COMMENTS AND ADDENDA

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Validity of the Boltzmann Equation for Systems with Both Electron-Phonon and Impurity Scattering

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A recent calculation of Mills indicating large deviations from Mathiessen's rule is shown to be in error because of the neglect of terms of the *same* order in perturbation theory which remove the reported divergency and leave only very small corrections to the Boltzmann equation. In addition, it is suggested that the experimental basis for these large deviations may have a different explanation.

In a recent Letter Mills[1] has presented a resistivity calculation based on the Boltzmann equation in which the scattering probability is carried to fourth order (second order in the impurity potential, second order in the phonon coupling). The results show that there are substantial deviations from Mathiessen's rule and seem to support the conjecture of Caplin and Rizzuto[2] that these deviations are caused by a breakdown in wave-vector conservation due to the presence of the impurities. On the other hand, the results are in disagreement with previous resistivity calculations and thus are rather suggestive that there may be something fundamentally wrong with all the usual treatments which employ the Kubo formalism and *ensemble-averaged* Green's functions. Indeed, in response to the calculation of Mills, several authors[3-5] have again shown that the Green's-function formalism does not lead to these large effects.

We show below that the Mills calculation does *not* in fact negate the usual Kubo-formula calculations of the resistivity. What has happened is that in his perturbation calculation Mills neglected certain other terms of the same order, and when all these contributions are considered together the calculation again reduces to the usual Green's-function approach and yields a very *small* correction to the lowest-order resistivity.[6] In what follows we illustrate the cancellation that occurs between the various terms and then establish the connection between this approach and the usual Green's-function approach. We conclude with a comment on the experimental situation.

To illustrate the cancellation that occurs we will consider only one of the two processes discussed by Mills and, furthermore, we will restrict ourselves initially to the much simpler calculation of the single-particle decay rate rather than the conductivity. The amplitude for the process shown in Fig. 1(a) is

$$V_{k,k'}\frac{1}{\epsilon_k-\epsilon_{k'}+i\eta}\,g_q\,,$$

where $V_{k,k'}$ and g_q are the impurity and phonon matrix elements. The single-electron decay rate is then given by

$$W(k)=2\pi\sum_q\sum_{k'}\langle|V_{k,k'}|^2\rangle\,|g_q|^2\left|\frac{1}{\epsilon_k-\epsilon_{k'}+i\eta}\right|^2$$

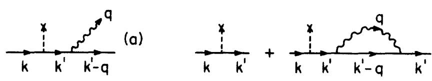

FIG. 1. Amplitudes that contribute in the same order (second order in both electron-phonon coupling and impurity potential) to the scattering probability. The solid lines represent electrons, the wavy lines represent phonons, and the dashed lines terminated (or interrupted) by a cross are impurity interactions.

$$\times\delta(\epsilon_k-\epsilon_{k'-q}-\omega_q)\ . \qquad (1)$$

The angular brackets ⟨ ⟩ indicate an ensemble average over impurity positions which we have taken after squaring the matrix element. We have not included the thermal-occupation factors in (1) since they play no role in the following argument. The important point, as Mills observed, is that this expression is divergent because of the structure of the energy denominator; that is, the poles in $|\epsilon_k-\epsilon_{k'}+i\eta|^{-2}$ lie on *opposite* sides of the real axis.

This term, however, is not the only process that contributes to second order in V *and* second order in g to the single-particle decay rate.[7] The lowest-order amplitude $V_{k,k'}$ [Fig. 1(b)] has a higher-order correction also shown in Fig. 1(b). The amplitude corresponding to this correction is

$$V_{k,k'}\frac{1}{\epsilon_k-\epsilon_{k'}+i\eta}\sum_q\left(g_q\frac{1}{\epsilon_k-\epsilon_{k'-q}-\omega_q+i\eta}\;g_q^*\right)$$

and the interference of this with the lowest-order amplitude leads to a correction to the decay rate given by

$$W'(k)=2\pi\sum_{k'}\langle|V_{k,k'}|^2\rangle\frac{1}{\epsilon_k-\epsilon_{k'}+i\eta}$$
$$\times\sum_q\left(g_q\frac{1}{\epsilon_k-\epsilon_{k'-q}-\omega_q+i\eta}\;g_q^*\right)\delta(\epsilon_k-\epsilon_{k'})\quad+\text{c.c.} \qquad (2)$$

Now this probability is also divergent, but if we combine this with the previous decay rate we get a finite answer. Schematically,

$$W(k)+W'(k)$$
$$\propto\left(\frac{1}{A^+}\,\frac{1}{A^-}\,\delta(B)+\frac{1}{A^+}\,\frac{1}{B^+}\,\delta(A)+\frac{1}{A^-}\,\frac{1}{B^-}\,\delta(A)\right)\ , \qquad (3)$$

where we have dropped all the common factors and defined

$$A^\pm=\epsilon_k-\epsilon_{k'}\pm i\eta\ ,\quad B^\pm=\epsilon_k-\epsilon_{k'-q}-\omega_q\pm i\eta\ .$$

Now $\delta(x)$ has the representation

$$\delta(x)=\frac{1}{2\pi i}\left(\frac{1}{x^-}-\frac{1}{x^+}\right)\ ,$$

so that we can rewrite (3) as

$$W(k)+W'(k)\propto\frac{1}{2\pi i}\left(\frac{1}{A^-B^-A^-}-\frac{1}{A^+B^+A^+}\right)\ . \qquad (4)$$

We note that the poles arising from the energy denominator are now on the *same* side of the real axis. If we integrate this expression over q and k', we get a very *small* correction since the density-of-states factors multiplying the energy denominator are smooth functions of energy.[8]

There is a very direct connection between this approach and the usual Green's-function method. In the Green's-function approach the single-particle decay rate is obtained from the imaginary part of the self-energy, which in our example is the self-energy shown in Fig. 2(a) and is given by

$$\Sigma(k,\ E)=\sum_{k'}\langle|V_{k,k'}|^2\rangle\left(\frac{1}{E-\epsilon_{k'}}\right)^2$$
$$\times\sum_q(1+n_q-f_{k'-q})|g_q|^2\frac{1}{E-\epsilon_{k'-q}-\omega_q}\ , \qquad (5)$$

where only the term resulting from the same process considered above has been written down. Except for the thermal-occupation factors the expression for the decay rate given earlier [Eq. (4)] is just

$$\frac{1}{2\tau}=-\operatorname{Im}\Sigma(k,\ \epsilon_k)$$
$$=\frac{1}{2i}\left[\Sigma(k,\ \epsilon_k-i\eta)-\Sigma(k,\ \epsilon_k+i\eta)\right]\ , \qquad (6)$$

so that the perturbation calculation does give the same results as the Green's-function approach, i.e., a negligible correction.[9]

The averaging over impurity positions deserves some comment. In both approaches the ensemble averaging was performed in the final stage of the calculation, that is, in the expressions for the physical quantities of interest. It was for this reason that we could compare the results of the two calculations and expect agreement. Note also that the averaging procedure has in fact played no role in either creating or resolving the divergence difficulties.

Although we have shown only that higher-order corrections to the single-particle decay rate are small, it seems plausible that the corrections to the resistivity are also small. This would certainly be the case if we were to use just the corrected matrix element in the ordinary Boltzmann equation. However, because of the semiclassical derivation of the Boltzmann equation one cannot be certain that this procedure does not neglect other equally important higher-order terms. If is therefore advisable to return to a first-principles calculation based on the Kubo formula in which the conductivity is written in terms of a current-current correlation function.

The current-current correlation function can be rewritten in terms of a two-particle Green's function, and again to make things tractable one performs an ensemble average over impurity positions. In a diagrammatic expansion a typical term would look as shown in Fig. 2(b). Note that the impurity aver-

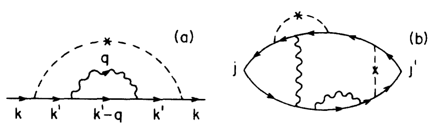

FIG. 2. (a) A self-energy contribution to the single-particle lifetime. (b) A particular "bubble" contribution to the conductivity.

aging leads not only to self-energy corrections but also to an effective particle-particle scattering amplitude. A calculation that keeps only the lowest-order interaction terms in *both* the irreducible self-energy of the single-particle Green's function *and* the irreducible particle-particle scattering amplitude yields the ordinary Boltzmann equation with first-order matrix elements. In establishing this equivalence we note that two things enter in a rather essential way. First, the approximate momentum independence of the self-energy enables us to use the Boltzmann equation with "particles" simply replaced by "quasiparticles." Second, it is important to treat the single-particle self-energy corrections and the particle-particle interactions consistently. For example, the neglect of the particle-particle interaction would lead to a conductivity proportional to a single-particle lifetime, rather than the transport lifetime τ_{tr}. On the other hand, the neglect of self-energy corrections would lead to a divergency of Mills's type since now the poles would lie on opposite sides of, and infinitesimally close to, the real axis.

The correction terms to these lowest-order results are of essentially three types. First, those terms involving multiple scattering off a single impurity site can be taken into account by simply replacing the potential matrix element by a t matrix. Those terms involving renormalizations of internal lines such as the example we discussed above are small. Finally, those involving crossed interaction lines are also very small because of the restrictions on the internal momentum sums.[10]

We conclude with a comment on the experimental situation. Caplin and Rizzuto[2] point out that the simple model used by Dugdale and Basinsky[11] to account for the effect of an anisotropic conduction-electron relaxation rate on the resistivity does not adequately describe the concentration and temperature dependence of the resistivity at low temperature. However, a preliminary analysis of the data[12] indicates that another simple model,[13] involving umklapp processes, can give a reasonable interpretation of the experimental results. Thus until such a time when solutions of the Boltzmann equation in a multiband metal such as aluminum are available to decide the validity of these and other model calculations, the conclusion of Caplin and Rizzuto—that an anisotropic relaxation time *cannot* account for the experimental data—is unwarranted.

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[1] D. L. Mills, Phys. Rev. Letters 26, 242 (1971).

[2] A. D. Caplin and C. Rizzuto, J. Phys. C 3, L117 (1970); I. A. Campbell, A. D. Caplin, and C. Rizzuto, Phys. Rev. Letters 26, 239 (1971).

[3] D. Sherrington, Phys. Letters 35A, 399 (1971).

[4] L. Dworin, Phys. Rev. Letters 26, 1244 (1971).

[5] D. A. Smith, J. Phys. C 4, L145 (1971).

[6] Note that this conclusion on the use of golden-rule perturbation theory differs from that of Ref. 3. Golden-rule perturbation theory can be used, provided one is careful to include all terms to a given order in the potential.

[7] That this was the case was also recognized by David C. Langreth (private communication).

[8] If the density-of-states factors were constant, this term would be identically zero, i.e., $\int_{-\infty}^{\infty} dx (x+i\eta)^{-2}=0$.

[9] What we have calculated here is just the first term in a series which can be considered as a renormalization of an internal propagator, and in fact the entire series yields a negligible correction to the lowest-order result. The crucial point is that the electronic density of states is essentially constant on the scale of possible level shifts caused by the perturbation. Therefore, renormalizations do not substantially change the values of the integrals representing the lowest-order process. See in this context Ref. 8.

[10] See, for example, A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 35, 1558 (1958) [Sov. Phys. JETP 8, 1090 (1959)]. Although the argument given there is only for impurity scattering at $T=0$, the arguments can be easily extended to include the electron-phonon interaction.

[11] J. S. Dugdale and Z. S. Basinsky, Phys. Rev. 157, 552 (1967).

[12] J. W. Ekin (private communication).

[13] A. C. Ehrlich, Phys. Rev. B 1, 4537 (1970).