho}_L(\mathbf{r})-\langle\rho_L(\mathbf{r})\rangle]\times v(\mathbf{r}-\mathbf{r}')\langle\rho_{\rm tot}(\mathbf{r}')\rangle\ . \tag{36}$$

This allows lattice fluctuations to experience only those restoring forces exerted by the rigid periodic average total density. The solutions of Eq. (36) are "bare" phonons which are not very close to the experimental phonon frequencies. The remaining two parts of $H_{\rm tot}$ are

$$H_{\rm int}=\tfrac{1}{2}\int d^3r\,d^3r'[\hat{\rho}_{\rm tot}(\mathbf{r})-\langle\rho_{\rm tot}(\mathbf{r})\rangle]v(\mathbf{r}-\mathbf{r}')\times[\hat{\rho}_{\rm tot}(\mathbf{r}')-\langle\rho_{\rm tot}(\mathbf{r}')\rangle]\ , \tag{37}$$

$$H_{\rm extra}=\tfrac{1}{2}\int dr\,dr'\langle\rho_L(\mathbf{r})\rangle v(\mathbf{r}-\mathbf{r}')\langle\rho_L(\mathbf{r}')\rangle-\tfrac{1}{2}\int dr\,dr'\langle\rho_{\rm el}(\mathbf{r})\rangle v(\mathbf{r}-\mathbf{r})\langle\rho_{\rm el}(\mathbf{r}')\rangle\ . \tag{38}$$

$H_{\rm int}$ contains all the interaction terms, and $H_{\rm extra}$ contains the positive "Madelung" energy of Coulomb repulsion between the nuclei, and a negative term which corrects for the fact that the Coulomb repulsion between electrons was double-counted in the Hartree term $H_{0,\rm el}$.

To solve the phonon part Eq. (36), it is convenient to introduce the Fourier-transformed density operator

$$\hat{\rho}_L(\mathbf{Q})=Z\sum_{\rm l} e^{-i\mathbf{Q}\cdot\mathbf{R}_{\rm l}} \tag{39}$$

and similarly for $\hat{\rho}_{\rm el}(\mathbf{Q})$. The average charge density is periodic

$$\langle\rho_{\rm tot}(\mathbf{r})\rangle=\frac{1}{\Omega}\sum\langle\rho_{\rm tot}(\mathbf{G})\rangle e^{i\mathbf{G}\cdot\mathbf{r}} \tag{40}$$

so only the reciprocal lattice vectors G appear. Here $\Omega$ is the crystal volume. Then the bare-phonon Hamiltonian becomes

$$H_{0,L}=\sum_{\rm l} P_{\rm l}^2/2M+\sum_{\rm G}[\hat{\rho}_L(-\mathbf{G})-\langle\rho_L(-\mathbf{G})\rangle]\times\frac{4\pi e^2}{\Omega G^2}\langle\rho_{\rm tot}(\mathbf{G})\rangle\ . \tag{41}$$

Now introduce the harmonic approximation by Taylor expanding $\rho_L(-\mathbf{G})$ to second order in $\mathbf{u}_l=\mathbf{R}_l-\mathbf{l}$:

$$\hat{\rho}_L(-\mathbf{G})-\langle\rho_L(-\mathbf{G})\rangle=Z\sum_l[e^{i\mathbf{G}\cdot(\mathbf{l}+\mathbf{u}_{\rm l})}-e^{i\mathbf{G}\cdot\mathbf{l}}]=Z\sum_l[i\mathbf{G}\cdot\mathbf{u}_{\rm l}-\tfrac{1}{2}(\mathbf{G}\cdot\mathbf{u}_{\rm l})^2+\cdots]\ . \tag{42}$$

When inserted into Eq. (41), the term linear in $\mathbf{u}_{\rm l}$ vanishes by symmetry leaving

$$H_{0,L}=\sum_{\rm l}(P_l^2/2M+\tfrac{1}{2}K^0_{\alpha\beta}u_{l\alpha}u_{l\beta})\ , \tag{43}$$

$$K^0_{\alpha\beta}=-\sum_G\langle\rho_{\rm tot}(\mathbf{G})\rangle\frac{4\pi Ze^2}{\Omega G^2}G_\alpha G_\beta\ . \tag{44}$$

This describes a system of Einstein oscillators. If we assume cubic symmetry, $K_{\alpha\beta}$ becomes $K_0\delta_{\alpha\beta}$, where the scalar force constant $K_0$ fixes the $3N$-fold degenerate bare frequency $\Omega_0$

$$M\Omega_0^2=K_0=-\frac{4\pi Ze^2}{3\Omega}\sum_{\rm G}\langle\rho_{\rm tot}(\mathbf{G})\rangle=-\frac{4\pi Ze^2}{3}\langle\rho_{\rm tot}(\mathbf{r}=0)\rangle\ . \tag{45}$$

The question of whether $\Omega_0^2$ is positive or even finite is not as relevant as might at first sight appear, and will be addressed in Sec. V.

Now that $H_{0,\rm el}$ and $H_{0,L}$ have been solved, we consider the density response functions, $\chi_0$, of this noninteracting system, and $\chi_{\rm MF}$ which takes interactions into account in a mean-field approximation. By definition, $\chi_0$ is to be the *exact* response function [calculated from Eq. (7)] of the complete Hamiltonian except for the term $H_{\rm int}$ [Eq. (37)]. Since $H_{\rm extra}$ is a constant, $\chi_0$ is the response function of

$H_{0,\mathrm{el}}+H_{0,L}$. The interactions are taken into account by the usual mean-field procedure of assuming that the system responds to a total potential $\delta V_{\mathrm{ext}}+\delta V_H$ just as the noninteracting system responds to the external potential alone [Eq. (3)]. The extra potential $\delta V_H$ is the classical or Hartree electrostatic potential of the charge-density fluctuation $\delta\rho_{\mathrm{tot}}$, which is self-consistently calculated, and denoted $\delta\rho_{\mathrm{MF}}$. Thus Eq. (3) is replaced by

$$\delta\rho_{\mathrm{MF}}(\mathbf{r}t)\equiv\int d^3r'\int_{-\infty}^{\infty}dt'\chi_{\mathrm{MF}}(\mathbf{r},\mathbf{r}',t-t')\delta V_{\mathrm{ext}}(\mathbf{r}',t')$$
$$=\int d^3r'\int_{-\infty}^{\infty}dt'\chi_0(\mathbf{r},\mathbf{r}',t-t')\left[\delta V_{\mathrm{ext}}(\mathbf{r}',t')+\int d^3r''v(\mathbf{r}'-\mathbf{r}'')\delta\rho_{\mathrm{MF}}(\mathbf{r}'',t')\right]. \tag{46}$$

In symbolic operator notation, this gives the equation for $\chi_{\mathrm{MF}}$

$$\chi_{\mathrm{MF}}=\chi_0+\chi_0v\chi_{\mathrm{MF}}=(1-\chi_0v)^{-1}\chi_0 \tag{47}$$

which is the usual RPA type of formula. Finally the mean-field dielectric function is defined as in Eq. (4), and can be solved explicitly

$$\epsilon_{\mathrm{MF}}^{-1}\equiv 1+v\chi_{\mathrm{MF}}\ ,$$
$$\epsilon_{\mathrm{MF}}=1-v\chi_0\ . \tag{48}$$

This is the usual RPA relation between the dielectric function and the noninteracting susceptibility. However, in the usual approach $\chi_0$ is the electronic part, and Eq. (48) includes an approximate treatment of the electron-electron Coulomb interaction only. The novelty of the present approach is that $\epsilon_{\mathrm{MF}}$ contains an approximate treatment of all Coulomb interactions between charge fluctuations: displacement-displacement and electron-phonon as well as electron-electron.

Finally let us use Eq. (7) to evaluate $\chi_0$. Separating $\hat{\rho}_{\mathrm{tot}}$ into $\hat{\rho}_{\mathrm{el}}$ and $\hat{\rho}_L$ there are three terms: (1) the purely electronic part $\chi_{0,\mathrm{el}}$, (2) the purely phonon part $\chi_{0,L}$, and (3) the mixed terms involving $[\hat{\rho}_{\mathrm{el}}(t),\hat{\rho}_L(0)]$ and vice versa. It is easy to verify that when $H_{\mathrm{int}}$ is omitted from the Hamiltonian which determines the $t$ dependence of $\hat{\rho}_{\mathrm{el}}$ and $\hat{\rho}_L$, the mixed commutator is zero at all $t$. Thus we have

$$\chi_0=\chi_{0,\mathrm{el}}+\chi_{0,L}\ . \tag{49}$$

We will require $\epsilon$ and $\chi$ in reciprocal space, so Eq. (7) can be replaced by its Fourier transformed version

$$\chi(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)=-\frac{i}{\hbar}\int_0^{\infty}dt\langle[\hat{\rho}_{\mathrm{tot}}(\mathbf{Q}+\mathbf{G},t),\hat{\rho}_{\mathrm{tot}}(-\mathbf{Q}-\mathbf{G}',0)]\rangle e^{i\omega t}\ , \tag{50}$$

where crystalline translational symmetry is now assumed. The electronic part of $\chi_0$ is a standard result

$$\chi_{0,\mathrm{el}}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)$$
$$=\sum_{k,k'}\langle k\mid e^{-i(\mathbf{Q}+\mathbf{G})\cdot\mathbf{r}}\mid k'\rangle\frac{f_k-f_{k'}}{\epsilon_k-\epsilon_{k'}-\hbar\omega}$$
$$\times\langle k'\mid e^{i(\mathbf{Q}+\mathbf{G}')\cdot\mathbf{r}}\mid k\rangle\ . \tag{51}$$

The lattice part can be calculated exactly if $H_{0,L}$ in Eq. (36) is replaced by its harmonic approximation. We only need to know $\chi_{0,L}$ to second order in $\mathbf{u}_l$, and to go to higher order would not be consistent with the harmonic approximation already made. Keeping only the lowest terms in the Taylor expansion Eq. (42), the lattice part $\chi_{0,L}$ is given by the displacement-displacement correlation function $D^0_{\alpha\beta}$

$$\chi_{0,L}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)=NZ^2(\mathbf{Q}+\mathbf{G})_\alpha D^0_{\alpha\beta}(\mathbf{Q},\omega)$$
$$\times(\mathbf{Q}+\mathbf{G}')_\beta\ , \tag{52}$$
$$D^0_{\alpha\beta}=-(i/\hbar)\int_0^{\infty}dt\langle[u_{Q\alpha}(t),u_{Q\beta}(0)]\rangle e^{i\omega t}\ . \tag{53}$$

The function $D^0_{\alpha\beta}$ is easily calculated from the results (43)–(45)

$$D^0_{\alpha\beta}(\mathbf{Q},\omega)=\sum_j\epsilon_\alpha(Qj)\epsilon_\beta(-Qj)/[M(\omega^2-\Omega_0^2)]$$
$$=\delta_{\alpha\beta}[M(\omega^2-\Omega_0^2)]^{-1}\ . \tag{54}$$

The sum in Eq. (54) is over the three degenerate modes which by completeness of the eigenvectors $\epsilon(Qj)$ yields the unit tensor $\delta_{\alpha\beta}$. Finally, Eq. (52) becomes

$$\chi_{0,L}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)=\frac{NZ^2(\mathbf{Q}+\mathbf{G})\cdot(\mathbf{Q}+\mathbf{G}')}{M(\omega^2-\Omega_0^2)}\ . \tag{55}$$

It is easy to verify the stability requirement that $\chi$ is a negative operator (when $\omega=0$). This takes the form

$$0\geq\langle f\mid\chi\mid f\rangle=\sum_{\mathbf{Q}}\sum_{\mathbf{G},\mathbf{G}'}f^*(\mathbf{Q}+\mathbf{G})\chi(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}')$$
$$\times f(\mathbf{Q}+\mathbf{G}')\ . \tag{56}$$

The electronic part [Eq. (51)] gives

$$\langle f \mid \chi_{0,\mathrm{el}} \mid f \rangle = \sum_{k,k',Q} \left| \sum_{G} f(\mathbf{Q}+\mathbf{G}) \langle k' \mid e^{i(\mathbf{Q}+\mathbf{G})\cdot\mathbf{r}} \mid k \rangle \right|^2 \times (f_k - f_{k'})/(\epsilon_k - \epsilon_{k'}) \tag{57}$$

which is negative because the first factor is positive and the second negative. Thus the mean field dielectric function (48) is positive when lattice response is omitted. The lattice part [Eq. (55)] gives

$$\langle f \mid \chi_{0,L} \mid f \rangle = -N \sum_{\mathbf{Q}} A(\mathbf{Q}) \cdot A(\mathbf{Q})^* / M\Omega_0^2 ,$$
$$\mathbf{A}(Q) = \sum_{\mathbf{G}} (\mathbf{Q}+\mathbf{G}) f(\mathbf{Q}+\mathbf{G}) . \tag{58}$$

This is also negative, provided of course, $\Omega_0^2 > 0$, which is an alternate way of demanding that the zeroth-order system is stable. We shall see later that $\Omega_0^2 > 0$ is not obeyed, so that $\epsilon_{\mathrm{MF}}$ is by no means necessarily positive.

## V. $\epsilon^{-1}$ AND COLLECTIVE MODES

To calculate the test-charge–test-charge interaction $V_{12} = v + v\chi v$ we need to invert the dielectric function calculated in the preceding section. This is most easily done in the symmetrized form

$$V_{12,\mathrm{MF}} = v_{1/2} \epsilon_{s,\mathrm{MF}}^{-1} v_{1/2} , \tag{59}$$

$$\epsilon_{s,\mathrm{MF}} = 1 - v_{1/2} \chi_0 v_{1/2} . \tag{60}$$

The operator $v_{1/2}$ is easily constructed in Fourier space, and the symmetric dielectric function $\epsilon_{s,\mathrm{MF}}$ is like $\epsilon_{\mathrm{MF}} = 1 - v\chi_0$ except that $v = 4\pi e^2/\Omega(\mathbf{Q}+\mathbf{G})^2$ is replaced by $4\pi e^2/\Omega \mid \mathbf{Q}+\mathbf{G} \mid \mid \mathbf{Q}+\mathbf{G}' \mid$. Then we have

$$\epsilon_{s,\mathrm{MF}} = \epsilon_{\mathrm{MF,el},s} - \sum f_\alpha(\mathbf{Q}+\mathbf{G}) D^0_{\alpha\beta}(\mathbf{Q},\omega) f_\beta(\mathbf{Q}+\mathbf{G}') , \tag{61}$$

$$f_\alpha(\mathbf{Q}+\mathbf{G}) = (4\pi N Z^2 e^2/\Omega(\mathbf{Q}+\mathbf{G})^2)^{1/2} (\mathbf{Q}+\mathbf{G})_\alpha , \tag{62}$$

where $\epsilon_{\mathrm{MF,el},s}$ is the purely electronic part, and $D^0_{\alpha\beta}$ is the displacement-displacement correlation function given by Eq. (54). If we assume that the inverse of $\epsilon_{0,\mathrm{el},s}$ is available, then the full inverse of Eq. (61) can also be found by use of the formula for matrices with factorizable parts. Given a matrix of the form

$$M_{ij} = A_{ij} - \sum_{\alpha,\beta} r^0_\alpha(i) t^0_{\alpha\beta} r^0_\beta(j) . \tag{63}$$

Then the inverse is

$$(M^{-1})_{ij} = (A^{-1})_{ij} + \sum_{\alpha,\beta} r_\alpha(i) t_{\alpha\beta} r_\beta(j) , \tag{64}$$

$$r_\alpha(i) = \sum_k (A^{-1})_{ik} r^0_\alpha(k) , \tag{65}$$

$$(t^{-1})_{\alpha\beta} = (t^0)^{-1}_{\alpha\beta} - \sum_{i,j} r^0_\alpha(i) (A^{-1})_{ij} r^0_\beta(j) . \tag{66}$$

The indices $ij$ translate into $G,G'$ in Eq. (61). If we use this to invert Eq. (60) and then construct the interaction Eq. (59), we get

$$V_{12,\mathrm{MF}} = V_{\mathrm{el}} + \sum_{\alpha,\beta} \phi_\alpha(\mathbf{Q}+\mathbf{G}) D_{\alpha\beta}(Q\omega) \phi_\beta(\mathbf{Q}+\mathbf{G}') , \tag{67}$$

where the first term is the purely electronic part of the screened interaction

$$V_{\mathrm{el}} = \epsilon^{-1}_{\mathrm{MF,el}}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega) \frac{4\pi e^2}{\Omega(\mathbf{Q}+\mathbf{G})^2} . \tag{68}$$

This corresponds to the first two graphs of Fig. 2. The second piece of Eq. (67) is the screened electron-phonon interaction corresponding to the third graph of Fig. 2. The dot on this graph is $\phi_\alpha$, the screened electron-phonon matrix element

$$\phi_\alpha(\mathbf{Q}+\mathbf{G}) = \sum_{\mathbf{G}_1} \epsilon^{-1}_{\mathrm{MF,el}}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}_1,\omega)(\mathbf{Q}+\mathbf{G}_1)_\alpha \times \frac{4\pi Z e^2}{\Omega(\mathbf{Q}+\mathbf{G}_1)^2} \tag{69}$$

which is the screened gradient of the electron-ion potential $Ze^2/r$. The wavy line in graph 3 of Fig. 2 is the renormalized phonon propagator $D_{\alpha\beta}$ given by

$$D^{-1}_{\alpha\beta} = M(\omega^2 - \Omega_0^2)\delta_{\alpha\beta} - \sum_{\mathbf{G}_1,\mathbf{G}_2} f_\alpha(\mathbf{Q}+\mathbf{G}_1)[\delta_{\mathbf{G}_1\mathbf{G}_2} + v_{1/2}(\mathbf{Q}+\mathbf{G}_1)\chi_{\mathrm{MF,el}}(\mathbf{Q}+\mathbf{G}_1,\mathbf{Q}+\mathbf{G}_2,\omega)v_{1/2}(\mathbf{Q}+\mathbf{G}_2)] f_\beta(\mathbf{Q}+\mathbf{G}_2) , \tag{70}$$

where $\epsilon^{-1}_{\mathrm{MF,el},s}$ has been written as $1 + v^{1/2}\chi_{\mathrm{MF,el}} v^{1/2}$. Writing out this propagator in more detail, Eq. (70) becomes

$$D^{-1}_{\alpha\beta}(\mathbf{Q},\omega) = M\omega^2\delta_{\alpha\beta} - K_{\alpha\beta}(\mathbf{Q},\omega) , \tag{71}$$

where $K_{\alpha\beta}(Q\omega)$ is the "dynamical matrix," given by

$$K_{\alpha\beta}(\mathbf{Q},\omega) = K^0_{\alpha\beta} + \sum_{\mathbf{G}} (\mathbf{Q}+\mathbf{G})_\alpha (\mathbf{Q}+\mathbf{G})_\beta \frac{4\pi Z^2 e^2}{\Omega(\mathbf{Q}+\mathbf{G})^2} + \sum_{\mathbf{G}_1,\mathbf{G}_2} (\mathbf{Q}+\mathbf{G}_1)_\alpha \frac{4\pi Z e^2}{\Omega(\mathbf{Q}+\mathbf{G}_1)^2} \chi_{\mathrm{el,MF}}(\mathbf{Q}+\mathbf{G}_1,\mathbf{Q}+\mathbf{G}_2,\omega) \times \frac{4\pi Z e^2}{\Omega(\mathbf{Q}+\mathbf{G}_2)} (\mathbf{Q}+\mathbf{G}_2)_\beta . \tag{72}$$

The second and third parts of Eq. (72) appear in the theory of phonon dynamics,[9-11] being the direct Coulomb force and the indirect electron mediated parts, respectively. The remaining piece, $K^0_{\alpha\beta}$ is given by Eq. (44), and does not yet have the standard form.

With the help of Eq. (39), Eq. (44) can be written as

$$K^0_{\alpha\beta} = -\sum_G G_\alpha G_\beta \frac{4\pi Ze^2}{\Omega_c G^2}[Z + \langle \rho_{\rm el}(\mathbf{G})\rangle/N] \ . \quad (73)$$

The first term of $K^0_{\alpha\beta}$ combines with the second term of Eq. (72) to give the total direct Coulomb part of the dynamical matrix. The second part of Eq. (73) can be rewritten as follows. Suppose the entire lattice is displaced by an arbitrary small amount $\eta\hat{\beta}$. The change in the electronic charge density is $\eta\nabla_\beta\langle\rho_{\rm el}(\mathbf{r})\rangle$. This change can be viewed as a response to a perturbation, $\eta\nabla_\beta V^0_{\text{el-ion}}(r)$, where the unscreened electron-ion interaction $V^0_{\text{el-ion}}$ is just $\sum Ze^2/|\mathbf{r}-\mathbf{l}|$, and the response function is $\chi_{\rm el}$. In Fourier space, this translates into

$$G_\beta\langle\rho_{\rm el}(\mathbf{G})\rangle = \sum_{G'} \chi_{\text{el,MF}}(\mathbf{G},\mathbf{G}')\frac{4\pi Ze^2}{\Omega G'^2}G'_\beta \ , \quad (74)$$

a relation known as the "acoustic sum rule" which the mean-field approximation obeys.[9,11] Using this in Eq. (73) gives a term which combines with the last term of Eq. (72). The complete dynamical matrix then has the form

$$K_{\alpha\beta}(\mathbf{Q},\omega) = \sum_{GG'}[(\mathbf{Q}+\mathbf{G})_\alpha \Phi(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)(\mathbf{Q}+\mathbf{G}')_\beta - G_\alpha\Phi(\mathbf{G},\mathbf{G}',0)G'_\beta] \ , \quad (75)$$

where the complete interaction $\Phi$ is

$$\Phi(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega) = \delta_{GG'}\frac{4\pi Z^2e^2}{\Omega(\mathbf{Q}+\mathbf{G})^2} + \frac{4\pi Ze^2}{\Omega(\mathbf{Q}+\mathbf{G})^2}\chi_{\text{el,MF}}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)\frac{4\pi Ze^2}{\Omega(\mathbf{Q}+\mathbf{G}')^2} \ . \quad (76)$$

Not surprisingly, this is the electronic part of the total screened interaction between two test charges $Z$. Equations (75) and (76) reproduce the theory of Refs. 9–11. *Thus the simple mean-field theory, Eq. (61), yields a fully developed theory for $\epsilon^{-1}$ and for the test-charge–test-charge interaction, Eq. (67), which has poles at the correct physical phonon frequencies.*

The total test-charge–test-charge interaction Eq. (67) is familiar in the theory of superconductivity, being the same as Fig. 2, graphs 1–3. Maksimov[12] in particular, has written this interaction out, and used it to *define* a total dielectric function $\epsilon^{-1}_{\rm tot}v = V_{12}$. Thus Maksimov's total dielectric function coincides with the mean-field result derived here.

Let us now return to the question of the sign and magnitude of the bare-phonon frequencies $\Omega_0^2$ of Eqs. (44) and (45), which are eigenfunctions of $K^0_{\alpha\beta}$ given in Eq. (73). The trace of this matrix is the sum of the bare-phonon frequencies of the three branches, which in cubic symmetry are all degenerate

$$M\Omega_0^2 = -\frac{4\pi Ze^2}{3\Omega}\sum_G[Z + \langle\rho_{\rm el}(\mathbf{G})\rangle/N] \ . \quad (77)$$

It is easy to see from Eq. (45) that this is negative and diverging to $-\infty$. Although these features seem undesirable, they are inevitable consequences of the simple mean-field procedure which as usual adds an unphysical self-force (which gets cancelled in the end). This aspect of mean field theory is explored further in the Appendix. There it is shown that the mean field treatment is exact for classical harmonic vibrations, and that the cancellation of self-interactions is exact. Because the particles are classical point charges, the self-force of the nucleus is infinite and repulsive. The starting noninteracting model violates the stability criterion. This should not be surprising: stability is only restored in the end when charge fluctuations interact, and only if the crystal structure parameters are chosen carefully to yield a stable structure. The divergence of the sum in Eq. (77) is also not bothersome. When the divergent sums are rearranged as in Eq. (75), convergence is rapid. A way to justify the matrix inversion procedure and rearrangement is as follows: arbitrarily terminate the matrix $\epsilon(\mathbf{G},\mathbf{G}')$ after a certain number of shells of reciprocal-lattice vectors, and keep the same set of shells in the computation of $K^0_{\alpha\beta}$ in Eq. (44). Then $\Omega_0^2$ is large and negative so $\chi_{0,L}$ Eq. (55) is small and positive. The inversion procedure is well defined and the rearrangement of Eq. (75) is legitimate. Finally, take the limit of this process as the number of shells goes to infinity.

An alternate route that leads to finite and sensible answers is to let $\langle\rho_L\rangle$ refer to an average taken with some finite rms thermal displacement included. Then $\rho_{\rm tot}(r=0)$ is finite [see Eq. (45)] and $\Omega_0^2$, although still negative, is finite.

The mean-field total dielectric function is apparently quite peculiar. It consists of an electronic part which in RPA has eigenvalues all $\geq 1$, in spite of the fact that stability also permits eigenvalues $<0$. In addition, there is a phonon part which is negative (i.e., has eigenvalues $\leq 0$) but each matrix element is infinitesimally small as the number of $G$ shells goes to infinity. However, this does not mean that $\epsilon_{\rm MF}$ has no negative eigenvalues, because the phonon contributions to $\epsilon_{\rm MF}$ do not diminish in size as $|\mathbf{G}|$, $|\mathbf{G}'|$, or $|\mathbf{G}-\mathbf{G}'|$ increases. It is an infinitely large matrix of infinitesimal elements, so the eigenvalues are not necessarily constrained by simple bounds. The final results for $\chi_{\rm MF}$ or $\epsilon^{-1}_{\rm tot}$ are very strongly altered by the infinitesimal elements of $\epsilon_{\rm MF}$, to the point that $\chi_{\rm MF}$ will surely have unstable behavior unless the crystal structure parameters are carefully chosen to yield stability. Thus, we have an extremely simple form for the pho-

non contribution to $\epsilon_{\rm MF}$. While it is not one which is computationally useful, it may prove to be useful analytically.

It is also instructive to examine the form of $\chi_{\rm MF}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)$ which emerges from this treatment. This can be found from $V_{12,\rm MF}$ by use of Eq. (23), i.e., $\chi_{\rm MF}=v^{-1}(V_{12,\rm MF}-v)v^{-1}$. The answer is

$$\chi_{\rm MF}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)=\chi_{\rm MF,el}+\chi_{{\rm MF},L}\ , \tag{78}$$

where $\chi_{\rm MF,el}$ is the result when the lattice is frozen. The lattice term can be written as in Eq. (52)

$$\chi_{{\rm MF},L}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega) =NZ^2(\mathbf{Q}+\mathbf{G})_{{\rm sc},\alpha}D_{\alpha\beta}(\mathbf{Q},\omega)(\mathbf{Q}+\mathbf{G}')_{{\rm sc},\beta}\ , \tag{79}$$

$$(\mathbf{Q}+\mathbf{G})_{{\rm sc},\alpha} =\sum_{\mathbf{G}_1}[\delta_{\mathbf{G},\mathbf{G}_1}+\chi_{\rm MF,el}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}_1) \times v(\mathbf{Q}+\mathbf{G}_1)](\mathbf{Q}+\mathbf{G}_1)_\alpha\ . \tag{80}$$

This has a simple interpretation. If the subscript sc for "screening" is omitted [i.e., $(Q+G)_{{\rm sc},\alpha}$ is replaced by $(Q+G)_\alpha$] then Eq. (79) is just the nuclear density–nuclear density correlation function, or the part of Eq. (50) quadratic in $\hat{\rho}_L$. The screening enters Eq. (79) as three additive corrections to the unscreened susceptibility. The first, $\chi_{\rm MF,el}v[(\mathbf{Q}+\mathbf{G}_1)_\alpha D_{\alpha\beta}(\mathbf{Q}+\mathbf{G}')_\beta]$ has $\chi_{\rm MF,el}$ to the left of $D_{\alpha\beta}$ and arises from the part of Eq. (50) with $[\hat{\rho}_{\rm el},\hat{\rho}_L]$. Another arises from $[\hat{\rho}_L,\hat{\rho}_{\rm el}]$, and a third arises from $[\hat{\rho}_{\rm el},\hat{\rho}_{\rm el}]$ and has $\chi_{\rm MF,el}$ on both sides of $D_{\alpha\beta}$. These corrections take into account the Coulomb coupling between electronic and lattice density fluctuations.

The Coulomb and electron-phonon interactions cause the phonon propagator $D_{\alpha\beta}$ to be fully renormalized. In terms of eact phonon eigenstates, $D_{\alpha\beta}$ is

$$D_{\alpha\beta}(\mathbf{Q},\omega)=\sum_j \epsilon^*_\alpha(\mathbf{Q}_j)[M\omega^2-M\omega^2_{\mathbf{Q}j}]^{-1}\epsilon_\beta(\mathbf{Q}_j)\ ,$$

where $\hat{\epsilon}(\mathbf{Q}j)$ is the eigenvector of $\mathbf{K}(\mathbf{Q},\omega)$ in Eq. (75), and $M\omega^2_{Qj}$ is the corresponding eigenvalue. In the limit $\omega=0$, $K$ is Hermitian, and $\omega^2_{Qj}$ and $\epsilon_\alpha(Qj)$ are real. A negative eigenvalue $M\omega^2_{Qj}$ would correspond to an unstable system. If the system is stable, $\omega^2_{Qj}>0$ holds for all modes $(\mathbf{Q}j)$ (except the three acoustic branches at $\mathbf{Q}=0$) and $\mathbf{D}$ is a nonpositive matrix (at $\omega=0$). Similarly $\chi_{{\rm MF},L}$ is nonpositive, following the algebra of Eq. (58) but with $(\mathbf{Q}+\mathbf{G})_{{\rm sc},\alpha}$ in place of $(\mathbf{Q}+\mathbf{G})_\alpha$ and $\omega^2_{Qj}$ in place of $\Omega_0^2$. The purely electronic part $\chi_{\rm MF,el}$ is also nonpositive. This follows from Eq. (57) which shows that $\chi_{0,\rm el}$ is negative and from Eq. (47) which can be written as $\chi^{-1}_{\rm MF}=\chi_0^{-1}-v$ and holds for the purely electronic part of $\chi$ as well as for the total $\chi$. The sum of two negative operators is negative. Thus the condition $\omega^2_{Qj}>0$ is sufficient to guarantee that $\chi$ is nonpositive and that $\epsilon$ and $\epsilon^{-1}$ obey the stability conditions.

These results enable us to see more vividly the way in which many real materials undoubtedly have negative eigenvalues of $\epsilon^{-1}_{\rm tot}$ and thus of $\epsilon_{\rm tot}$ at $\omega=0$. In order to avoid negative eigenvalues of $\epsilon^{-1}$, $v_{1/2}\chi v_{1/2}$ must not have eigenvalues less than $-1$. But $\chi_{{\rm MF},L}$ has the factor $-M\omega^2_{Qj}$ in the denominator. If the system has any "soft modes," there will be a strong tendency for large negative eigenvalues of $\chi$. In the limit that an eigenfrequency goes to zero, $\chi$ and $\epsilon^{-1}$ will have eigenvalues diverging to $-\infty$, and $\epsilon$ will have eigenvalues approaching zero from the negative side. Thus, well before any "soft mode" goes unstable, there will be negative eigenvalues of $\epsilon_{\rm tot}$.

## VI. CONCLUSIONS

Previous work relating stability requirements to restrictions on the total dielectric function have been generalized to the case of inhomogeneous materials. It is concluded that the eigenvalues of the inverse dielectric matrix, $\lambda_i$, satisfy $\lambda_i<1$. A consequence of this is that the electron-electron interaction (as determined by test charges) which enters BCS theory is not restricted to positive values by general stability requirements, i.e., $\mu-\lambda$ can be negative.

The total dielectric function for a combined system of electron plus lattice is calculated in mean-field theory with remarkably simple results, Eqs. (51) and (55). The poles of the inverse dielectric function are shown to be at the phonon frequencies determined by the usual dynamical matrix.

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## APPENDIX: RENORMALIZED AND BARE FREQUENCIES IN RPA

The treatment given in Secs. IV and V uses a natural version of the RPA to generate renormalized phonon frequencies from a noninteracting reference system. However, the reader may be puzzled by the fact that the "bare" squared phonon frequencies $\Omega_0^2$ differ from other definitions which arise in other contexts. More disconcerting is the fact that $\Omega_0^2$ remains in the RPA formula for $\epsilon$, and it is negative and diverging to minus infinity. This divergence comes about because of a nonphysical self interaction $v(r_i-r_j)$ which blows up when $r_i=r_j$. Almost by magic, the true finite frequencies $\omega_Q^2$ emerge as poles of $\chi$ after $\epsilon^{-1}$ is constructed. This Appendix attempts to demystify these features by tracing their appearance in a much simpler problem.

Consider a classical one-dimensional model for a diatomic molecule

$$H = p_1^2/2M + p_2^2/2M + v(r_1 - r_2) , \tag{A1}$$

where the potential $v$ has a stable minimum at a separation $r_0$ (for example, $v$ might be a Lennard-Jones interaction.) We know that the two eigenmodes of this system have $\omega_1^2 = 0$ and $\omega_2^2 = v''(r_0)/(M/2)$ where the first mode is the uniform translation of the center of mass, and the second mode is the vibration of the relative coordinate $r_2 - r_1$, with reduced mass $M/2$. Let us derive these by a mean-field treatment of the response function. Ultimately we want to do the susceptibility, but it is illuminating first to calculate the displacement response function $D_{ij}(\omega)$, defined as

$$\langle u_i(t) \rangle = \sum_j D_{ij}(\omega) F_j e^{-i\omega t} . \tag{A2}$$

That is, $D$ gives the displacement of the $i$th atom when forces $F_1, F_2$ are applied to each atom at the same frequency $\omega$. $D$ is the phonon Green's function, and has poles at the resonant frequencies of the system.

We work in harmonic approximation around the stable minimum, which permits us to replace (A1) by

$$H = p_1^2/2M + p_2^2/2M + \tfrac{1}{2} v''(r_0)(u_2 - u_1)^2 , \tag{A3}$$

where $u_i$ are the displacements from the minima at $R \pm r_0/2$, and $R$ is the center of mass. A mean field theory can be made by replacing $u_i$ by $\langle u_i \rangle + \delta u_i$ (where $\delta u_i$ is $u_i - \langle u_i \rangle$) and temporarily ignoring the term quadratic in $\delta u_i$. Now since $\langle u_i \rangle = 0$ in the absence of external forces, the reference system is just free particles with $H_0 = (p_1^2 + p_2^2)/2M$. The response function is $D_{ij}^0 = -\delta_{ij}/M\omega^2$, just like the Drude response of the noninteracting electron gas. Now the interaction $v''$ is taken into account in the usual mean field fashion, by assuming that the actual response of the particles is the noninteracting response to the total force consisting of the external force plus the harmonic force caused by the mean displacement of the atoms.

$$\begin{aligned} \langle u_i \rangle &= \sum_j D_{ij}^0(\omega) \\ &\quad \times \left[ F_j - \left\langle \frac{\partial}{\partial u_j} \frac{1}{2} v''(u_2 - u_1)^2 \right\rangle \right] e^{-i\omega t} \\ &= \sum_j D_{ij}^0(\omega) \left[ F_j - \sum_k R_{jk} \langle u_k \rangle \right] e^{-i\omega t} , \end{aligned} \tag{A4}$$

where the matrix $\underline{R}$ is

$$\underline{R} = \begin{bmatrix} v'' & -v'' \\ -v'' & v'' \end{bmatrix} . \tag{A5}$$

The solution is easily found

$$\underline{D}^{-1} = \underline{D}_0^{-1} + \underline{R} = \begin{bmatrix} -M\omega^2 + v'' & -v'' \\ -v'' & -M\omega^2 + v'' \end{bmatrix} . \tag{A6}$$

The eigenvalues are $-M\omega^2$ and $-M\omega^2 + 2v''$, and the correponding eigenvectors

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad |2\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix} , \tag{A7}$$

i.e., the uniform translation and the optic vibration. The corresponding poles of $\underline{D}$ are at $\omega^2 = 0$ and $\omega^2 = 2v''/M$, exactly as expected.

The following lessons can be drawn from this example. (1) Mean-field theory gives an *exact* treatment of dynamics in harmonic approximation. (2) The reference system does not have to be close to the true system, or even stable. In this example, the reference system was free particles with no restoring forces; the "bare" frequencies $\Omega_0^2$ were zero. (3) The generalization to large or infinite systems of bound particles with harmonic interactions is immediate. The "bare frequencies" are zero, the noninteracting response function is $\underline{D}_0^{-1} = -M\omega^2$ and the mean field answer, which is exact, is $\underline{D}^{-1} = -M\omega^2 + \underline{K}$ where $K$ is the force constant matrix, given by

$$K_{ij} = \frac{\partial^2}{\partial u_i \partial u_j} \left[ \sum_{\langle mn \rangle} \tfrac{1}{2} v''(r_{mn}^0)(u_m - u_n)^2 \right] , \tag{A8}$$

and $\langle mn \rangle$ indicates that the sum goes over each bond once.

Now let us solve for the susceptibility $\chi$ by a mean field theory analogous to Sec. IV. For the 1D diatomic classical model, the nuclear density is

$$\rho(r) = \delta(r - r_1) + \delta(r - r_2) , \tag{A9}$$

and the Hamiltonian (A1) becomes

$$\begin{aligned} H = p_1^2/2M + p_2^2/2M + \tfrac{1}{2} \int dr\, dr' \rho(r) v(r - r') \rho(r') \\ - v(r = 0) , \end{aligned} \tag{A10}$$

where the last piece subtracts off the self-interactions contained in the previous piece. Now replace the density $\rho(r)$ by $\langle \rho(r) \rangle + \delta\rho(r)$. The part quadratic in $\delta\rho(r)$ is the interaction $H_{\text{int}}$, and the remaining part is

$$\begin{aligned} H_0 = (p_1^2 + p_2^2)/2M \\ + \int dr\, dr' \langle \rho(r) \rangle v(r - r') [\rho(r') - \langle \rho(r') \rangle] + \text{const.} \end{aligned} \tag{A11}$$

The average density $\langle \rho(r) \rangle$ is just the static molecule $\delta(r - r_1^0) + \delta(r - r_2^0)$. Apart from constant terms, the potential in (A11) consists of an identical single-particle potential for each atom

$$\sum_{ij} v(r_i^0 - r_j) - v(r_i^0 - r_j^0) \cong \sum_{ij} \tfrac{1}{2} v''(r_{ij}^0) u_j^2 . \tag{A12}$$

This reference system has each atom vibrating independently. The eigenfrequencies are the same for each atom

$$M\Omega_0^2 = v''(r = 0) + v''(r = r_0) . \tag{A13}$$

The displacement correlation function is

$$\underline{D}_0^{-1}(\omega) = M(\Omega_0^2 - \omega^2)\underline{1} . \tag{A14}$$

We now consider the effect of an external potential and of the interactions

$$H_{\text{ext}}=\int dr\,\delta\rho(r)V_{\text{ext}}(r)e^{-i\omega t}\,, \tag{A15}$$

$$H_{\text{int}}=\tfrac{1}{2}\int dr\,dr'\delta\rho(r)v(r-r')\delta\rho(r')\,. \tag{A16}$$

The mean field treatment of the susceptibility assumes that the system reponds as the noninteracting reference system does, except driven by $V_{\text{ext}}$ plus a Hartree-type field.

$$\langle\delta\rho(r)\rangle e^{-i\omega t} = \int dr'\chi_0(r,r',\omega) \times\left[V_{\text{ext}}(r')+\int dr''v(r'-r'')\langle\delta\rho(r'')\rangle\right]e^{-i\omega t}\,. \tag{A17}$$

The resulting susceptibility obeys

$$\chi^{-1}(r,r',\omega)=\chi_0^{-1}(r,r',\omega)-v(r-r')\,. \tag{A18}$$

Rather than compute (A18) directly, we find a relation between $\chi^{-1}$ and $\underline{D}^{-1}$. The external perturbation can be expressed either through a potential or through a force

$$H_{\text{ext}}=\int dr\,\delta\rho(r)V_{\text{ext}}(r)=-\sum_i u_iF_i\,. \tag{A19}$$

By inverting the definitions of $\chi$ and $D$, (A19) can be written as

$$\int dr\,dr'\delta\rho(r)\chi^{-1}(r,r')\delta\rho(r')=-\sum_{ij}u_iD_{ij}^{-1}u_j\,. \tag{A20}$$

The density $\delta\rho(r)$ is $\sum u_i\nabla_i\rho$, which enables us to identify

$$D_{ij}^{-1}=-\nabla_i\nabla_j\chi^{-1}(R_i,R_j,\omega)\,. \tag{A21}$$

Then Eq. (A18) becomes

$$D_{ij}^{-1}=D_{0ij}^{-1}+\left[\frac{\partial^2v(r-r')}{\partial r\partial r'}\right]_{r=R_i,r'=R_j} \tag{A22}$$

$$=\begin{bmatrix}-M\omega^2+v_0''+v_{r_0}'' & 0\\ 0 & -M\omega^2+v_0''+v_{r_0}''\end{bmatrix}+\begin{bmatrix}-v_0'' & -v_{r_0}''\\ -v_{r_0}'' & -v_0''\end{bmatrix}\,. \tag{A23}$$

Equation (A23) agrees exactly with (A6), so we have again correctly found the vibrational eigenfrequencies.

The lessons to be drawn from this second calculation are the following.

(1) As in the calculation of $D$ in Eqs. (A1)–(A7), the mean field treatment of $\chi$ gives the exact dynamics of a harmonic system.

(2) Again the reference system is very different from the true system, and is typically unstable. When density rather than displacement is used as the dynamical variable, the reference system contains unphysical self forces, expressed as $v''(r=0)$ in Eq. (A13). When the poles of $\chi$ are found by mean field theory, the self forces cancel. The bare frequencies $\Omega_0^2$ are generally unstable and divergent. For example, the Lennard-Jones system has $v(r)\cong\epsilon(\sigma/r)^{12}$ so that $\Omega_0^2$ is more severely divergent than the Coulomb case in Secs. IV and V.

(3) The generalization to large systems is again immediate, and it is easy to see that the answer (A22) is equivalent to (A8).

It is useful to consider the form of the bare frequencies when (A12) is applied to a periodic system.

$$\sum_{ij}\tfrac{1}{2}v''(r_{ij}^0)u_j^2=\sum_i\tfrac{1}{2}M\Omega_0^2u_i^2$$
$$M\omega_0^2\delta_{\alpha\beta}=-\sum_G v(G)G_\alpha G_\beta\,. \tag{A24}$$

This is the precise analog of Eq. (44). When the complete problem of the periodic lattice with potential $v(r-r')$ is solved by any of the methods above, followed by Fourier transforming, a $3\times3$ dynamical matrix $K_{\alpha\beta}(Q)$ is found

$$K_{\alpha\beta}(Q)=\sum_G[\,v(Q+G)(Q+G)_\alpha(Q+G)_\beta - v(G)G_\alpha G_\beta]\,, \tag{A25}$$

which is the analog of Eqs. (75) and (76).

It is natural to wonder whether the form for $\epsilon$ given by Eqs. (48), (51), and (55) is compulsory. More precisely, can we avoid the peculiarity that the lattice part $\chi_{0,L}$ of Eq. (55) is infinitesimal owing to the diverging bare frequencies of Eqs. (44) and (45)? The answer seems to be no. We are stuck with these forms. We can make $\Omega_0^2$ large but finite by truncation or a smooth cutoff, but we cannot replace these formulas by something different. The form of $\epsilon^{-1}$ in Sec. V is not at all peculiar, and in fact quite compelling. Then the form of $\epsilon$ is dictated by the fact that an inverse, if it exists, is unique.

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