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Interaction of slow electrons with density fluctuations in condensed materials: Calculation of stopping power

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The calculation of the energy-resolved scattering of slow ($\lesssim 3$ eV) electrons from density fluctuations is extended from crystalline semiconductors to amorphous, condensed materials (solid or liquid). In the Born approximation, the scattering is proportional to $S(\mathbf{q},\omega)$, the "dynamical structure factor" of the material. This factor, which exhibits some basic similarities and differences between solids and liquids, is determined by hydrodynamical parameters in the low-q range relevant to slow electrons. For solids, the scattering law remains unchanged when extended from crystalline to amorphous states, so the stopping power remains unchanged also. The scattering law changes when extended to liquids, but the calculated stopping power remains effectively unchanged.

I. INTRODUCTION

After ionizing radiation impinges on a condensed material, the absorbed energy is dissipated via many different channels. A substantial fraction ($\sim$10–20%) of the total energy eventually ends up as kinetic energy of quasifree, subexcitation electrons.[1] Although fast electrons interact with individual constituents of the material, slower ($\lesssim 3$ eV) electrons are not localized enough to do the same. They tend, instead, to interact with collective modes of the material. In the calculation of the energy degradation of slow electrons in crystalline semiconductors, interactions with phonons have traditionally provided a major contribution.[2] These interactions generate scattering events consisting of single-phonon processes, whose probabilities may be evaluated in the first Born approximation. In general, the calculation of the transition amplitude would involve a detailed knowledge of the lattice geometry, microscopic force constants of the atomic oscillations, and electron-atom potential.[3]

However, the calculation simplifies greatly for an electron whose wavelength encompasses many atoms of the crystal (the condition $E < 3$ eV ensures that the electron wavelength exceeds 7 Å), using the method of "deformation potentials." In this energy regime, the electron couples only with modes of the crystal that change its density over distances comparable to the electron wavelength.[4] Hence, the electron couples only with longitudinal-acoustic phonons. The resultant probability of scattering, per unit volume in $\mathbf{k}$ space, can be expressed in terms of a few macroscopic parameters of the electron-crystal system:[5]

$$\frac{E_1^2 q}{4\pi\hbar\rho c}[(N_\omega+1)\delta(\omega-cq)+N_\omega\delta(\omega+cq)] \ . \tag{1}$$

Here, E_1 ($\sim 1-20$ eV) is the shift of conduction-band edge per unit dilatation of the lattice, and provides the coupling between the quasifree electron and the phonons. Also, $\hbar\mathbf{q}=\hbar(\mathbf{k}_i-\mathbf{k}_f)$ is the momentum transfer, $\hbar\omega=E_i-E_f$ is the energy transfer, ρ is the mass density, c is the spherically averaged longitudinal sound velocity, $N_\omega=1/(e^{\hbar\beta\omega}-1)$, and $\beta=(k_BT)^{-1}$. In the energy-loss calculation, phonon-creation and phonon-destruction probabilities are comparable, but their nonunit ratio $[(N_\omega+1)/N_\omega=e^{\hbar\beta\omega}\cong 1+\hbar\beta\omega]$ yields the net result that $\langle \dot{E}\rangle < 0$ for epithermal electrons, as would be expected.

Extending this theoretical treatment from crystals to general amorphous materials (solid or liquid) seems to meet conceptual difficulties in the aforementioned requirement for knowledge of lattice geometry, force constants, and potentials, owing either to the ill definition of these quantities or to their experimental inaccessibility. However, these problems are subsumed in the "dynamical structure factor," $S(\mathbf{q},\omega)$, introduced by Van Hove[6] to interpret neutron scattering. This function depends on *density fluctuations* in a material, in the following sense. If $\delta\rho(\mathbf{r},t)$ is the fluctuation of density from equilibrium, measured at the point $\mathbf{r}$ at time t, then $\langle\delta\rho(\mathbf{r},t)\rangle=0$. However, the dimensionless quantity

$$G(\mathbf{r},t)\equiv\langle\delta\rho(0,0)\delta\rho(\mathbf{r},t)\rangle/\rho^2 \tag{2}$$

is nonzero and is called the density autocorrelation function. Due to the noncommutability of the operators $\delta\rho(\mathbf{r},t)$ for different values of t, the density autocorrelation function is complex valued, with the symmetry

$$G(-\mathbf{r},-t)=[G(\mathbf{r},t)]^* \ . \tag{3}$$

The dynamical structure factor, characteristic of any material (crystalline or amorphous) and independent of the scattering particle, is related to $G(\mathbf{r},t)$ by

$$S(\mathbf{q},\omega)=\frac{n}{2\pi}\int_{-\infty}^{+\infty}dt\int d^3r\,G(\mathbf{r},t)e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)} \ , \tag{4}$$

where n is the equilibrium number density of atoms. As a consequence of Eq. (3), the dynamical structure factor is a real-valued function. The "static structure factor" $S(\mathbf{q})$, familiar in x-ray scattering experiments, is related to $S(\mathbf{q},\omega)$ by

$$S(\mathbf{q})=\int_{-\infty}^{+\infty} d\omega\, S(\mathbf{q},\omega)=n\int d^3r\, G(\mathbf{r},t=0)e^{i\mathbf{q}\cdot\mathbf{r}}\ .$$

For an isotropic material, $G(\mathbf{r},t)=G(r,t)$ and $S(\mathbf{q},\omega)=S(q,\omega)$.

Although $S(q,\omega)$ is not easily calculable from first principles, it is measured in several different types of scattering experiments: with photons, electrons, or neutrons. The general result is that the scattering of long-wavelength radiation, per unit volume in **k** space, is equal to

$$\frac{\alpha^2 S(\mathbf{q},\omega)}{nh^2}P(\theta)\ , \tag{5}$$

where $P(\theta)$ is a polarization factor and α is a coupling constant with the dimension of energy. Using this notation, the rate of radiation energy loss is given by an integral of the form

$$\langle \dot{E}\rangle \propto \int dq \int \omega\, d\omega\, S(q,\omega)\ .$$

In this integral, $S(q,\omega)>0$, but ω can be positive or negative, because the radiation can either gain or lose energy in a single-scattering process. A net energy loss is assured, formally, by the fact that, for a material at thermal equilibrium, $S(q,\omega)$ satisfies the "detailed balance" condition:

$$S(q,-\omega)=e^{-\hbar\beta\omega}S(q,\omega)\ . \tag{6}$$

The ω-reflection asymmetry of $S(q,\omega)$ is due to the imaginary part of $G(r,t)$.

The quantity α characterizes each type of scattering process by quantifying the interaction which couples the radiation to the density fluctuations of the material. For visible light, $\alpha\propto\partial\epsilon/\partial n$, where $\epsilon(n)$ is the density-dependent dielectric constant, and $P(\theta)=1+\cos^2\theta$, for unpolarized incident light. For slow electrons, $P(\theta)=1$, if one ignores the spin dependence of low-energy electron interactions. For slow electrons in a semiconductor, $\alpha=E_1$. Similarly, for slow electrons in an amorphous material, $\alpha=n[\partial V_0(n)/\partial n]$, where $V_0(n)$ is the density-dependent energy of a long-wavelength electron.[7] Since an amorphous material possesses no spatial periodicity, its band structure is an ill-defined quantity. However, it still is sensible to talk about the energy of a long-wavelength electron. Thus, $n[\partial V_0(n)/\partial n]$ is essentially the same quantity as E_1, which was previously defined to be the shift of the conduction-band edge per unit dilatation.

The quantity α represents the effect of the average net interaction between the quasifree electron and the atoms of the material. One might divide the interaction into a long-range part and a short-range part, using the electron wavelength to separate the two components. As suggested in a recent note,[8] these two components should be treated differently. The long-range part represents the polarization of the material by the charge of the electron. The combination of the electron and the material's dielectric response is referred to as a "polaron," and traverses the material, dissipating energy. In this paper, however, I am not concerned with polarons, so I require that $V_0(n)$ and E_1 contain contributions from only the short-range part of the electron-atom interaction. For $n\lesssim 10^{20}\ \mathrm{cm}^{-3}$ (i.e., in the gas phase), $E_1(n)=V_0(n)=2\pi an\hbar^2/m$, where a is the average scattering length per atom due to the short-range part of the electron-atom interaction.[9] For $n\gtrsim 10^{22}\ \mathrm{cm}^{-3}$ (i.e., in the condensed phase), however, this simple functional form no longer holds.[10] In fact, it is evident that there are values of n where $E_1(n)=0$, in which case the scattering given by Eq. (5) vanishes, so higher-order perturbation theory must be used. Much physics goes into the calculation and/or measurement of $V_0(n)$ and $E_1(n)$ for condensed materials, but that is not the subject of this paper, except for the purpose of a rough estimate.

II. DYNAMICAL STRUCTURE FACTOR

Shockley's calculation of electron scattering from phonons was done mechanistically, not thermodynamically [except for the appearance of β in the phonon distribution $N_\omega=1/(e^{\hbar\beta\omega}-1)$]. Essentially, it involved a calculation of $S(q,\omega)$ with the assumption that, in the absence of excess electrons, the phonons would have infinite lifetimes. Due to the uncertainty principle, the lifetime τ is related to the width $\Delta\omega$ of the peaks in $S(q,\omega)$ by $\tau\Delta\omega\sim 1$. The result [Eq. (1)] displayed two "phonon peaks" in the energy-resolved scattering calculation, at $\omega=\pm cq$. However, energy-resolved light-scattering data from liquids exhibit a third peak, at $\omega=0$, called a "heat peak," not interpretable in terms of phonon processes.[11] This peak represents the fact that, if a localized density fluctuation exists in a fluid at $t=0$, it can either propagate away (as phonons) or diffuse away (by heat conduction) for $t>0$. The ratio of the intensity of the heat peak to the summed intensities of the phonon peaks is $\gamma-1$, where γ is the ratio of the specific heats. The dimensionless quantity $\gamma-1$ is called the "Landau-Placzek ratio." From thermodynamics, $\gamma-1=\alpha^2T/K_TC_V>0$, where α is the thermal coefficient of expansion (not to be confused with the coupling constant α defined in Sec. I), K_T is the isothermal compressibility, and C_V is the constant-volume heat capacity per unit volume. For solids (crystalline and amorphous), $\gamma-1\ll 1$, but for most fluids, $\gamma-1$ is on the order of unity. Thus, Shockley's scattering result for low-energy electrons in crystalline semiconductors can be extended to amorphous solids [making the connection that $E_1=n(\partial V_0/\partial n)$] but is not valid for most fluids, due to the presence of the peak at $\omega=0$.

The importance of the heat peak depends on the quantity being considered. In the calculation of stopping power, the energy-transfer cross section is the important quantity. In the "infinite-lifetime approximation," the three scattering peaks have zero width, so the energy-transfer cross section due to the heat peak vanishes identically. However, a more careful calculation of $S(q,\omega)$ gives a nonzero width to the heat peak (as well as to the phonon peaks). For this reason, the peak centered at $\omega=0$ might contribute to the energy transfer, thereby making Shockley's energy-loss calculation (which is strictly due to phonons) invalid for liquids. In Sec. III, it will be shown that the heat peak does not make a substantial contribution to the stopping power, compared to the phonon contribution. However, for treating physical problems where the momentum transfer is important, the heat peak is just as important as the phonon peaks. This is the case, for instance, in the calculation of electron-drift mobility,[7] in which case the mobility μ is given by $\mu^{-1} \propto \int d\omega\, S(q,\omega) = S(q) \approx S(0)$.

Much work has been done on the theoretical calculation of $S(q,\omega)$, especially in the small (q,ω) regime, relevant for the scattering of light or of slow electrons. In this regime, hydrodynamics is applicable. The fluctuation-dissipation theorem[12] relates $S(q,\omega)$ (the "fluctuation") to the behavior of a many-particle system after being disturbed from equilibrium (the "dissipation"). The "dissipation" term of the theorem can be evaluated using the linearized Navier-Stokes equations, since the fluctuations from equilibrium are quite small.[13] (Note that this is *not* valid in the neighborhood of the gas-liquid critical point, where the density fluctuations are large.) The evaluation involves setting initial conditions for the hydrodynamic variables and using the fluid equations to propagate solutions from $t=0$ to $t=\infty$. Three independent hydrodynamic quantities are needed to describe a single-component fluid, with possible choices: the mass-density fluctuation $\delta\rho(\mathbf{r},t)$, the momentum density $\mathbf{g}(\mathbf{r},t)$, and the entropy-density fluctuation $\delta s(\mathbf{r},t)$. The solutions can be obtained analytically, and the solution for $\delta\rho(\mathbf{r},t)$, along with its initial condition, is inserted into Eqs. (2) and (3), the formulas for $G(\mathbf{r},t)$.

The resulting formula for $S(q,\omega)$ depends on the initial conditions of the hydrodynamic variables, because quantities of the form $\langle |\delta\rho(q,t=0)|^2\rangle$ or $\langle \delta\rho^*(q,t=0)\delta s(q,t=0)\rangle$ factor out of the Fourier integrals. These factors are quadratic, and the fluctuation Hamiltonian can also be shown to contain terms of this form, so their values can be calculated using the equipartition theorem, in terms of thermodynamic coefficients. The nontrivial result is[14]

$$S(q,\omega) = \frac{S(0)}{4\gamma\pi}\left[\frac{\hbar\beta\omega}{1-e^{-\hbar\beta\omega}}\right] \times \left\{ \frac{\Gamma_s(\omega)q^2}{(\omega-cq)^2+\left[\dfrac{\Gamma_s(\omega)q^2}{2}\right]^2} + \frac{\Gamma_s(\omega)q^2}{(\omega+cq)^2+\left[\dfrac{\Gamma_s(\omega)q^2}{2}\right]^2} + \frac{4(\gamma-1)D_T(\omega)q^2}{\omega^2+[D_T(\omega)q^2]^2} \right\} . \tag{7}$$

The origin of the factor $\hbar\beta\omega/(1-e^{-\hbar\beta\omega})$ [≈ 1 for $\omega \ll (\hbar\beta)^{-1}$] is intimately related to the fluctuation-dissipation theorem,[15] but it will suffice here to regard this factor as necessary to satisfy the detailed-balance condition [Eq. (6)]. This formula for $S(q,\omega)$ exhibits the three peaks (at $\omega=0$, $\pm cq$) predicted by Landau and Plazcek. The total integrated intensity is

$$\int_{-\infty}^{+\infty} d\omega\, S(q,\omega) \equiv S(q) \approx \text{const} = S(0) .$$

The quantity $S(0)$ represents the "pair correlation function"—$G(r,t=0) \equiv G(r)$—integrated over all space. For fluids, $S(0) = nk_BTK_T$,[16] but for solids,

$$S(0) = \gamma k_B T/Mc^2 \approx k_B T/Mc^2$$

(Ref. 17), where M is the average atomic mass. These two formulas differ slightly because, for a fluid $\rho c^2 = K_S^{-1}$, but for a solid $\rho c^2 = (K_S^{-1} + \frac{4}{3}G)$, where G is the shear modulus (which vanishes for a fluid). The size of $S(0)$ is dictated by the degree of uncorrelation in a material, which allows for density fluctuations. For gases, $S(0) \approx 1.0$; for liquid argon at 85 K, $S(0) \approx 0.05$; and for silica glass, $S(0) \approx 0.003$.

Thus, a more accurate way of stating the Landau-Placzek result is that $S(q,\omega)$ consists of three sharply peaked Lorentzians, with widths $D_T(\omega_0)q^2$ or $\Gamma_s(\omega_0)q^2$, where ω_0 is the location of the peak. $\Gamma_s(\omega)$ and $D_T(\omega)$, frequency-dependent transport coefficients which are even functions of ω, may be viewed as the temporal Fourier transforms of "memory functions."[18] For $\omega \ll \omega_{\max} \equiv \tau_c^{-1}$, where τ_c ($\sim 10^{-12}$–10^{-11} s) (Ref. 19) is a microscopic relaxation time, $D_T(\omega) = \kappa/C_P$, the heat diffusion coefficient; and $\Gamma_s(\omega) = (4\eta/3+\zeta)/\rho + (\gamma-1)D_T$, the sound attenuation coefficient, where κ is the heat conductivity, η is the shear viscosity, and ζ is the bulk viscosity. The quantities D_T and Γ_s summarize the effects of the coupling of the hydrodynamic modes to the microscopic modes, in the form of dissipation. The functions $D_T(\omega)$ and $\Gamma_s(\omega)$ are constant for small ω, but are understood to drop off sufficiently fast in the neighborhood of $|\omega| \approx \omega_{\max}$, to ensure a rapid decrease of $S(q,\omega)$ as $|\omega| \to \infty$. It is this fact which allows the three peaks to be equivalent to properly normalized δ functions, dropping off to zero well before the factor $\hbar\beta\omega/(1-e^{-\hbar\beta\omega})$ begins to depart substantially from unity. Hence, the areas under the peaks are obtained analytically, and the ratio of the heat-peak intensity to the summed phonon-peak intensities is $\gamma-1$, the Landau-Placzek ratio, as predicted.

III. ENERGY LOSS

The calculation of the energy loss of a slow electron with kinetic energy $E = \hbar^2k^2/2m^*$ (where m^* is the effective electron mass) through scattering by a condensed material involves an integral over all electron final states $\mathbf{k}_f$, of the scattering probability [given by Eq. (5)]. The integrand is weighted by the energy transfer $\hbar\omega$, yielding

$$\langle \dot{E} \rangle = \frac{-E_1^2}{h^2 n} \int d^3k_f\, \hbar\omega S(q,\omega) . \tag{8}$$

To evaluate the integral in Eq. (8),[20] I change coordinates from $\mathbf{k}_f$ to (q,θ), where θ is the angle between $\mathbf{k}_f$

and q. Next, I change coordinates from θ to ω, to obtain

$$\langle \dot{E} \rangle = \frac{-m^* E_1^2}{2\pi n \hbar^2 k} \int_0^\infty q\, dq \times \int_{-\hbar kq/m^* - \hbar q^2/2m^*}^{\hbar kq/m^* - \hbar q^2/2m^*} \omega\, d\omega\, S(q,\omega) \ . \tag{9}$$

A few physical aspects of this integral deserve pointing out. First, the endpoints of the ω integral, the k^{-1} prefactor, and the q (as opposed to q^2) integrand are all due to the change of variables from θ to ω. Second, since the fractional energy transfers are small ($\sim 10^{-3}$–10^{-1}), the ω integral can be assumed to vanish when q becomes so large ($\gtrsim 2k$) that the range of the ω integration does not enclose the origin. This condition lowers the upper limit of the q integration from infinity to $2k$. Third, for small q ($\ll 2k$), the limits of the ω integration are roughly equal and opposite. Thus, the presence of the linear factor of ω in the integrand essentially "measures" the ω-reflection asymmetry of $S(q,\omega)$, which is quantified by the detailed-balance condition, in Eq. (6). This ultimately yields the result that $\langle \dot{E} \rangle < 0$, when E is sufficiently larger than $k_B T$. Fourth and last, the fact that the lower limit of the ω integration is slightly larger (in absolute value) than the upper one becomes important when E is near, at, or below $k_B T$. The result is that $\langle \dot{E} \rangle$ approaches zero and becomes positive as E decreases. This is related to the fact that subsonic electrons can absorb phonons but cannot emit them ("acoustic Cherenkov effect").

The next step involves inserting Eq. (7), the dynamic structure factor, into Eq. (9), the energy-loss equation. Since $S(q,\omega)$ separates logically into two different parts, the phonon peaks and the heat peak, I separate the energy loss into two parts: $\langle \dot{E} \rangle = \langle \dot{E} \rangle_{\text{phonon}} + \langle \dot{E} \rangle_{\text{heat}}$. First, $\langle \dot{E} \rangle_{\text{phonon}}$ is obtained. The first two Lorentzians in Eq. (7) are quite narrow. Typically, the ratio of their width to their displacement from the origin is

$$\frac{\Gamma_s q^2}{cq} \sim \frac{(10^{-3}\ \text{cm}^2/\text{s})(0.1\ \text{Å}^{-1})^2}{(10^5\ \text{cm/s})(0.1\ \text{Å}^{-1})} = \frac{0.1\ \text{GHz}}{1\ \text{GHz}} = 0.1\ .$$

Momentum transfers larger than 0.1 Å^{-1} are certainly possible, but the function $\Gamma_s(\omega)$, evaluated at $\omega = cq$, will decrease for $q \gtrsim 0.1\ \text{Å}^{-1}$, thereby keeping the phonon peaks sufficiently narrow. Thus, the Lorentzian form of the phonon peaks can be replaced by delta functions, in which case their contribution to $\langle \dot{E} \rangle$ is

$$\langle \dot{E} \rangle_{\text{phonon}} = \frac{-2\sqrt{2} E_1^2 m^{*5/2}}{\pi \rho \hbar^4} \sqrt{E}\,(E - 2k_B T)$$

$$= \frac{-E_1^2 m^* k^3}{\pi \rho \hbar} \left[1 - \frac{2k_B T}{E} \right] , \tag{10}$$

which is equivalent to

$$\left\langle \frac{d(\ln E)}{dx} \right\rangle_{\text{phonon}} = \frac{-2E_1^2 m^{*3}}{\pi \rho \hbar^4} \left[1 - \frac{2k_B T}{E} \right] . \tag{11}$$

This equation is interpreted most easily by multiplying it by l, the phonon scattering mean free path. The calculation of the mean free path involves an integral of the form $l^{-1} \propto \int d^3k_f S(q,\omega)$. This is evaluated[21] much more easily than $\langle \dot{E} \rangle_{\text{phonon}}$, to yield

$$l_{\text{phonon}} = \frac{\pi \hbar^4 n \gamma}{m^{*2} E_1^2 S(0)} \ . \tag{12}$$

For liquid argon at 85 K, using Eq. (12) and setting m^* equal to the free-electron mass yields $l_{\text{phonon}} \sim 10$–$50$ Å, depending on the value of E_1 that is used.[10] Multiplying Eqs. (11) and (12) together yields

$$l_{\text{phonon}} \left\langle \frac{d(\ln E)}{dx} \right\rangle_{\text{phonon}} = \frac{2\gamma m^* \left[1 - \frac{2k_B T}{E} \right]}{M S(0)}$$

$$= -2 \left[\frac{c}{v_T} \right]^2 \left[1 - \frac{2k_B T}{E} \right] , \tag{13}$$

where v_T is the electron thermal velocity. At room temperature, $v_T = (k_B T/m^*)^{1/2} \approx 6.6 \times 10^4$ m/s, using the free-electron mass. This velocity is 1 or 2 orders of magnitude higher than sound velocities in condensed materials, so Eq. (13), which represents the average fractional energy loss per collision, is a very small number. Since $S(q) \approx S(0)$ and E_1 are independent of q, and since the fractional energy transfers are small, the scattering is roughly isotropic. Thus, the energy-loss process is diffusive, in that the electron changes directions many times before losing a substantial portion of its energy.

The calculation of the heat-peak mean free path is a trivial reproduction of the calculation of l_{phonon}, yielding the simple result $l_{\text{phonon}}/l_{\text{heat}} = \gamma - 1$. However, the calculation of the heat peak's contribution to the energy loss is tricky, because it depends on the (effective) size of $\omega_{\max}$, not a very accessible quantity. The analog of Eq. (10) is

$$\langle \dot{E} \rangle_{\text{heat}} = \left[\frac{-E_1^2 m^*}{2\pi n \hbar^2 k} \right] \pi^{-1} S(0)(1 - \gamma^{-1}) \int_0^\infty q\, dq \int_{-\hbar kq/m^* - \hbar q^2/2m^*}^{\hbar kq/m^* - \hbar q^2/2m^*} \omega\, d\omega \left[\frac{\hbar\beta\omega}{1 - e^{-\hbar\beta\omega}} \right] \frac{D_T(\omega) q^2}{\omega^2 + [D_T(\omega) q^2]^2} \ . \tag{14}$$

Since the Lorentzian peak located at the origin is weighted by ω in the energy-loss integral, it cannot be simply replaced by a δ function, which would yield exactly zero energy loss. The $\omega_{\max}$ cutoff, as mentioned in Sec. II, is essential to the evaluation of the ω integral. If $D_T(\omega)$ were independent of ω, the integrand $\omega S(q,\omega)$ would approach a constant in the range $D_T q^2, (\hbar\beta)^{-1} \ll \omega \ll \hbar k_0^2/2m^*$, making the integral in

Eq. (14) considerably larger than for phonons. Instead, $D_T(\omega)$ is expected to vanish in the neighborhood of $|\omega| = \omega_{\max} \ll \hbar k^2/2m^*$.

In my calculation, I assume that $D_T(\omega)$ cuts off sharply at $\omega_{\max} \ll (\hbar\beta)^{-1}$. This leads to

$$\langle \dot{E} \rangle_{\text{heat}} \approx \frac{-m^* E_1^2 (1-\gamma^{-1}) K_T}{8\pi^2 \hbar k D_T} \times \int_0^{\omega_{\max}} \omega^2 d\omega \ln \left[1 + \frac{(4D_T k^2)^2}{\omega^2} \right] , \tag{15}$$

which is valid for $E \gg k_B T$. The q integration was evaluated from 0 to $2k$ by conservation of momentum and quasiconservation of energy. In estimating the integral in Eq. (15), it is important to know the relative size of $\omega_{\max}$ and $D_T k^2$. For $D_T \approx 10^{-3}$ cm^2/s and E ranging from thermal energy to 3 eV, the quantity $D_T k^2$ ranges from 0.1 to 10 THz. Thus, $\omega_{\max}$ might be significantly larger or smaller than $D_T k^2$. Evaluation of the integral in Eq. (15) yields, in both of these limits,

$$\int_0^{\omega_{\max}} \omega^2 d\omega \ln \left[1 + \frac{(4D_T k^2)^2}{\omega^2} \right] = \begin{cases} \frac{2}{3}\omega_{\max}^3 [\ln(4D_T k^2/\omega_{\max}) + \frac{1}{3}] & \text{if } \omega_{\max} \ll D_T k^2 , \\ (4D_T k^2)^2 \omega_{\max} & \text{if } \omega_{\max} \gg D_T k^2 . \end{cases} \tag{16}$$

Hence, the ratio of Eq. (14) to Eq. (9) is, for electron energies much larger than $k_B T$,

$$\frac{\langle \dot{E} \rangle_{\text{heat}}}{\langle \dot{E} \rangle_{\text{phonon}}} \cong \begin{cases} (\gamma - 1)[\ln(4D_T k^2/\omega_{\max}) + \frac{1}{3}]\omega_{\max}^3 / 2[12\pi(ck)^2 D_T k^3] & \text{if } \omega_{\max} \ll D_T k^2 , \\ 2(\gamma-1) D_T \omega_{\max}/\pi c^2 & \text{if } \omega_{\max} \gg D_T k^2 . \end{cases} \tag{17}$$

As an example, I will consider liquid argon at 85 K, at its saturation vapor pressure, using the data[22]

$$D_T = 8.5 \times 10^{-4}\ \text{cm}^2/\text{s} = 8.5\ \text{Å}^2\ \text{THz} ,$$

$$c = 8.5 \times 10^4\ \text{cm/s} = 8.5\ \text{Å THz} ,$$

$$\gamma = 2.14 .$$

In order to get an upper bound on the ratio in Eq. (17), I assume that $E = 0.05$ eV, that m^* is the free-electron mass, and that $\omega_{\max} = 1$ THz. This yields

$$D_T k^2 = 0.11\ \text{THz} \ll \omega_{\max} \ll (\hbar\beta)^{-1} = 11\ \text{THz} \ll \frac{\hbar k^2}{2m^*} = 76\ \text{THz} ,$$

which leads to

$$\frac{\langle \dot{E} \rangle_{\text{heat}}}{\langle \dot{E} \rangle_{\text{phonon}}} = \frac{2(\gamma-1) D_T \omega_{\max}}{\pi c^2} \approx 0.09 . \tag{18}$$

Thus, the heat-peak contribution seems rather unimportant. For $E > 0.05$ eV or $\omega_{\max} < 1$ THz, this ratio will be lower still. Thus, Shockley's energy-loss calculation, as given in Eq. (10), is valid for liquids, in addition to solids.

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[16] See, e.g., R. R. Pathria, *Statistical Mechanics* (Pergamon, Ox-

ford, 1972), Chap. 13.

[17] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart, and Winston, Philadelphia, 1976), Appendix N.

[18] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976), Chap. 11.

[19] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions,* Ref. 14, p. 11; N. W. Ashcroft and N. D. Mermin, *Solid State Physics,* Ref. 17, p. 398.

[20] See, e.g., W. Shockley, Bell Syst. Tech. J. **30**, Appendix 5 (1951); or E. M. Conwell, *High Field Transport in Semiconductors* (Academic, New York, 1967), pp. 119–127. The result [Eq. (9)] is valid for general forms of $S(\mathbf{q},\omega)$, but in the case that $S(\mathbf{q},\omega)$ consists of two infinitely narrow phonon peaks, this integral is essentially calculated in these two references, resulting in Eq. (10).

[21] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

[22] *Handbook of Chemistry and Physics,* 56th ed., edited by R. C. Weast (Chemical Rubber Co., Cleveland, 1975), p. E-11; and B. Chu and P. W. Schmidt, in *Simple Dense Fluids,* edited by H. L. Frisch and Z. W. Salsbury (Academic, New York, 1968), pp. 111–118.