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Abstract

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SEMICLASSICAL APPROXIMATION IN THE THEORY OF ELECTRICAL CONDUCTIVITY

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The calculation of transport coefficients by constructing kinetic equations can by no means always be justified. Kinetic equations, for example equations of the Boltzmann type, in fact represent certain approximations describing a definite asymptotic behavior of the correlation function ([1]). Therefore, in calculating kinetic coefficients it is expedient from the very beginning to start from expressions relating the characteristics of a nonequilibrium state to correlation functions in the state of statistical equilibrium. For the electrical-conductivity tensor, as is known, we have ([2,3])

$$\operatorname{Re}\sigma_{\nu\mu}(\omega) = \frac{1}{2\omega}\left(e^{\beta\omega} - 1\right)\int_{-\infty}^{+\infty} \langle J_\nu(0) J_\mu(t)\rangle e^{i\omega t}\, dt, \tag{1}$$

where $\beta = 1/kT$; $J(t) = e^{iHt} J(0) e^{-iHt}$; ω is the frequency of the external field; the symbol $\langle ...\rangle$ denotes averaging over the grand canonical Gibbs ensemble.

The kinetic equation corresponds to the case in which $\langle J(0)J(t)\rangle \sim \exp(-t/\tau)$ for large t. In the case where the dynamical connection predominates, another simplest approximation is more suitable: $\langle J(0)J(t)\rangle \sim e^{-t^2/\Delta}$; here Δ is the width of the Gaussian distribution ([4]). The meaning of such an approximation is that the main contribution to the integral of the correlation function is made by small times. It may be thought that precisely the latter case is realized in systems with low mobility of the current carriers. Direct calculation shows that the kinetic equation is applicable if the mobility $u \gg 1$ cm^2/V $\cdot$ sec. Much experimental data for organic semiconductors indicate that very often $u < 10^{-2}$ cm^2/V $\cdot$ sec, and thus calculations of transport coefficients performed for such compounds on the basis of the kinetic equation are very difficult to justify. Below we consider an approximation which is meaningful precisely when the ordinary kinetic equation is inapplicable, and which reduces to the simplest approximation of the correlation function mentioned at the beginning of the article.

Let us consider a system with Hamiltonian ([5,6])

$$H = \sum(\varepsilon - \mu) a_m^+ a_m + \sum B(\mathbf{g}) a_{m+g}^+ a_m +$$

$$+\sum A_q e^{i\mathbf{qm}}(b_q + b^+_{-q})a^+_m a_m + \sum \omega_q b^+_q b_q; \tag{2}$$

$$H = H_0 + H_1; \qquad H_1 = \sum A_q e^{i\mathbf{qm}}(b_q + b^+_{-q})a^+_m a_m;$$

μ is the chemical potential.

For the current operator in the nearest-neighbor approximation we have

$$\mathbf{J} = -ie\sum B(\mathbf{g})\,\mathbf{g}\,a^+_{m+g}a_m. \tag{3}$$

It can be shown that in the interaction representation

$$a_m(t) = \sum_{n_1 n_2 n_3} I_{n_1}(-2iB_1 t)I_{n_2}(-2iB_2 t)I_{n_3}(-2iB_3 t)\,a_{m+n}(0)e^{it(\varepsilon-\mu)}; \tag{4}$$

here I_n is the Bessel function. In the case of a small concentration of current carriers

$$\langle a_m(t)a^+_n(t')\rangle = e^{i(\varepsilon-\mu)(t-t')}I_{m-n}(2iB(t-t')), \qquad \langle a^+_n(t')a_m(t)\rangle \simeq 0. \tag{5}$$

We note that the Hamiltonian (2) takes into account hopping processes (5), which, generally speaking, may turn out to be essential for systems with narrow bands.

Since $[H_0 J] = 0$, we have

$$\langle J(0)J(t)\rangle = \left\langle J(0)e^{iHt}e^{-iH_0 t}J(0)e^{iH_0 t}e^{-iHt}\right\rangle.$$

If we introduce the notation

$$S(t) = e^{iH_0 t}e^{-iHt}, \tag{6}$$

then

$$X(t) = \langle J(0)J(t)\rangle =$$

$$= -e^2\sum B(g)B(g')\,gg'\,\left\langle a^+_{m+g}(0)a_m(0)S^+(t)a^+_{m'+g'}(0)a_{m'}(0)S(t)\right\rangle.$$

The approximation under consideration consists in neglecting the commutators $[H_1 H_0]$, i.e., $S(t)$ is chosen in the form

$$S(t) \simeq e^{-iH_1 t}. \tag{7}$$

Then

$$X(t) = -e^2 \sum B(g)B(g')\, gg' \; \Big\langle a^+_{m+g}(0) a_m(0) a^+_{m'+g'}(0) a_{m'}(0) \times$$

$$\times \exp\left[-it \sum A_q e^{iq(m'+g')}(b_q + b^+_{-q})\right] \exp\left[it \sum A_q e^{iqm'}(b_q + b^+_{-q})\right]\Big\rangle , \tag{8}$$

since

$$e^{iH_1 t} a_p e^{-iH_1 t} = a_p(0) \exp\left[it \sum A^{iqp}_{qe}(b_q + b^+_{-q})\right] . \tag{9}$$

For simplicity, let us consider for the moment the case in which one may approximately put $S(i\beta) \simeq 1$. The latter, in any case, is always fulfilled in the high-temperature limit. We readily obtain:

$$X(t) = -e^2 \sum B(g)B(g')\, gg' \cdot I_{g+g'}(2B\beta) \times$$

$$\times \exp\left[-t^2 \sum A^2 (1 - \cos qg')(2\bar{n}_q + 1)\right] . \tag{10}$$

For $\operatorname{Re} \sigma_{xx}(\omega)$ we find:

$$\operatorname{Re} \sigma_{xx}(\omega) = \frac{e^2 B^2}{\omega} (e^{\beta\omega} - 1) e^{\beta(\mu - \varepsilon)} I_0^2(2B\beta)(I_0(2\beta B) -$$

$$- I_2(2\beta B)) \left[\pi \Big/ \sum A_q^2 (1 - \cos qa)(2\bar{n}_q + 1)\right]^{1/2} \times$$

$$\times \exp\left[-\omega^2 \Big/ 4 \sum A_q^2 (1 - \cos qa)(2\bar{n}_q + 1)\right] . \tag{11}$$

Strictly speaking, in (11) one should have put $\omega = 0$, since the strong frequency dependence of the electrical conductivity following from (11) is due rather to the approximation $S(i\beta) = 1$ than to the actual state of affairs. Moreover, since the high-temperature approximation can by no means always be justified, especially for organic semiconductors, it is necessary to calculate $\sigma(\omega)$ taking into account at least several terms in the expansion of $S(i\beta)$.

The result can be obtained considerably more simply if one uses the method of moments. Indeed, if the exact value is $X(t) = \langle J(0)e^{iHt}J(0)e^{-iHt}\rangle$, then in the semiclassical approximation $X_{\text{semicl}}(t) =$

$$= \langle J(0)e^{iH_1t}J(0)e^{-iH_1t}\rangle,$$

and for the unnormalized moments we have

$$\begin{aligned}
a_1 &= \langle J(0)[HJ]\rangle = \langle J(0)[H_1J]\rangle = a_{1\ \text{semicl}},\\
a_2 &= \langle J(0)[H[HJ]]\rangle = a_{2\ \text{semicl}} + \langle J(0)[H_0[H_1J]]\rangle, \qquad (12)\\
a_3 &= a_{3\ \text{semicl}} + \langle J(0)[H_0[(H_0+H_1)[H_1J]]]\rangle + \langle J(0)[H_1[H_0[H_1J]]]\rangle.
\end{aligned}$$

Thus, the first exact and semiclassical moments always coincide; the corresponding second moments coincide exactly only in the approximation $S(i\beta) \simeq 1$. It is not difficult to see, however, that although their difference does not decrease to zero with increasing temperature, it becomes relatively less significant. The same is true for higher moments (7).

Taking into account all that has been said, we finally obtain for σ

$$\operatorname{Re}\sigma(\omega) = \frac{1}{2\omega}(e^{\beta\omega}-1)e^{\beta(\mu-\varepsilon)}\frac{a_0}{\sqrt{\overline{a}_2}}\exp\left[-\frac{(\omega-\overline{a}_1)^2}{2\overline{a}_2}\right]. \qquad (13)$$

Here $\overline{a}_i$ are normalized moments. In the semiclassical approximation this is a practically exact formula. Of course, an exact calculation of $\overline{a}_1$ and $\overline{a}_2$ is difficult, and in principle it would be very desirable to determine these quantities directly from experiment. Calculation in the first approximation leads to the following result for the first moments:

$$\overline{a}_1 = \sum\frac{A_q^2}{\omega_q}(1-\cos qa)\left(2\overline{n}_q\sinh\beta\omega_q + 1 - e^{-\beta\omega_q}\right); \qquad (14)$$

$$\overline{a}_2 = 2\sum A_q^2(2\overline{n}_q+1)(1-\cos qa). \qquad (15)$$

For σ at $\omega = 0$ we evidently have an activated character of the mobility. It is interesting to compare formulas (11) and (13). For the case of weak coupling (but such that the semiclassical approximation is still applicable), the mobility, as is easy to see, decreases with temperature, whereas from (13) it follows that in some temperature interval it increases. The considerations presented, probably, may be useful in interpreting electrical-conductivity data in the case where carriers of different signs are present. Since the strength of coupling to the lattice may be somewhat different for holes and electrons, the temperature dependence of the mobility may have not only quantitative but also qualitative differences. It is possible that precisely this is the reason for the different temperature dependence of the mobility for holes and electrons recently observed in anthracene (8).

The method of moments can naturally also be used to obtain approximate criteria for the applicability of the semiclassical approximation considered. Indeed, in the approximation $S(i\beta) = 1$ the first two moments (exact and semiclassical) coincide. The difference between the exact and semiclassical third-order moments as $T \to \infty$ becomes small in comparison with the second moment raised to the power 3/2 (7). Thus, the approximation we have considered is applicable if

$$\langle J[H_1[H_0[H_1 J]]]\rangle / a_0 \ll (\overline{a}_2)^{3/2}. \tag{16}$$

Relation (16) can be rewritten in the form

$$\left|(2\overline{n}+1)BA^2 - A^2\omega\right| \ll A^3(2\overline{n}+1)^{3/2}. \tag{17}$$

Here $\overline{n}$, A are the Planck mean averaged over phonon momenta and the electron–phonon coupling parameter. It follows from (17) that the semiclassical approximation is not applicable to the case of too weak coupling (this is also natural, since then the ordinary kinetic equation is applicable). It follows directly from (17) that upon passing from $B \gg \omega$ to $B \ll \omega$ the condition imposed on the coupling strength becomes weaker, i.e., for a given A the semiclassical approximation is most applicable when $B \ll \omega$.

The last inequality signifies a strong "nonadiabaticity." In addition, criterion (17) depends on the temperature, and especially sharply when $B \ll \omega$.

It is evident that the condition $B \ll \omega$ or $B \sim \omega$ cannot be satisfied for metals or for most ordinary semiconductors, since in this case B is, in order of magnitude, several electron-volts. A completely opposite picture is observed in organic semiconductors, where $B \sim \omega$ for interaction with the acoustic branch and $B \ll \omega$ for interaction with the optical vibrational branches.

If it turns out that the present approximation is applicable sufficiently often, then the problem arises of considering transport processes specifically for this approximation. The treatment in this particular case will differ substantially from the traditional one, based on the solution of the Boltzmann kinetic equation. For example, when using diagram techniques, instead of asymptotic time estimates it is necessary to use estimates of time integrals as $t \to 0$.

The semiclassical approximation, in one form or another, may also be applied to a number of other problems, such as impurity scattering and spin diffusion.

The approximation considered, if necessary, can be improved (9). For example, setting

$$H_1(S) = \sum A_q a_m^+(0) a_m(0) e^{i\mathbf{qm}} (b_q(s) + b_{-\mathbf{q}}^+(s)), \tag{18}$$

i.e., neglecting the development in time of the electron density in comparison with the development in time of the phonon motions, and considering small electron concentrations, we have

$$S^{+}(t) a_p S(t) = a_p T \exp\left[i \int_0^t \sum A_q e^{i\mathbf{pq}} (b_q(s) + b^{+}_{-\mathbf{q}}(s))\, ds \right]. \tag{19}$$

Substituting (19) into the expression for $X(t)$, we obtain, for example, for $S(i\beta) = 1$:

$$X(t) = -e^2 \sum B(\mathbf{g}) B(\mathbf{g}')\, \mathbf{gg}'\, I_{g+\mathbf{g}'}(2B\beta) \exp\left\{ -\sum_q \frac{2A_q^2}{\omega_q} \left[(2n_q + 1)(1 - \cos \mathbf{qg}') \times \right.\right.$$

$$\left.\left. \times (1 - \cos \omega_q t) + i \sin \omega_q t - i\omega_q t \right] \right\}. \tag{20}$$

At high temperatures $X(t)$ tends to the Gaussian form ([10]). In the general case, when conditions of the type (17) are satisfied, the main contribution to $\sigma(\omega)$ will again be determined at small t, i.e., the semiclassical approximation will still be suitable.

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