Quasiparticle transport equation with collision delay. I. Phenomenological approach

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For a system of non-interacting electrons scattered by resonant levels of neutral impurities, we show that virial and quasiparticle corrections have nearly equal magnitudes. We propose a modification of the Boltzmann equation that includes quasiparticle and virial corrections and discuss their interplay on a dielectric function.

I. INTRODUCTION

Elastic scattering of electrons by impurities is the simplest but still very interesting dissipative mechanism in semiconductors. Its simplicity follows from the absence of the impurity dynamics, so that individual collisions are described by a motion of an electron in a fixed potential. On the other hand, due to a large variety of impurities and their accessible concentrations, impurity-controlled transport regimes span from simple response characterized by a mean-free path to a weak localization.

Let us recall a quasiclassical picture of impurity controlled transport. The basic effect of impurities on transport in crystals consists in abrupt changes of directions of electron trajectories. Within the Boltzmann equation (BE), this effect is described by scattering integrals. At higher concentrations, impurities influence a band structure. This correction can be built into the BE if one accepts that elementary excitations are not simple electrons but electron-like quasiparticles in the spirit of the Landau theory of Fermi liquids [1]. Finally, impurities attract/expel electrons to/from their vicinity what reduces/increases a density of freely traveling electrons. Such changes in effective density of electrons are covered by virial corrections that are accounted for via non-local (in time and space) corrections to scattering integrals. Although quasiparticle and virial corrections to the BE are known for decades, transport theory that would include both non-locality and their accessible concentrations, impurity-controlled transport regimes span from simple response characterized by a mean-free path to a weak localization.

In this paper we focus on an intuitive approach. In Appendix A, we show that virial corrections to transport coefficients. In Sec. VII we summarize. In Appendix A, we show that non-self-consistent treatment used in this paper and more advanced self-consistent treatment are equivalent within assumed precision. In Appendix B, we derive the derived optical theorem which explains comparable magnitudes of the virial and the quasiparticle corrections. In Appendix C, we verify that the presented modification of the BE is consistent with the equation of continuity and the energy conservation.

II. CLASSICAL COLLISION

Since the quantum-mechanical theory with intuitively clear virial corrections is still missing, the only experience for non-equilibrium systems one can gain from virial corrections to the BE in the classical statistical theory of moderately dense gases. Within accuracy to the second order virial coefficient, these corrections were introduced already on the break of centuries by Clausius [2]. Here we modify his approach in two aspects. First, instead of binary collisions of molecules we assume electron-impurity events. Second, instead of space non-locality, we reformulate virial corrections in terms of time non-locality.

According to Clausius [2], one has to take into account that two colliding molecules are not at the same space point, but at a distance of sum of their radii. In other words, the scattering integral has to be non-local in space.

Similar argument about non-locality of scattering event applies to collisions of electrons with impurities. A sketch of a classical trajectory of a colliding electron is in Fig. 1. Before the electron reaches the impurity potential of a finite range, its trajectory is a straight line. Then it makes a curve in the impurity potential and again follows a straight line in a new direction. Within the BE, this process is approximated by an effective event that is local in time and space. Of course, within the local approximation, one has to sacrifice dynamics of the electron during the collision. More serious neglect follows from the fact...
that within the local approximation the asymptotic motion along outgoing line cannot be properly matched with the motion along the incoming line.

Let us find a correct matching of incoming and outgoing lines. To this end, we extrapolate the incoming and outgoing lines and find their crossover $X$. In general, such a crossover need not exist, however, it always exists for spherical potentials to which we limit our attention. The crossover $X$ gives us the coordinate at which we have to place the effective event. As one can see in Fig. 1, the outgoing lines and find their crossover. To this end, we extrapolate the incoming and outgoing lines. Using intuitive arguments, the collision delay $\Delta t$ can be incorporated into the scattering integrals of the BE. A balance equation of the Boltzmann type for scattering by impurities reads

$$\frac{\partial f}{\partial t} + \frac{k}{m} \frac{\partial f}{\partial r} - \frac{\partial \phi f}{\partial \Delta t} = \int \frac{dp}{(2\pi)^3} P_{kp} f (p, r, t_{in}^{kp}) - \int \frac{dp}{(2\pi)^3} P_{kp} f (k, r, t_{in}^{kp}),$$

(1)

where $f(k, r, t)$ is a distribution function in the phase space, $r$ is a coordinate, $t$ is a time, $k$ and $p$ are momenta, $P_{kp}$ is the scattering rate from $k$ to $p$. Since distributions in the scattering integrals correspond to initial conditions, $t_{in}^{kp}$ is a time at which an electron enters the scattering from $k$ to $p$.

In the scattering-out event [the second term on the r.h.s. of (1)], an electron of momentum $k$ enters a collision at $t_{in}^{kp}$ leaving at $t_{out}^{kp}$ with momentum $p$. The scattering-out integral gives a probability that at time $t$ an electron leaves the momentum $k$. This happens at the beginning of the collision, thus $t_{in}^{kp} = t$.

In the scattering-in event [the first term on the r.h.s of (1)], an electron of momentum $p$ enters a collision at $t_{in}^{kp}$ leaving at $t_{out}^{kp}$ with momentum $k$. The scattering-in integral gives a probability that at time $t$ an electron enters the momentum $k$. This happens at the end of the collision, thus $t_{out}^{kp} = t$. From $t_{out}^{kp} + t_{in}^{kp} = \Delta t(p,k)$, one finds that $t_{in}^{kp} = t - \Delta t(p,k)$. The time argument in the scattering-in is thus shifted by the collision delay $\Delta t(p,k)$. A modified BE then reads

$$\frac{\partial f}{\partial t} + \frac{k}{m} \frac{\partial f}{\partial r} - \frac{\partial \phi f}{\partial \Delta t} = \int \frac{dp}{(2\pi)^3} P_{kp} f (p, r, t - \Delta t)$$

$$- \int \frac{dp}{(2\pi)^3} P_{kp} f (k, r, t).$$

(2)

Electrons trapped by impurities are excluded from free motion. With a finite collision delay, one has to deal with two distinguished local densities of electrons. Beside the physical density $n = N/\Omega$ (number of electron $N$ per volume $\Omega$), there is an effective density

$$n_{\text{free}} (r,t) = \int \frac{dk}{(2\pi)^3} f(k, r, t)$$

(3)

which equals the local density in the free space between impurities.

For finite collision delay $\Delta t$, a share of electrons trapped by impurities can change in time. Accordingly, the free density $n_{\text{free}}$ does not conserve. From (2) one finds that in a homogeneous but non-stationary system

$$\frac{\partial n_{\text{free}}}{\partial t} = \int \frac{dk}{(2\pi)^3} \frac{dp}{(2\pi)^3} P_{kp} (f(p, t - \Delta t) - f(p, t))$$

$$- \int \frac{dk}{(2\pi)^3} \frac{dp}{(2\pi)^3} P_{kp} \frac{\partial f(p, t)}{\partial t}$$

$$- \frac{\partial \phi}{\partial t} \int \frac{dk}{(2\pi)^3} \frac{dp}{(2\pi)^3} P_{kp} \Delta t f(p, t).$$

(4)

The quantity that conserves is the physical density

$$n = n_{\text{free}} + n_{\text{corr}}$$

(5)

which differs from the free density by the density

$$n_{\text{corr}} = \int \frac{dk}{(2\pi)^3} \frac{dp}{(2\pi)^3} P_{kp} \Delta t f(p, t)$$

(6)

that is correlated with impurity positions.

Note that the scattering mechanism enters relation between density $n$ and distribution $f$. Without virial correction (here represented by correlated density), the functional $n[f]$ is independent of scattering, since $n = n_{\text{free}}$. In the presence of virial corrections one has to keep in mind that a density of freely traveling electrons does not equal the physical density.
B. Hard spheres

As the second example, we discuss hard-sphere impurities. In this case, the incoming and outgoing lines have a crossover at the sphere surface. The times match exactly, \( t^{\text{out}} = t^{\text{in}} \). The only misfit results from the fact that the crossover is not at the centre of the impurity but shifted by the sphere radius. Here we show that the crossover offset can be reformulated in terms of an effective time mismatch so that one can use unified description of collisions with point traps and with hard spheres.

A collision with a hard sphere is schematically shown in Fig. 2. The real electron trajectory follows the full line. The scattering integral of the BE describes this event by an electron following the dashed line. This effective trajectory (from \( \Lambda \) to \( \Lambda B \)) is longer than the real one (from \( \Lambda \) to \( \Lambda B \)) by \( \Delta s = 2\sqrt{R^2 - b^2} \).

One can include the finite size of impurities into the transport equation in a manner to parallel traps. We approximate the trajectory of the electron by the effective trajectory \( AB \). Since, following the a real trajectory \( AB \), the electron reaches a next collision sooner by a time \( \Delta s/u \), we introduce into transport equation (2) a negative time delay \( \Delta t = -\Delta s/u \). Here \( u \) is an electron velocity.

For the hard-sphere impurities, transport equation (2) with the negative collision delay is only an approximation. Let us check how this approximation works for the correlated density. The classical scattering rate on hard spheres reads

\[
P_{pk} = \frac{(2\pi)^3}{k^2} \delta(|k| - |p|) c' u R^2 \sin \vartheta, \tag{7}
\]

where \( c' = N_{\text{imp}}/\Omega \) is an impurity concentration (number of impurities \( N_{\text{imp}} \) per volume \( \Omega \)), \( u = k/m \) is an electron velocity, and \( \vartheta \) is a scattering angle, \( p k = |k||p| \cos \vartheta \). The inverse lifetime follows from (7) as

\[
\frac{1}{\tau} = \int \frac{dp}{(2\pi)^3} \frac{1}{2} \rho_{pk} = c' u \pi R^2. \tag{8}
\]

The collision delay \( \Delta t = -\Delta s/u \) in angular coordinates reads

\[
\Delta t = -\frac{2}{u} \sqrt{R^2 - b^2} = -\frac{2}{u} R \sin \frac{\vartheta}{2}. \tag{9}
\]

The correlated density from (8) results

\[
n_{\text{corr}} = -\int \frac{dp}{(2\pi)^3} f(p,r,t) \times \frac{1}{(2\pi)^3} \int_0^\infty k^2 dk \int_0^{2\pi} d\varphi \int_0^\pi d\theta P_{pk} \Delta t
\]

\[
= -c' \frac{4\pi}{3} R^3 \int \frac{dp}{(2\pi)^3} f(p,r,t)
\]

\[
= -c' \frac{4\pi}{3} R^3 n_{\text{free}}
\]

\[
= -\frac{\Omega_{\text{imp}}}{\Omega} n_{\text{free}}. \tag{10}
\]

Here, we have denoted \( \Omega_{\text{imp}} = \Omega c' \frac{4\pi}{3} R^3 = N_{\text{imp}} \frac{4\pi}{3} R^3 \) the total volume of impurities.

The physical content of the correlated density can be demonstrated on the equation of state. The number of electrons which hit the surface of the sample is given by the density of freely traveling electrons \( n_{\text{free}} \), therefore the pressure \( P \) is given by the equation of state

\[
P = n_{\text{free}} k_B T. \tag{11}
\]

From (8) and (10) we find relation between the free density and the total number of particles \( N \)

\[
n_{\text{free}} = \frac{N}{\Omega - \Omega_{\text{imp}}}. \tag{12}
\]

The equation of state (11) thus takes the form of the van der Waals equation

\[
P(\Omega - \Omega_{\text{imp}}) = N k_B T. \tag{13}
\]

Briefly, the negative collision delay simulates for the excluded volume in the van der Waals equation of state.

Note that the correlated density (10) is negative. The density \( n_{\text{free}} \) in the free space between impurities is higher than the physical density \( n \) what reflects that electrons are expelled from the volume of impurities. It is important to distinguish which density \( (n_{\text{free}} \text{ or } n) \) is relevant for individual physical quantities. For instance, the charge density is given by \( n \), while pressure relates to \( n_{\text{free}} \).

III. COLLISION DELAY TIME IN QUANTUM MECHANICS

The classical statistics shows that the non-locality of scattering events is approximatively described by the collision delay. This concept is easily transferred to the quantum mechanics, where the collision delay has already been introduced by Wigner. He used the maximum of wave packet to identify motion of an electron. Now we apply Wigner’s approach to a neutral impurity to estimate a magnitude of virial corrections.

The scattering of electron by a single impurity is described by the Schrödinger equation

\[
(\omega - H_0 - V)(\psi_{\text{in}} + \psi_{\text{out}}) = 0, \tag{14}
\]

where \( \psi_{\text{in}}(r) = \exp ikx \) is an incoming plane wave, with \( r \equiv (x, y, z) \), \( \psi_{\text{out}} \) is the outgoing part, \( H_0 \) is Hamiltonian of unperturbed crystal and \( V \) is the impurity potential. The incoming plane wave has to be an eigen state of the crystal, \( (\omega - H_0)\psi_{\text{in}} = 0 \), thus the energy equals the kinetic energy of the incoming plane wave, \( \omega = \epsilon_k \). Then (14) simplifies as

\[
(\epsilon_k - H_0)\psi_{\text{out}} = V(\psi_{\text{in}} + \psi_{\text{out}}). \tag{15}
\]

A formal solution of equation (15) reads
\[ \psi_{\text{out}} = G_0^R(\epsilon_k)T^R(\epsilon_k)\psi_{\text{in}}, \]  

(16)

where

\[ G_0^R(\omega) = \frac{1}{\omega - H_0 + i\epsilon}, \]

(17)

is the retarded Green’s function of the host crystal, and

\[ T^R = V + VG_0^R G^R, \]

(18)

is the T-matrix.

As a model potential of the neutral impurity we use the one proposed by Koster and Slater: 

\[ V = |0\rangle v \langle 0|, \]

(19)

where \(|0\rangle\) is a single orbital at the impurity site. We will use the convention that lowercase denotes local elements of operators (that are in uppercase) throughout the paper. For the Koster-Slater potential, the T-matrix is also restricted to the selected orbital, \( T^R = |0\rangle \langle 0| T^R \langle 0| \).

To obtain the collision delay, we place the impurity in the initial of coordinates and express the wave function in the time representation

\[ \psi(r, t) = e^{ikx - i\epsilon_k t} - \frac{m}{2\pi|p|} t^R(\epsilon_k) e^{ik|p| - i\epsilon_k t}. \]

(21)

We have used an asymptotic Green’s function for large \( r \), see Ref. 4.

\[ \langle r | G_0^R(\epsilon_k) | 0 \rangle = - \frac{m}{2\pi|p|} e^{ik|p|}, \]

(22)

to evaluate the outgoing wave from (14). This approximation holds for energies \( \epsilon_k \) in the parabolic region of the band structure, \( \epsilon_k = k^2/2m \). The first term in (21) is the incoming wave \( \psi_{\text{in}} \) and the second one is the outgoing part \( \psi_{\text{out}} \).

To see the time delay, we take a linear combination of wave functions \( \psi \) so that the incoming part \( \psi_{\text{in}} \) forms a wave packet of a narrow momentum width \( \kappa \to 0 \),

\[ \psi_{\text{in}}(r, t) = \frac{1}{\sqrt{\pi \kappa}} \int dp e^{-\frac{(x-p)^2}{\kappa^2}} e^{ipx - i\epsilon_p t} \]

\[ \approx e^{ikx - i\epsilon_k t} \exp \left\{ -\frac{\kappa^2}{4} (x - ut)^2 \right\}, \]

(23)

where \( u = k/m \) is an electron velocity. This wave packet passes the initial of coordinates at \( t = 0 \). A corresponding outgoing wave \( \psi_{\text{out}} \) reads

\[ \psi_{\text{out}}(r, t) = -\frac{m}{2\pi|p|} \frac{1}{\sqrt{\pi \kappa}} \int dp e^{-\frac{(x-p)^2}{\kappa^2}} t^R(\epsilon_p) e^{ip|p| - i\epsilon_p t} \]

\[ \approx -\frac{m}{2\pi|p|} t^R(\epsilon_k) e^{ik|p| - i\epsilon_k t} \]

\[ \times \exp \left\{ -\frac{\kappa^2}{4} \left( |p| - u \left( t + \frac{i}{t^R} \frac{\partial t^R}{\partial \omega} |_{\omega = \epsilon_k} \right) \right)^2 \right\}. \]

(24)

The outgoing wave passes the initial of coordinates with the collision delay

\[ \Delta_t = \text{Im} \frac{1}{t^R} \frac{\partial t^R}{\partial \omega} |_{\omega = \epsilon_k}. \]

(25)

The collision delay (25) depends only on the energy of electron. This is because the Koster-Slater impurity has a single scattering channel of the s-symmetry. For a general potential \( V \), collision delay \( \Delta_t \) depends also on the scattering angle as the classical collision delay (9).

The collision delay (25) is a quantum counterpart of the classical collision delay (9). Following analogy between the quantum and classical approaches to the Boltzmann-like transport equations, we introduce the collision delay (25) into the scattering integral in exactly the same way as in the classical case. In other words, we expect the transport equation to be of form (2), however, scattering rates \( P_{kp} \) and collision delay \( \Delta_t \) are extracted from quantum collisions.

The rate of scattering by Koster-Slater impurities of concentration \( c \) (probability that impurity occupy a site) follows from the Fermi golden rule as

\[ P_{pk} = c |t^R(\epsilon_k)|^2 \pi \delta(\epsilon_k - \epsilon_p). \]

(26)

This scattering rate does not depend on the scattering angle, thus it can be also expressed in terms of the lifetime \( \tau \)

\[ P_{pk} = \frac{1}{\tau} \frac{2\pi^2}{k^2} \delta(|p| - |k|), \]

(27)

where \( \tau \) is conveniently evaluated from the T-matrix

\[ \frac{1}{\tau} = c(-2) \text{Im} t^R(\epsilon_k). \]

(28)

A. Estimate of virial corrections

\( \delta \)From a scattering by a single impurity one can estimate magnitude of virial corrections. Using formula (1) with the quantum scattering rate (27) and collision delay (25), one finds correlated density

\[ n_{\text{corr}} = \int \frac{dk}{(2\pi)^3} f(k) \frac{\Delta_t}{\tau}. \]

(29)

The magnitude of virial corrections is thus measured by a ratio \( \Delta_t/\tau \).

Note that the collision delay is independent from the impurity concentration, while the lifetime is inversely proportional to the concentration. Accordingly, \( \Delta_t/\tau \sim c \), i.e., magnitude of virial corrections is controlled by the impurity concentration \( c \). To be specific, we will assume impurity concentrations \( \sim 10^{-6} \) per site.

Now we estimate \( \Delta_t/\tau \) for a model local Green’s function (4).
\[ \langle 0 | G_0^R(\omega) | 0 \rangle = \frac{2}{W} \left( -\frac{b_1}{2} - \frac{b_3}{8} + z + \left( b_1 - \frac{b_3}{2} \right) z^2 + b_3 z^4 \right) + \theta(1 - z^2) \frac{2}{W} (1 + b_1 z + b_3 z^3) \sqrt{1 - z^2} \bigg|_{z = \frac{\mu}{\hbar}}. \]  

Here, \( W = 6 \) eV is a half-width of a conductivity band, and parameters \( b_1 = 1.2 \) and \( b_1 = -0.4 \) serve to model the local density of state to a shape resembling III-V semiconductors, see Fig. 3.

The collision delay is very sensitive to a value of the impurity potential \( v \). Using (20), one can rearrange the collision delay (25) as

\[ \Delta_t = -\text{Im} \left[ t^R \frac{\partial}{\partial \omega} \frac{1}{t^R} \right] = \text{Im} \frac{v \frac{\partial}{\partial \omega} \langle 0 | G_0^R(\omega) | 0 \rangle}{1 - v \langle 0 | G_0^R(\omega) | 0 \rangle}. \]

Apparently, the collision delay will be long for potentials for which the denominator \( 1 - v \langle 0 | G_0^R(\omega) | 0 \rangle \) goes to zero. For these values of potential \( v \), the impurity behaves like a resonant level close to the conductivity band edge.

For model function (30), the real part of the local density of state to a shape resembling III-V semiconductors because it is compensated by a shift of chemical potentials. Since

\[ \Sigma^R = cT^R. \]

Since \( T^R = \sum_r |r\rangle t^R(r) \langle r| \), we can write the self-energy as

\[ \Sigma^R = \sum_r |r\rangle \sigma^R(r) \langle r|. \]

\section{IV. QUASIPARTICLE PICTURE}

From analysis of the scattering by the Koster-Slater impurity, we have found that the largest virial corrections appear for resonant levels. Resonant levels, however, also result in large values of the T-matrix, as one can see in Fig. 4. At the band edge \( \text{Re} t^R \sim -400 \) eV and \( \text{Im} t^R \sim -30 \) eV. In particular, the real part of the T-matrix is large compared to potential \( v = -5.35 \) eV. For such large values of the T-matrix, the impurity scattering affects the electronic band structure. To take this effect into account, we have to treat electrons as quasiparticles.

\subsection{A. Averaged T-matrix approximation}

The multiple scattering by impurities has been described in detail already in 1960’s within Green’s functions. In the averaged T-matrix approximation (ATA) that corresponds to our approximation of scattering rates, the self-energy equals the averaged value of the T-matrix,

\[ \Sigma^R = cT^R. \]

The quasiparticle energy that describes propagation given by effective “Hamiltonian” \( H_0 + cT \) reads

\[ \varepsilon_k = \epsilon_k + \text{Re} \sigma^R(\epsilon_k). \]

The imaginary part of the self-energy provides the lifetime

\[ \frac{1}{\tau} = -2\text{Im} \sigma^R(\epsilon_k), \]

which is identical to the Fermi golden rule value (27).

The major effect is the overall shift of the band. This shift does not influence bulk properties of homogeneous crystals because it is compensated by a shift of chemical potential.

The energy renormalization leads to quasiparticle corrections to velocity

\[ u = \frac{\partial \varepsilon_k}{\partial k} = \frac{k}{m}. \]

Taking the momentum derivative from (34) one finds the renormalized velocity as

\[ u = \frac{z k}{m}, \]

where \( z \) is the wave-function renormalization

\[ z(k) = 1 + \frac{\partial \text{Re} \sigma^R(\omega)}{\partial \omega} \bigg|_{\omega = \epsilon_k}. \]

\section{B. Energy renormalization}

With respect to transport properties, the velocity renormalization is the most important quasiparticle correction as it determines drift of quasiparticles between collisions. The wave-function renormalization as a function of the impurity potential is presented in Fig. 5.

There is a striking similarity of the wave-function renormalization and the magnitude of virial corrections.

In the above discussion we have ignored selfconsistency. In Appendix A it is shown that for the weak scattering, \( \frac{1}{\tau} \rightarrow 0 \), the above formulas are identical to those resulting from selfconsistent treatment. In Appendix B we also derive a formula that connects virial correction \( 1 + \Delta_t/\tau \) with quasiparticle renormalization \( z \). This formula explains similar magnitudes of these two corrections.
V. QUASIPARTICLE BOLTZMANN EQUATION WITH COLLISION DELAY

Similarity of magnitudes of quasiparticle and virial corrections show that both corrections have to be included in the transport equation within the same accuracy. It is quite easy to guess such a transport equation. The quasiparticle renormalization affects the drift between collisions, therefore it enters the transport equation as a renormalization of velocity (3). The virial corrections enter the scattering integrals like in (3). The transport equation that includes both corrections reads

\[
\frac{\partial f}{\partial t} + \frac{z k}{m} \frac{\partial f}{\partial r} - \frac{\partial \phi}{\partial r} \frac{\partial f}{\partial k} = - \frac{f}{\tau} + \frac{1}{\tau} \frac{2 \pi^2}{k^2} \int \frac{dp}{(2\pi)^3} \delta(|p| - |k|) f(p, r, t - \Delta t). \quad (39)
\]

Although this equation has the classical form (3), its components \(z, \tau, \) and \(\Delta t\) are given by quantum-mechanical microscopic dynamics. One can also view (39) as a phenomenologic equation with momentum-dependent parameters \(z, \Delta t, \) and \(\tau.\)

Beside the transport equation, one also needs relation of observables to distribution function \(f.\) From the equation of continuity one finds that the physical density includes only virial corrections,

\[
n = \int \frac{dk}{(2\pi)^3} \left(1 + \frac{\Delta t}{\tau}\right) f, \quad (40)
\]

while the density of particle current has only quasiparticle corrections

\[
j = \int \frac{dk}{(2\pi)^3} \frac{k}{m} f = \int \frac{dk}{(2\pi)^3} \frac{\partial \varepsilon}{\partial k} f. \quad (41)
\]

\(\varepsilon\)From the energy conservation one finds that the energy density includes both corrections

\[
E = \int \frac{dk}{(2\pi)^3} \left(1 + \frac{\Delta t}{\tau}\right) (\varepsilon + \phi) f. \quad (42)
\]

Both conservation laws are in Appendix C.

\(\varepsilon\)From the set of equations (39-42) one can evaluate properties of electron gas or liquid in a similar manner as one uses the BE to this end. To demonstrate such an application, in the next section we evaluate the dielectric function.

VI. DIELECTRIC FUNCTION

The virial corrections influence a response of the system to perturbations. The time non-locality of the scattering integral emerges in non-stationary processes. The simplest but important process is linear screening of external field described by dielectric function \(\kappa_r.\)

The virial corrections enter the dielectric function in two ways, from the transport equation (39) and from functional (11). To demonstrate both mechanisms, we evaluate \(\kappa_r\) from its definition.

An electrostatic external potential

\[
\phi_0(r, t) = \phi_0 e^{i\omega t - i\omega t} \quad (43)
\]

creates a perturbation in the electron density

\[
\tilde{n}(r, t) = \tilde{n}(r, t - i\omega t). \quad (44)
\]

The perturbation in density creates Coulomb potential

\[
\tilde{\phi}(r, t) = \tilde{\phi} e^{i\omega t - i\omega t} = \frac{\varepsilon^2}{\kappa q^2} \tilde{n} e^{i\omega t - i\omega t} \quad (45)
\]

that adds to the external one so that the internal field reads

\[
\phi = \phi_0 + \tilde{\phi} = \phi_0 + \frac{\varepsilon^2}{\kappa q^2} \tilde{n}. \quad (46)
\]

Here, \(\kappa\) is permittivity of the host crystal. From definition

\[
\phi = \frac{\tilde{\phi}_0}{\kappa_r} \quad (47)
\]

one finds the dielectric function to be

\[
\kappa_r = 1 - \frac{\varepsilon^2 \tilde{n}}{\kappa q^2 \tilde{\phi}}. \quad (48)
\]

A. Perturbation of quasiparticle distribution

To evaluate perturbation \(\tilde{n}\) of the physical density \(n,\) we have to find the linear perturbation of the quasiparticle distribution,

\[
\tilde{f}(k, r, t) = \tilde{f}(k) e^{i\omega t - i\omega t} \quad (49)
\]

caused by potential \(\phi.\) To this end we use linearized transport equation (39)

\[
\left( -i \omega + iz \frac{k q}{m} + \frac{1}{\tau} \right) \tilde{f}(k) - iq \phi \frac{\partial f_0(k)}{\partial k} = \frac{1}{\tau} \frac{2 \pi^2}{k^2} \int \frac{dp}{(2\pi)^3} \delta(|p| - |k|) e^{i\omega \Delta t} \tilde{f}(p). \quad (50)
\]

The momentum derivative of the equilibrium distribution \(f_0(k) = f_{FD}(\varepsilon_k)\) reads

\[
\frac{\partial f_0(k)}{\partial k} = \frac{z}{m} \frac{\partial f_{FD}(\varepsilon_k)}{\partial \varepsilon_k}. \quad (51)
\]

The perturbation \(\tilde{f}\) depends only on the absolute value of momentum \(|k|\) and the angle between momentum \(k\)
and wave vector q. We denote $s = \frac{ik}{|k|} m$ and $s' = \frac{ik'}{|k'|} m$, and integrate over the energy conserving $\delta$ function so that the transport equation simplifies to

$$
\left( -i\omega + i sz \frac{|k|}{m} + \frac{1}{\tau} \right) \tilde{f}(|k|, s) - i sz \frac{|k|}{m} \phi \frac{\partial f_{FD}(\varepsilon_{|k|})}{\partial \varepsilon_{|k|}} = \frac{1}{2\tau} e^{i\omega \Delta t} \int_{-1}^{1} ds' \tilde{f}(|k|, s').
$$

With abbreviations $\frac{|k|}{m} \equiv u$, $|q| \equiv q$, and skipping argument $|k|$ in distributions, equation (54) reads

$$
\left( -i\omega + i squ \frac{1}{\tau} \right) \tilde{f}(s) - i squ \phi \frac{\partial f_{FD}}{\partial \varepsilon} = \frac{1}{2\tau} e^{i\omega \Delta t} \int_{-1}^{1} ds' \tilde{f}(s').
$$

The angular dependence of the distribution is easily found from (54)

$$
\tilde{f}(s) = \frac{i squ \phi \frac{\partial f_{FD}}{\partial \varepsilon} + \frac{1}{2} e^{i\omega \Delta t} \tilde{F}}{-i\omega + isqu + \frac{1}{\tau}},
$$

where

$$
\tilde{F} = \frac{1}{2} \int_{-1}^{1} ds' \tilde{f}(s'),
$$

is an angle-averaged distribution. Integrating over s, one finds from (54) a condition for the angle-averaged distribution

$$
\tilde{F} = (1 + (1 - i\omega \tau) J) \phi \frac{\partial f_{FD}}{\partial \varepsilon} e^{i\omega \Delta t} \tilde{F},
$$

where

$$
J = \frac{i}{2qu\tau} \ln \left( \frac{\omega + \frac{i}{\tau} - qu}{\omega + \frac{i}{\tau} + qu} \right).
$$

Since the BE holds only for slowly varying fields, we can linearize in $\Delta t$, $e^{i\omega \Delta t} \approx 1 + i\omega \Delta t$. The angle-averaged distribution from (54), then results

$$
\tilde{F} = \phi \frac{\partial f_{FD}}{\partial \varepsilon} \frac{1 + (1 - i\omega \tau) J}{1 + (1 + i\omega \Delta t) J}.
$$

Now the perturbation of the quasiparticle distribution is fully determined by (54) and (58).

### B. Perturbation of density

Perturbation of the electron density is found from (40)

$$
\tilde{n} = 2 \int \frac{dk}{(2\pi)^3} \tilde{f}(k) = \frac{1}{\pi^2} \int_{0}^{\infty} dk k^2 \tilde{F}(k) \left( 1 + \frac{\Delta t}{\tau} \right).
$$

The factor of two stands for sum over spins. For simplicity we assume the limit of low temperature

$$
\frac{\partial f_{FD}}{\partial \varepsilon} \to -\delta(\varepsilon - E_F) = -\frac{m}{\pi^2} \delta(k - k_F),
$$

where one can easily integrate out the momentum

$$
\tilde{n} = -\phi \frac{mk}{\pi^2 z} \left( 1 + \frac{\Delta t}{\tau} \right) \frac{1}{1 + (1 + i\omega \tau)J} \int_{k=k_F}.
$$

Using (51) in (58) one directly obtains the dielectric function.

### C. Long wave length limit

Now we focus on long wave length limit, $q \to 0$. To evaluate this limit from (51) we first rearrange (57) as

$$
J = -\frac{1}{1 - i\omega \tau} \sum_{x=\pm} \frac{1}{x} \ln(1 + x) \to -\frac{1}{1 - i\omega \tau} \left[ 1 - \frac{1}{3} \left( \frac{qu\tau}{1 - i\omega \tau} \right)^2 \right].
$$

In the long wave length limit, the dielectric function reads

$$
\kappa_r = 1 + \frac{e^2 mk_F}{\kappa_{\pi^2 z}} \left( 1 + \frac{\Delta t}{\tau} \right) \frac{1 + \Delta t}{1 - i\omega \tau} - 3\omega \left( \omega + \frac{i}{\tau} \right) \left( 1 + \frac{\Delta t}{\tau} \right) \frac{mk_F^2}{\kappa_{\pi^2 z}},
$$

where $z$, $\tau$ and $\Delta t$ are values at the Fermi level. In the static case $\omega = 0$, the dielectric function is of form $\kappa_r = 1 + \frac{\Delta t}{\tau}$. From (53) one finds that the Thomas-Fermi screening length $1/q_s$ is

$$
q_s^2 = \frac{e^2 mk_F}{\kappa_{\pi^2 z}} \frac{1}{z} \left( 1 + \frac{\Delta t}{\tau} \right).
$$

Part $\frac{e^2 mk_F}{\kappa_{\pi^2 z}}$ gives standard Thomas-Fermi screening, factors $\frac{\Delta t}{\tau}$ and $1 + \frac{\Delta t}{\tau}$ provide quasiparticle and virial corrections, respectively. As one can see from Fig. 3, quasiparticle and virial corrections nearly equal, therefore they mutually compensate in the Thomas-Fermi screening length (53)

$$
q_s^2 \approx \frac{e^2 mk_F}{\kappa_{\pi^2 z}}.
$$

For homogeneous perturbations, $q = 0$, the dielectric function is of form $\kappa_r = 1 - \frac{\omega^2}{\omega_0^2 (\omega + i/\tau)}$. From (53), the plasma frequency $\omega_p$ results

$$
\omega_p^2 = \frac{e^2 k_F}{3\kappa_{\pi^2 m} z}.
$$

There is only the quasiparticle correction $z$. 7
Note that virial corrections to the Thomas-Fermi screening $q_s$ and plasma frequency $\omega_p$ appear in rather paradoxical way. While the static screening has virial corrections [due to $n[f]$, Eq. (63)], the plasma frequency describing non-stationary behavior has none. This is because in the homogeneous case, $q = 0$, the virial corrections from $n[f]$ and the scattering integral mutually cancel due to particle conservation law.

D. Virial correction to Fermi momentum

The Thomas-Fermi screening length (64) and the plasma frequency (66) are expressed in terms of the Fermi momentum. Additional virial corrections to those quantities appear if one rewrite them in terms of physical density $n$.

In general, the Fermi momentum is a parameter of the quasiparticle distribution $f$, therefore it is always related to the free density. For the parabolic band, the Fermi momentum results from (3) as

$$k_F = \frac{2}{\sqrt{3} \pi^2 n_{\text{free}}}.$$

(67)

For sufficiently low density $n$, the ratio $\Delta \tau / \tau$ changes a little from zero to the Fermi momentum. In our case, $\Delta \tau / \tau$ changes by 7% for density $n = 10^{16}$ cm$^{-3}$. This weak dependence allows us to take approximation

$$\frac{\Delta \tau(k)}{\tau(k)} = \frac{\Delta \tau(k_F)}{\tau(k_F)}.$$  

(68)

\[ \text{From (64)} \text{ one finds that the free and physical densities relate as} \]

$$n = n_{\text{free}} \left(1 + \frac{\Delta \tau}{\tau}\right),$$

(69)

and the Fermi momentum reads

$$k_F = \frac{3}{\sqrt{3} \pi^2 n_{\text{free}}}.$$

(70)

In terms of the physical density, the Thomas-Fermi screening length (65) regains corrections

$$q_s^2 \approx \frac{e^2 m}{\kappa \pi^2} \sqrt{\frac{3 \pi^2 n}{1 + \frac{\Delta \tau}{\tau}}}.$$  

(71)

In opposite, the plasma frequency in terms of physical density regains its free-particle value

$$\omega_p^2 = \frac{e^2 n}{\kappa m} \frac{1}{1 + \frac{\Delta \tau}{\tau}} \approx \frac{e^2 n}{\kappa m},$$

(72)

\[ \text{E. dc conductivity} \]

Compensation of virial and quasiparticle corrections also appears for dc conductivity $\sigma_{dc}$. Although this compensation is a direct consequence of the dielectric function, we discuss it in detail for its experimental importance.

The conductivity relates to dielectric function $\kappa_r$ as

$$\sigma_{dc} = \lim_{q, \omega \to 0} -i \omega \kappa_r (\kappa_r - 1).$$

(73)

This known relation can be recovered from the equation of continuity (C2) that yields $i \omega \tilde{n} - i q j = 0$, where $j$ is flow of particles. The electric field $F$ results from the electrostatic potential as $eF = iq \phi$. The conductivity then reads

$$\sigma_{dc} = \frac{e^2 k_F^3 \tau}{3 \pi^2 n}.$$

(74)

Comparing (74) with (48) one recovers (73).

Sending $q \to 0$ and $\omega \to 0$ one finds standard relaxation time formula with the quasiparticle correction

$$\sigma_{dc} = \frac{e^2 n \tau}{m} \frac{z}{1 + \frac{\Delta \tau}{\tau}} \approx \frac{e^2 n \tau}{m}.$$

(76)

virial and quasiparticle corrections mutually compensate.

\[ \text{VII. SUMMARY} \]

We have shown that for scattering by resonant levels of neutral impurities the virial and quasiparticle corrections are of the same magnitude. We have proposed an intuitive modification of the BE that includes both corrections. Proposed modification of the BE has quasiparticle corrections in the drift term (as in the Landau theory) and virial corrections in the scattering integral (as in the classical theory of dense gases). The modified BE can be solved as simply as the standard BE.

An interplay of virial and quasiparticle corrections has been discussed on the dielectric function. Various compensations of virial and quasiparticle corrections has been demonstrated on the static screening, plasma frequency and dc conductivity. Careful measurements of the dielectric function in III-V semiconductor with resonant levels can reveal this interplay. Sensitivity of resonant levels to a hydrostatic pressure makes possible to control magnitude of virial and quasiparticle corrections in a single sample.
The way we have introduced the transport equation does not guarantee its validity. There are two fundamental questions one has to ask: (i) Has the time non-locality of the quantum-mechanical scattering integral really the same form as the classical collision delay? (ii) Are quasiparticle and virial corrections included in consistent manner? No intuitive argument can give satisfactory answers to these questions. To prove yes-answers for both questions one has to recover the transport equation from quantum statistics. Such a microscopic theory is in the second paper of this sequence.

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APPENDIX A: SELF-CONSISTENT ATA

Here we show that for weak scattering, $\frac{1}{\tau} \rightarrow 0$, non-self-consistent formulas from Sec. VB result also from the self-consistent generalization of the self-energy.

The effect of impurities on the band structure affects propagation of the electron in the region between impurities. This change should be included in the propagator that enters the T-matrix. Instead of the unperturbed propagator $G^R$, the T-matrix in the self-energy should be constructed from the full propagator $G^R$

$$t^R_{\text{self}} = v + V \langle 0 \mid G^R \mid 0 \rangle t^R_{\text{self}},$$

where $G^R$ is given by the Dyson equation

$$G^R = G^R_0 + G^R_0 \Sigma^R_{\text{self}} G^R,$$

and

$$\sigma^R_{\text{self}} = \sigma^R_{\text{self}}.$$ (A3)

This approximation is called the self-consistent ATA.

For the KS impurity, where the self-energy has no momentum dependence, the self-consistency is simply achieved by a complex shift of the energy argument

$$G^R(\omega) = G^R_0 (\omega - \sigma^R_{\text{self}}).$$ (A4)

From (A3) one finds that $t^R_{\text{self}}(\omega) = t^R(\omega - \sigma^R_{\text{self}})$, therefore

$$\sigma^R_{\text{self}}(\omega) = \sigma^R(\omega - \sigma^R_{\text{self}}).$$ (A5)

1. Energy

Within the self-consistent treatment the quasiparticle energy is defined as

$$\varepsilon_k = \varepsilon_k + \text{Re} \sigma^R_{\text{self}}(\varepsilon_k).$$ (A6)

Using (A3), one can rewrite (A6) as

$$\varepsilon_k = \varepsilon_k + \text{Re} \sigma^R(\varepsilon_k - \text{Re} \sigma^R_{\text{self}}).$$ (A7)

In argument of the self-energy we use definition (A6) to recover

$$\varepsilon_k = \varepsilon_k + \text{Re} \sigma^R(\varepsilon_k).$$ (34)

2. Wave-function renormalization

Within the self-consistent treatment, the wave-function renormalization results as

$$z = \frac{1}{1 - \frac{\text{Re} \sigma^R}{\partial \omega} \bigg|_{\omega = \varepsilon_k}}.$$ (A8)

From (A3) follows

$$\frac{\partial \text{Re} \sigma^R}{\partial \omega} \bigg|_{\omega = \varepsilon_k} = \frac{\text{Re} \sigma^R}{\partial \omega} \bigg|_{\omega = \varepsilon_k} \left(1 - \frac{\partial \text{Re} \sigma^R_{\text{self}}}{\partial \omega} \bigg|_{\omega = \varepsilon_k}\right),$$

which can be rewritten as

$$\frac{1}{1 - \frac{\partial \text{Re} \sigma^R}{\partial \omega} \bigg|_{\omega = \varepsilon_k}} = 1 + \frac{\partial \text{Re} \sigma^R}{\partial \omega} \bigg|_{\omega = \varepsilon_k}. (A9)$$

The wave-function renormalization (A8) is thus identical to (38).

3. Lifetime

Within the self-consistent treatment, the inverse lifetime results as

$$\frac{1}{\tau} = z \text{Im} \sigma^R_{\text{self}}(\varepsilon_k).$$ (A11)

From (A3) and (A6) one finds

$$\sigma^R_{\text{self}}(\varepsilon_k) = \sigma^R(\varepsilon_k - \text{Re} \sigma^R_{\text{self}} - i \text{Im} \sigma^R_{\text{self}})$$

$$= \sigma^R(\varepsilon_k - i \text{Im} \sigma^R_{\text{self}})$$

$$= \sigma^R(\varepsilon_k) - i \text{Im} \sigma^R_{\text{self}}(\varepsilon_k) \frac{\partial \sigma^R}{\partial \omega} \bigg|_{\omega = \varepsilon_k}. (A12)$$

In the last line we have used linear approximation in the imaginary part of the argument which holds for weak scattering, $\frac{1}{\tau} \rightarrow 0$. 

Imaginary part of (A12)

$$\text{Im}\sigma^R_{\text{self}}(\varepsilon_k) = \text{Im}\sigma^R(\varepsilon_k) - \text{Im}\sigma^R_{\text{self}}(\varepsilon_k) \frac{\partial \text{Re}\sigma^R}{\partial\omega} \bigg|_{\omega=\varepsilon_k} \tag{A13}$$

can be rearranged as

$$\varepsilon \text{Im}\sigma^R_{\text{self}}(\varepsilon_k) = \text{Im}\sigma^R(\varepsilon_k). \tag{A14}$$

Formula (A11) is thus identical to (B3).

**APPENDIX B: QUASIPARTICLE VERSUS VIRIAL CORRECTIONS**

Although virial and quasiparticle corrections describe different features of the quasiparticle transport, both of them are linked to energy derivatives of the T-matrix. From this link follows similarity of their magnitudes.

One can rearrange formula (B2) in the way that reveals the relation of virial correction $1 + \Delta t$ to wave-function renormalization $z$. Writing (B2) as $\Delta t = \text{Im}\frac{\partial R}{\partial\omega} = \frac{1}{2i} \left( \frac{1}{t^A} \frac{\partial t^R}{\partial\omega} - \frac{1}{t^R} \frac{\partial t^A}{\partial\omega} \right)$ and the inverse lifetime (28) as

$$\frac{1}{\tau} = \frac{\partial\text{Re} \sigma^R}{\partial\omega} + \frac{c}{2} \left( \frac{t^A}{t^R} \frac{\partial t^R}{\partial\omega} - \frac{t^R}{t^A} \frac{\partial t^A}{\partial\omega} \right), \tag{B1}$$

where we have used that $\text{Re}\sigma^R = \frac{\varepsilon}{2} (t^R + t^A)$. From (B1) one finds

$$\frac{\partial t^R}{\partial\omega} = t^R \frac{\partial}{\partial\omega} \text{Re} \frac{\partial}{\partial\omega} |0\rangle G^R_0 |0\rangle, \tag{B2}$$

which substituted into (B1) provides

$$\frac{\Delta t}{\tau} = \frac{\partial\text{Re}\sigma^R}{\partial\omega} - c |t^R|^2 \text{Re} \frac{\partial}{\partial\omega} |0\rangle G^R_0 |0\rangle. \tag{B3}$$

Formula (B3) makes connection between virial and quasiparticle corrections. One can see that at least two limiting regimes can be distinguished according to relative values of the first and the second terms in (B3).

For weak potentials when the self-energy can be treated in the Born approximation $t^R \approx v$, i.e., $\sigma^R = cv^2 |0\rangle G^R_0 |0\rangle$, the virial corrections vanish because the first and the second terms mutually cancel. In contrast, the quasiparticle corrections remain. Since most of quasiclassical transport equations have been derived within the Born approximation (or single-loop approximation for particle-particle interaction), it is quite natural that they do not include virial corrections.

The scattering by resonant levels is far from the Born approximation, for model and parameters we consider here $|t^R| \sim 100 \times |v|$. In this case, the second term of (B3) is of the order of $10^{-3}$ while the first one is of the order of $10^{-1}$. Accordingly, the second term can be neglected, i.e., virial and quasiparticle corrections are of the same magnitude.

**APPENDIX C: CONSERVATION LAWS**

1. **Equation of continuity**

In inhomogeneous and non-stationary system, there are currents $j$ due to which local density of electrons $n$ changes. Here we prove that density (40) and current (41) are consistent with the BE (39) obeying the equation of continuity.

Under integration over momentum, term $\frac{\partial f}{\partial r}$ turns into $\frac{\partial n}{\partial r}$, and the scattering integrals turn into $-\frac{\partial n}{\partial r}$, see Sec. II. Equation (39) then yields

$$\frac{\partial n}{\partial t} + \int \frac{dk}{(2\pi)^3} \left( \frac{\varepsilon}{m} \frac{\partial f}{\partial k} - \frac{\partial f}{\partial r} \frac{\partial f}{\partial k} \right) = 0. \tag{C1}$$

The second term in the brackets vanishes what follows from its integration by parts,

$$\frac{\partial n}{\partial t} + \frac{\partial f}{\partial r} \int \frac{dk}{(2\pi)^3} \frac{\varepsilon}{m} f = 0. \tag{C2}$$

The second term is the divergency of the current $j$ given by (41). Equation (C2) is thus the equation of continuity.

2. **Conservation of energy**

Here we prove that for homogeneous system the energy of electrons (42) changes with the field $\phi$ in a consistent way, i.e., $\frac{\partial E}{\partial t} = \frac{\partial n}{\partial t} \frac{\partial f}{\partial \phi}$. First we take time derivative of equation (42),

$$\frac{\partial E}{\partial t} = \int \frac{dk}{(2\pi)^3} \frac{\partial f}{\partial t} \left( 1 + \frac{\Delta t}{\tau} \right)$$

$$+ \int \frac{dk}{(2\pi)^3} \left( \varepsilon + \phi \frac{\partial f}{\partial k} \right) \frac{\partial f}{\partial t} \left( 1 + \frac{\Delta t}{\tau} \right). \tag{C3}$$

The second term of (C3) vanishes. To show this, we multiply the BE (39) with the quasiparticle energy $\varepsilon + \phi$ and integrate over momentum

$$\int \frac{dk}{(2\pi)^3} (\varepsilon + \phi) \frac{\partial f}{\partial t} = - \int \frac{dk}{(2\pi)^3} (\varepsilon + \phi) \frac{\partial f}{\partial t} \frac{\Delta t}{\tau}. \tag{C4}$$

We have used that contributions of non-gradient terms of the scattering integrals mutually cancel because of the energy-conserving $\delta$ function.
In the first term of (C3) we take out the field, the rest of the integral is just density (40). We have thus proved that the total energy changes in thermodynamically consistent way

\[ \frac{\partial E}{\partial t} = n \frac{\partial \phi}{\partial t}. \]  

(C5)

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Except for a shift by an order of magnitude, the collision delay (full line) has nearly the same energy dependence as the lifetime (dashed line).

Virial correction (dashed line) is greater than 1 for resonant levels, $v > -5.4$ eV, what corresponds to positive collision delay. Quasiparticle renormalization $z$ (dotted line) nearly equals the virial correction. In fact they differ less than by 0.8%.

Quasiparticle energy (full line) for resonant levels, $v = -5.35$ eV, of concentration $c = 10^{-6}$. Bare kinetic energy $\epsilon_k$ (dotted line) serves as an eye guide.