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# Nonequilibrium statistical mechanics of drifting particles

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This paper describes a method for obtaining nonequilibrium one-particle energy distributions of fermions or bosons. For the program to be carried out, particle transport should occur in the drifting mode in which the average velocity is much lower than the instantaneous velocity. Under this condition, the spectral current density has a drift-diffusion structure involving a mobility-diffusion relationship unrelated to statistics. When a local-equilibrium energy distribution is used, the linear response theory is recovered. Next, the particle–medium energy exchange is treated within a Fokker–Planck framework in order to obtain the nonequilibrium energy distribution; a nonlinear framework is used to account for the quantum-statistical correlations. Explicit formulas are obtained for homogeneous distributions at steady state. The rate of change of entropy is a simple generalization of the second law of thermodynamics. The positivity of the total entropy production stems from the positive definiteness of the diffusion tensors. Minimal entropy production is not necessarily achieved in the stationary state.

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## I. SCOPE OF THE PAPER

Nonequilibrium phenomena are often dealt with as perturbations of a local equilibrium state with a well-defined temperature. In previous papers[1–3] we showed how to handle particle transport in a medium without reference to equilibrium or temperature. Specifically, the Lorentz model of electrical conduction was addressed in the case of a high applied field, as occurs in semiconductors or insulators. The Boltzmann–Lorentz kinetic equation dealing with the phase–space occupation was replaced by a much simpler equation of the Fokker–Planck type dealing with the particle density in the energy-position manifold, in the limit of a vanishing drift-to-instantaneous velocity ratio. (The drift velocity is obtained by averaging the particle motion over times larger than the velocity–correlation time.) The analytical proof for the replacement was further supported by Monte Carlo evidence. Here we want to bring out the generality of our approach which may be envisioned as a generalization of equilibrium statistical mechanics. The particles considered so far were classical in the sense that they were not subjected to the quantum constraints of indistinguishability, so that their equilibrium energy distribution was given by the Boltzmann–Gibbs statistics. Obviously it is desirable to extend the approach to quantum particles whose equilibrium statistics is of the Fermi–Dirac or Bose–Einstein type. This is compatible with the semiclassical Boltzmann transport equation (dealing with populations alone) if inelastic scattering events are frequent enough to erase the coherence. The approach would enable physicists to address the transport of fermions and bosons in the energy-position manifold, arbitrarily far from equilibrium, in a mathematically simple way.

Section II shows that the expression for the spectral current density derived previously holds for any kind of drifting particle, and that the relations between current densities and generalized forces in irreversible thermodynamics are recovered as instantiations of this expression. Section III explains how the Fokker–Planck framework yields the nonequilibrium energy occupation function of quantum particles exchanging energy with reservoirs, and a simple application to degenerate electrons is given. Section IV discusses the behavior of entropy in the formalism, and Sec. V gathers the conclusions.

## II. THE DRIFT AND DIFFUSION OF QUANTUM PARTICLES

### A. Definitions and classical result

The spectral particle density $\underline{n}(E,\mathbf{r},t)$ (in $\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$) may be written as

$$\underline{n}(E,\mathbf{r},t)=N(E)f_0(E,\mathbf{r},t), \tag{1}$$

where $N(E)$ is the density of one-particle states per unit energy per unit volume of material, and $f_0$ is the energy occupation function at location $\mathbf{r}$ at time $t$. The particle density $n(\mathbf{r},t)$ (in $\mathrm{cm}^{-3}$) is the integral of $\underline{n}$ over energy.

The spectral current density $\mathbf{J}$ (in $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}\,\mathrm{eV}^{-1}$) is obtained from the current density $\mathbf{j}$ (in $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$) by picking out the contribution from the energy shell $[E,E+dE]$, that is

$$\mathbf{j}=\int_0^{+\infty}\mathbf{J}\,dE, \tag{2}$$

and the following expression was arrived at [1]:

$$J^i=qF_j\mu^{ij}(E)\underline{n}(E,\mathbf{r},t)-\frac{\partial}{\partial E}[qF_jD^{ij}(E)\underline{n}(E,\mathbf{r},t)]-\frac{\partial}{\partial x^j}[D^{ij}(E)\underline{n}(E,\mathbf{r},t)], \tag{3}$$

where Einstein's summation convention is understood, $q\mathbf{F}(\mathbf{r},t)$ is the force acting upon the particle, and energy-dependent diffusion and mobility tensors are defined as

$$D^{ij}(E)\equiv\overline{(v_g^i(\mathbf{p})\lambda^j(\mathbf{p}))}_E, \tag{4a}$$

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$$N(E)\mu^{ij}(E) \equiv \frac{d}{dE}[N(E)D^{ij}(E)]. \tag{4b}$$

In Eq. (4a) $v_g(\mathbf{p})$ is the group velocity $\partial E/\partial \mathbf{p}$ of the particle of momentum or pseudomomentum $\mathbf{p}$, and $\boldsymbol{\lambda}(\mathbf{p})$ is the vector mean free path, which is the solution to an integral equation

$$\boldsymbol{\lambda}(\mathbf{p}) - \tau(\mathbf{p}) \int\int\int \boldsymbol{\lambda}(\mathbf{p}') W_{\mathbf{p}',\mathbf{p}} \frac{d^3\mathbf{p}'}{h^3} = \mathbf{v}_g(\mathbf{p})\tau(\mathbf{p}), \tag{5}$$

involving the scattering mechanism specified by the probability per unit time $W_{\mathbf{p},\mathbf{p}'} d^3\mathbf{p}'/h^3$ that the particle of momentum $\mathbf{p}$ be scattered to the momentum–space volume $d^3\mathbf{p}'$ about $\mathbf{p}'$, and $h$ is Planck's constant. In Eq. (5)

$$1/\tau(\mathbf{p}) = \int\int\int W_{\mathbf{p},\mathbf{p}'} \frac{d^3\mathbf{p}'}{h^3} \tag{6}$$

is the total scattering rate. Finally, $\overline{(..)}_E$ denotes the microcanonical average over the constant-energy surface $E(\mathbf{p}) = E$ in momentum space, that is

$$\overline{(..)}_E = \frac{\int\int\int (..)\,\delta(E(\mathbf{p})-E)\,d^3\mathbf{p}}{\int\int\int \delta(E(\mathbf{p})-E)\,d^3\mathbf{p}}. \tag{7}$$

Equation (4b), in which the mobility is the ratio of a velocity to a *force*, is a mobility-diffusion linkup of a geometric nature generalizing the Nernst–Townsend relation [4].

Equation (3) was derived under the assumption that the departure $f_1(\mathbf{p},\mathbf{r},t)$ of the momentum–space occupation $f(\mathbf{p},\mathbf{r},t)$ from its microcanonical average

$$f_0(E,\mathbf{r},t) \equiv \overline{(f)}_E, \tag{8}$$

be small. The *drift property* $|f_1| \ll f_0$, or state of near isotropy, entails an average (drift) velocity much lower than the instantaneous (group) velocity, and amounts to assuming that momentum or group velocity is relaxed at a faster rate than energy. In other words, the Boltzmann–Lorentz scattering operator is the sum of a large energy-conserving contribution and of a small energy-relaxing term, and this view is the starting point of a singular-perturbative expansion [5] of the Boltzmann transport equation. The alternative statement that scattering is more frequently elastic than inelastic has been used in developing the so-called lucky-drift model [6,7]. The drift property does not require the absence of deeply inelastic events, but it requires that they should occur infrequently [3,8].

### B. Quantum particles

In deriving Eq. (3) particles were taken to be statistically independent, so that the $\mathbf{p} \to d^3\mathbf{p}'$ traffic in momentum space contributes $W_{\mathbf{p},\mathbf{p}'} f(\mathbf{p}) d^3\mathbf{p}'/h^3$ to the scattering integral. If account is taken of the quantum nature of the particles, the traffic is altered by an exclusion factor $1-f(\mathbf{p}')$ in the case of fermions, and by an enhancement factor $1+f(\mathbf{p}')$ in the case of bosons. Then the scattering operator is no longer of the Lorentz type (i.e., linear in $f$). However, Shockley [9] has shown (in the case of fermions, but the reasoning is equally valid for bosons) that the *overall* traffic within an energy shell is unchanged by the occupancy *in the nearly elastic-scattering approximation*, allowing one to consider that the relaxation of the velocity is unaffected. Thus, the definition of the mean free path is not modified nor is the connection between $f_1(\mathbf{p},\mathbf{r},t)$ and $f_0(E,\mathbf{r},t)$, wherefore our Eq. (3) for the spectral current density retains its validity for quantum particles.

It is interesting to check this conclusion in the well-known case of degenerate electrons near equilibrium. The occupation function is the Fermi function

$$f_0(E) = [1+\exp((E-E_F)/kT)]^{-1} \equiv f_{\mathrm{FD}}((E-E_F)/kT), \tag{9}$$

where the origin of energies is the bottom of the conduction band, $E_F$ is the Fermi energy, or the chemical potential, and $T$ is the temperature. Integration of $\mathbf{J}$ over energy yields $\mathbf{j}$ as the sum of a drift term and a diffusion term, namely

$$j^i = qF_j \mu^{ij} n(\mathbf{r},t) - \frac{\partial}{\partial x^j}[D^{ij} n(\mathbf{r},t)],$$

where

$$\mu^{ij} n = \int_0^{+\infty} \mu^{ij}(E)\, \underline{n}(E,\mathbf{r},t)\, dE, \tag{10a}$$

and similarly for $D^{ij}n$. Integrating Eq. (10a) by parts and using Eq. (4b) $[N(E)D^{ij}(E)|_{E=0} = 0$ and $f_0(+\infty) = 0]$,

$$\mu^{ij} n = \int_0^{+\infty} N(E) D^{ij}(E)(-\partial f_0/\partial E)\, dE. \tag{10b}$$

At a vanishing temperature, $-\partial f_0/\partial E = \delta(E-E_F)$, whence

$$\mu^{ij} n = N(E_F) D^{ij}(E_F). \tag{11}$$

Equation (11) expresses the well-known property that the drift of degenerate electrons only depends on Fermi-surface properties. The drift-current versus particle-density relationship is not linear, since the Fermi level depends on $n$ through

$$n = \int_0^{E_F} N(E)\, dE. \tag{12}$$

Similarly, according to the definition of the diffusion tensor, at zero temperature

$$D^{ij} n = \int_0^{E_F} N(E) D^{ij}(E)\, dE, \tag{13}$$

so that the diffusion current density

$$-\frac{\partial (D^{ij}n)}{\partial x^j} = -N(E_F) D^{ij}(E_F) \frac{\partial E_F}{\partial x^{j'}},$$

$$= -D^{ij}(E_F) \frac{\partial n}{\partial x^{j'}}, \tag{14}$$

shows that the fermions diffuse with the effective tensor $D^{ij}(E_F)$. Here again, the diffusion-current versus particle-density relationship is not linear. Vassiliev [10] remarks that only the current-density versus particle-density relationship makes sense in the degenerate case, and that the conventional mobility and diffusion tensors are concepts of little usefulness, as can be seen in mesoscopic transport physics [11].

The mobility-diffusion relation (4b) holds regardless of space dimensionality, as a consequence of the basic theorem of exterior differentiation. In two dimensions $N(E)$ is independent of $E$ for nearly free electrons, and the zero-temperature conductivity tensor $\sigma$ derived from Eq. (11) is

$$\sigma^{ij} = q^2 N D^{ij}(E_F), \tag{15}$$

a result sometimes called [11] ''the Einstein relation in two dimensional metal physics.''

In summary, the usual properties of degenerate fermions are contained in Eq. (3), which is easy to handle at finite temperatures by using Sommerfeld's expansion. Section II C shows that thermoelectric or thermodiffusive transport properties are obtained as well.

### C. Linear and nonlinear responses

In a solid it may often be assumed that the local occupation function of the electrons is thermal, namely

$$f_0(E,\mathbf{r},t) = f_{\mathrm{FD}}([E - E_F(\mathbf{r},t)]/kT(\mathbf{r},t)), \tag{16}$$

where $E_F(\mathbf{r},t)$ and $T(\mathbf{r},t)$ are, respectively, the local chemical potential and temperature. From $\mathbf{J}$ it is easy to obtain the particle-number current density, Eq. (2), and the energy current densities

$$j_E = \int_0^{+\infty} E\mathbf{J}\,dE, \quad j_{\mathcal{E}} = \int_0^{+\infty} \mathcal{E}\mathbf{J}\,dE, \tag{17}$$

where $\mathcal{E} = E + qV$ includes the potential energy of the force $q\mathbf{F} = -\partial(qV)/\partial\mathbf{r}$. The calculation of $\mathbf{j}$ and $\mathbf{j}_{\mathcal{E}}$ from Eq. (3) yields

$$j^i = L_{00}^{ij}\frac{\partial}{\partial x^j}\left(\frac{-\tilde{\mu}}{kT}\right) + L_{01}^{ij}\frac{\partial}{\partial x^j}\left(\frac{1}{kT}\right), \tag{18a}$$

$$j_{\mathcal{E}}^j = L_{10}^{ij}\frac{\partial}{\partial x^j}\left(\frac{-\tilde{\mu}}{kT}\right) + L_{11}^{ij}\frac{\partial}{\partial x^j}\left(\frac{1}{kT}\right), \tag{18b}$$

where $\tilde{\mu} = E_F + qV$ is the electrochemical potential, and

$$L_{kl}^{ij} = \int_0^{+\infty} \mathcal{E}^{k+l} N(E) D^{ij}(E)\left[-f'_{\mathrm{FD}}\left(\frac{E - E_F(\mathbf{r},t)}{kT(\mathbf{r},t)}\right)\right] dE. \tag{18c}$$

These are the equations describing thermoelectric phenomena usually derived from kinetic theory and simplifying assumptions, or (excepting $L_{kl}^{ij}$) from linear irreversible thermodynamics. The equations of thermodiffusion may be obtained similarly. The advantages of the present derivation are many: (i) it is mathematically straightforward as only simple integrals over energy are involved; (ii) it does not require the relaxation-time approximation or the cubic symmetry [12,13]; (iii) time-varying $T$ and $E_F$ are allowed up to a maximum frequency $1/2\pi\tau_E$, where $\tau_E$ is the energy-relaxation time. The Fokker–Planck formalism in the energy-position manifold can also be used if the local energy distribution significantly departs from thermal equilibrium (as is the case of high-field thermoelectric effects in semiconductors [14]). Hence *it is not restricted to the linear response*: it is a nonperturbative generalization of Onsager's linear response theory. The only basic requirement is that the fermion motion proceed by drift, that is, the momentum–space occupation $f(\mathbf{p},\mathbf{r},t)$ departs little from the energy-shell average $f_0(E,\mathbf{r},t)$.

If the energy distribution is not a local-equilibrium one, it should be determined from the particle–medium energy exchange, and this calculation is tackled in Sec. III. We shall also indicate how to handle nonstationary effects occurring over time scales shorter than $\tau_E$.

### D. Boson transport

Our previous examples dealt with fermions. What can we say about the transport of bosons? We do not know of charged bosons capable of undergoing drift under an electric force (Cooper pairs in superconductors undergo *coherent* transport, better named propagation, for which this framework is inappropriate). However, elementary excitations in superconductors do respond to the gradient of a potential energy, and the approach based on the Boltzmann kinetic equation [15] may conveniently be replaced by a Fokker–Planck treatment.

In the absence of a force, diffusion phenomena are present, to which the Fokker–Planck description in the energy-position manifold is ideally suited, just like in neutronics. Photons in vacuum travel ballistically, so that diffusion is meaningless. However, electromagnetic radiation in a random medium is known to lose its coherence and the notion of a ''random walk of photons'' is pertinent [16,17]. Similar diffusion-related concepts emerge in multiple strong scattering of acoustic waves (phonons) [18]. Because our approach is spectral and local, it has a much broader compass than the extant ones, for instance if the temperature of the medium is inhomogeneous. Finally, consider hot phonons, the statistics of which usually call for the Boltzmann equation: that equation may be replaced by a Fokker–Planck approach, e.g., when electron and phonon distributions are coupled.

As we shall show in Sec. III, the evolution of the particle density is governed by an equation expressing local conservation in the energy-position manifold (and possibly nonlocal in energy if some deeply inelastic scattering is present). Since the number of bosons is not always conserved, the equation has to be generalized, e.g.,

$$\frac{\partial \underline{n}}{\partial t} + \frac{\partial J^\alpha}{\partial x^\alpha} = -\frac{\underline{n}(E,\mathbf{r},t)}{\tau_{abs}(E,\mathbf{r},t)'}$$

where $x^0 = E$, $J^0$ is the component along the $x^0$ axis, and $1/\tau_{abs}$ is the absorption rate of bosons of energy $E$ at location $\mathbf{r}$ at time $t$ (in the case of first-order kinetics). The present framework is general and flexible enough to support a variety of modifications and additions needed to handle special situations.

## III. NONEQUILIBRIUM QUANTUM STATISTICS

### A. Energy exchange with the medium

The occupation of the one-particle quantum states is controlled by the exchange of energy with the surrounding medium. Until Sec. III C the exchange is assumed to take place in the form of small energy jumps, and large energy jumps will be subsumed in a second stage. Owing to the central-limit theorem [19], the evolution of $f_0$ over times longer than the collision time only involves the rates of the mean and the variance of the energy change. The former rate, or drift coefficient, is denoted by $W_m(E)$, and the latter, or twice the diffusion coefficient, by $2D_m(E)$. Let $\delta E_{\mathbf{p},\mathbf{p}'}$ denote the energy change of a particle scattered from the state of momentum $\mathbf{p}$ to the state of momentum $\mathbf{p}'$. We begin with the diffusion coefficient. The drift property allows us to write it as a microcanonical average

$$D_m(E)=\overline{(D_m(\mathbf{p}))_E},$$

where

$$2D_m(\mathbf{p})=\int\int\int(\delta E_{\mathbf{p},\mathbf{p}'})^2 W_{\mathbf{p},\mathbf{p}'}\frac{d^3\mathbf{p}'}{h^3}[1\pm f_0(E')]. \tag{19}$$

In Eq. (19) we have accounted for the enhancement (upper sign)/exclusion (lower sign) factor of the final state (the $\mathbf{r}$, $t$ dependence is not written explicitly). Since

$$f_0(E')\approx f_0(E)+\delta E\left(\frac{\partial f_0}{\partial E}\right),$$

an error of third order in the inelasticity $\delta E$ ensues if we take

$$D_m(E)=[1\pm f_0(E)]\mathcal{D}_m(E), \tag{20}$$

where $\mathcal{D}_m(E)$ denotes the classical diffusion coefficient. Next, the drift coefficient $W_m(E)$ is the microcanonical average of

$$W_m(\mathbf{p})=\int\int\int\delta E_{\mathbf{p},\mathbf{p}'}W_{\mathbf{p},\mathbf{p}'}\frac{d^3\mathbf{p}'}{h^3}[1\pm f_0(E')], \tag{21a}$$

while for classical particles one would write

$$\mathcal{W}_m(\mathbf{p})=\int\int\int\delta E_{\mathbf{p},\mathbf{p}'}W_{\mathbf{p},\mathbf{p}'}\frac{d^3\mathbf{p}'}{h^3}. \tag{21b}$$

Retaining terms up to second order in $\delta E$, we get

$$W_m(E)=[1\pm f_0(E)]\mathcal{W}_m(E)\pm 2\left(\frac{\partial f_0}{\partial E}\right)\mathcal{D}_m(E). \tag{22}$$

Three remarks are in order. First, in keeping with the Fokker–Planck methodology we have written *local* expressions for the drift and diffusion coefficients, at energy $E$. Second, while the classical coefficients are independent of the energy–space occupation, the quantum ones do depend on $f_0$. Third, while the inelasticity is absent in the *position*–space drift and diffusion coefficients dealt with in Sec. II B, it is conveyed in the *energy*–space coefficients, and it is in the latter that the Fermi or Bose nature of the particle plays a role.

The instantaneous energy flow from the medium to the particles is embodied in the spectral energy-current density [2]

$$J_E=W_m(E)\underline{n}-\frac{\partial}{\partial E}[D_m(E)\underline{n}]. \tag{23}$$

The *overall* flow (in eV s$^{-1}$ cm$^{-3}$), obtained by integration of $J_E dE$, only involves the drift term. The derivative, or diffusion term, is involved in the *detailed* exchange (in eV s$^{-1}$ cm$^{-3}$ per eV). The drift-diffusion current density, Eq. (23), describes the exchange over times longer than the typical collision time, in order that the central-limit theorem be applicable. As a result of the quantum-statistical correlation of the particles, $J_E$ is nonlinear in $\underline{n}$ or $f_0$.

In the case of classical particles, the capacity of the medium to thermalize the particles at the temperature $T$ is expressed by a $\mathcal{W}_m$–$\mathcal{D}_m$ relationship

$$N(E)\mathcal{W}_m(E)=\frac{\partial}{\partial E}[N(E)\mathcal{D}_m(E)]-\frac{1}{kT}[N(E)\mathcal{D}_m(E)] \tag{24}$$

meaning that the detailed exchange $\mathcal{J}_E=\mathcal{W}_m(E)\underline{n}-\partial/\partial E[\mathcal{D}_m(E)\underline{n}]$ vanishes for the equilibrium $\underline{n}(E)\propto N(E)\exp(-E/kT)$. Assuming the linkup, Eq. (24), between the classical energy-exchange coefficients, what relation ensues between the quantum coefficients? The question is readily answered using Eqs. (20) and (22), to give

$$\begin{aligned}N(E)W_m(E)={}&\frac{\partial}{\partial E}[N(E)D_m(E)]-\frac{1}{kT}[N(E)D_m(E)]\\&\pm\left(\frac{\partial f_0}{\partial E}\right)\frac{N(E)D_m(E)}{1\pm f_0(E)}.\end{aligned} \tag{25}$$

If the spectral energy flow is written in terms of $f_0$ instead of $\underline{n}$,

$$\begin{aligned}J_E&=-N(E)D_m(E)\left[\frac{f_0}{kT}+\frac{1}{1\pm f_0(E)}\left(\frac{\partial f_0}{\partial E}\right)\right]\\&=-N(E)\mathcal{D}_m(E)\left[\frac{f_0(E)[1\pm f_0(E)]}{kT}+\left(\frac{\partial f_0}{\partial E}\right)\right],\end{aligned} \tag{26}$$

whence it is apparent that $J_E=0$ if and only if $f_0$ is the equilibrium occupancy,

$$f_0(E)=\frac{1}{\exp(E/kT)\mp 1}.$$

To conclude this subsection, we recall that not all interactions have the ability to thermalize the particle, so that Eqs. (25) and (26) are not universally valid. A conduction electron in a solid can reach a thermal energy distribution through interaction with zone-center acoustic phonons [20], but *not* with optical phonons [21] (unless [2] their energy is infinitesimal with respect to $kT$). When energy exchange is mediated by finite quanta, nonequilibrium statistical properties such as transport cannot be described within irreversible thermodynamics [22]. However, the Fokker–Planck framework handles both cases, either separately [22] or jointly [3].

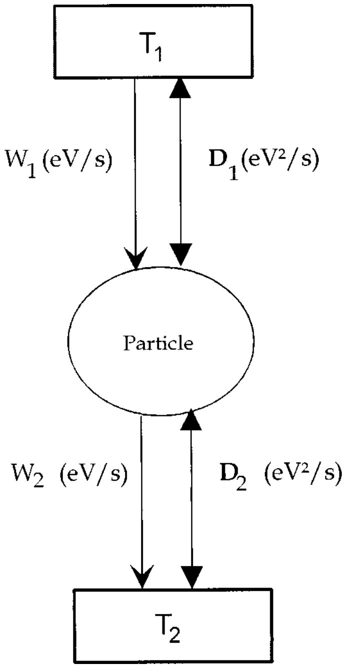

FIG. 1. The particle exchanges energy with two reservoirs, at temperatures $T_1$ and $T_2$. Each exchange is specified by means of the average energy input per unit time (drift coefficient *W*) and the energy half-variance per unit time (diffusion coefficient *D*). Position dependence is not considered in this diagram.

### B. Detailed energy balance and nonequilibrium occupancy

Suppose that the particle is in contact with two systems; then the particle's energy inflow $J_E$ is the sum of two currents having the structure, Eq. (23), $J_E=J_1+J_2$ (Fig. 1). Energy balance at steady state means a vanishing $J_E$. It is a *detailed* energy balance equation, in contrast to the frequently used ‘‘*average* energy balance equation,’’

$$W_1(E)+W_2(E)=0,$$

meaning $J_E|_{\text{drift}}=0$, that is, the fluctuating part of the exchange is waived to yield a single value of $E$ that serves as an estimate of $\langle E\rangle$.

In a nonsteady state, $J_E\neq 0$ and the evolution of $\underline{n}$ is governed by

$$\frac{\partial \underline{n}}{\partial t}+\frac{\partial J_E}{\partial E}=0, \tag{27}$$

and the steady state is reached after the largest energy-relaxation time of the two or more reservoirs.

If the two systems have well-defined temperatures $T_1$ and $T_2$, and if both energy exchanges are of the thermalizing type, the occupation function at steady state is easily obtained from Eq. (26)

$$\frac{f_0(E)}{1\pm f_0(E)}=\exp\left\{-\int_{E_0}^{E}\left[\frac{1}{kT_1}\frac{D_1(E')}{D_1(E')+D_2(E')}\right.\right.$$
$$\left.\left.+\frac{1}{kT_2}\frac{D_2(E')}{D_1(E')+D_2(E')}\right]dE'\right\}, \tag{28}$$

where the integration constant (with respect to $E$, but not necessarily to $\mathbf{r}$, $t$) $E_0$ is the condensation level ($f_0\rightarrow+\infty$) for bosons and the demarcation level $[f_0(E_0)=1/2]$ for fermions (‘‘quasi-Fermi level’’). It is seen that, unless $D_1$ and $D_2$ are proportional functions of $E$, the particle does not have a well-defined temperature. If an energy-dependent effective temperature $T_e(E')$ is defined as a local weighted harmonic mean

$$\frac{1}{T_e(E')}=\frac{1}{T_1}\frac{D_1(E')}{D_1(E')+D_2(E')}+\frac{1}{T_2}\frac{D_2(E')}{D_1(E')+D_2(E')}, \tag{29}$$

where $D_1/D_2=\mathcal{D}_1/\mathcal{D}_2$ is independent of $f_0$, then

$$f_0(E)=\frac{1}{\exp(\int_{E_0}^{E}dE'/kT_e(E'))\mp 1}. \tag{30}$$

Generalization to thermal contact with more than two reservoirs is straightforward.

If system No. 2 is a force field, the energy-exchange coefficients are [2,4]

$$W_F(E)=qF_iqF_j\mu^{ij}(E), \quad D_F(E)=qF_iqF_jD^{ij}(E),$$

and the field temperature should be considered infinite. In Eq. (26) $\mathcal{D}_m(E)\rightarrow\mathcal{D}_F(E)=D_F(E)$ yields the field-particle energy flow

$$J_F=-N(E)D_F(E)\left(\frac{\partial f_0}{\partial E}\right). \tag{31}$$

It is positive where $f_0$ is a decreasing function of $E$. The steady-state occupation function is given by Eq. (30), where

$$\frac{1}{T_e(E')}=\frac{1}{T}\frac{\mathcal{D}_m(E')}{\mathcal{D}_m(E')+D_F(E')}. \tag{32}$$

As a simple example, consider nearly free electrons isotropically exchanging acoustic phonons with the lattice at a rate $1/\tau$. It can be shown that [2]

$$D^{ij}(E)=\tfrac{1}{3}v^2(E)\tau\delta^{ij}, \tag{33a}$$

$$\mathcal{D}_m(E)=\frac{2mv_s^2E}{\tau}, \tag{33b}$$

where $m$ is the effective mass, $v^2(E)=2E/m$, and $v_s$ is the speed of sound. If the collision time $\tau$ is taken to be independent of $E$ (instead of the mean free path $v\tau$), $\gamma\equiv D_F(E)/\mathcal{D}_m(E)=\frac{1}{3}(qF\tau/mv_s)^2$ is independent of energy, and

$$\frac{f_0}{1-f_0}=\exp\left(-\frac{E-E_0}{(\gamma+1)kT}\right), \tag{33c}$$

where $E_0$ is an integration constant. Thus a Fermi–Dirac function with a higher, field-dependent temperature $(\gamma+1)T$ arises as a generalization of the result of classical kinetic theory [10].

### C. Miscellaneous remarks

In the inhomogeneous case where $\underline{n}$ depends on **r**, $\underline{n}$ is the solution to the full Fokker–Planck equation [1]

$$\frac{\partial \underline{n}}{\partial t}+\frac{\partial J_E}{\partial E}+\frac{\partial J^i}{\partial x^i}=0, \tag{34}$$

where $J_E$ is the spectral energy-current density considered so far, and $J^i$ is the spectral current density Eq. (3). In general, the energy and position dependences are coupled. For instance, in a Gaussian packet of classical particles traveling in a uniform field, the energy distribution is ''hotter'' on the leading edge [22] (although negligibly so in the ohmic regime). For smoothly varying densities $n(\mathbf{r},t)$, a perturbative expansion [22,23] involving the derivatives $(\partial^p n/\partial x^i \partial x^j \ldots)_{p\geqslant 0}$ may be used to obtain $f_0(E,\mathbf{r},t)$.

Only nearly elastic particle–medium interactions (i.e., small energy jumps) have been addressed so far, but deeply inelastic interactions can be subsumed [3] by augmenting Eq. (34) with finite-difference or energy-integral terms in which the quantum nature of the statistics should be taken into account. For instance, if the particles are lit by a monochromatic radiation, they will absorb and emit light quanta $\hbar\Omega$ at rates $1/\tau_a(E)$ and $1/\tau_e(E)$ (linked by the Einstein relation involving the light intensity), and the additional terms at the right-hand side of Eq. (34) are

$$\begin{aligned}&\frac{\underline{n}(E)[1\pm f_0(E-\hbar\Omega)]}{\tau_e(E)}+\frac{\underline{n}(E+\hbar\Omega)[1\pm f_0(E)]}{\tau_e(E+\hbar\Omega)},\\ &\frac{\underline{n}(E)[1\pm f_0(E+\hbar\Omega)]}{\tau_a(E)}+\frac{\underline{n}(E-\hbar\Omega)[1\pm f_0(E)]}{\tau_a(E-\hbar\Omega)},\end{aligned} \tag{35}$$

where the **r**, $t$ dependences are allowed although not written explicitly.

## IV. ENTROPY

### A. Homogeneous system

Neither in our discussion of transport in position space (in Sec. II) nor in our determination of nonequilibrium statistics (in Sec. III) has entropy been introduced. Entropy is conjugate to temperature, which *in general* is not defined far from equilibrium, meaning that the occupancy is not of the Fermi–Dirac or Bose–Einstein type. In some problems, however, the notion of temperature can be rescued. For example, thermoelectric phenomena in metals are nonequilibrium processes for which there exists a local equilibrium giving rise to a locally defined $T(\mathbf{r},t)$. Another example is met when interparticle energy exchange overwhelms that with the surrounding: an assembly of degenerate electrons may thus have a well-defined temperature distinct from that of the lattice [24].

In contradistinction, our approach deals with energy exchange arising from occupational changes (''heat'') with no reference to temperature, in the form of a spectral density of energy inflow $J_E$. It is interesting to use the general definition of entropy and examine its behavior in the present framework. Transposing the momentum-space definition involving $f(\mathbf{p})$ to one involving $f_0(E)$ owing to the drift property, the entropy per unit volume is

$$\begin{aligned}\mathcal{S}\{f_0\}=-\int_0^{+\infty}&\{f_0(E)\ln f_0(E)\\ &\mp[1\pm f_0(E)]\ln[1\pm f_0(E)]\}N(E)dE.\end{aligned} \tag{36}$$

Its time derivative is easily calculated to be

$$\frac{\partial \mathcal{S}}{\partial t}=-\int_0^{+\infty}\ln\frac{f_0(E)}{1\pm f_0(E)}\left(\frac{\partial f_0}{\partial t}\right)N(E)dE. \tag{37}$$

Applying the Fokker–Planck equation in the homogeneous case Eq. (27), and integrating by parts, one obtains

$$\frac{\partial \mathcal{S}}{\partial t}=\frac{1}{k}\int_0^{+\infty}\frac{J_E(E)dE}{T_e(E)}, \tag{38}$$

where the nonequilibrium distribution function has been parametrized by means of the effective temperature [Eq. (30)]. The spectral energy inflow divided by the $E$-dependent effective temperature generalizes the expression $\delta\dot{Q}/T$ from the Second law of thermodynamics. If the system is colder than the surrounding, $J_E(E)dE$ generally will be positive and increase the system's entropy unless the effective-temperature function $T_e(E)$ favors energy ranges where the inflow is negative.

### B. Inhomogeneous system

If the system is not homogeneous, the time derivation, Eq. (37), involves the divergence of the four-current

$$\frac{\partial \mathcal{S}}{\partial t}=\int_0^{+\infty}\ln\frac{f_0(E)}{1\pm f_0(E)}\left(\frac{\partial J_E}{\partial E}+\frac{\partial J^i}{\partial x^i}\right)dE. \tag{39}$$

If $x^0=E$ denotes the energy coordinate and Greek indices run from 0 to 3, integration by parts gives

$$\begin{aligned}\frac{\partial \mathcal{S}}{\partial t}=&-\int_0^{+\infty}J^\alpha\frac{\partial}{\partial x^\alpha}\ln\left(\frac{f_0}{1\pm f_0}\right)dE\\ &+\frac{\partial}{\partial x^i}\int_0^{+\infty}J^i\ln\left(\frac{f_0}{1\pm f_0}\right)dE.\end{aligned} \tag{40}$$

The physical meaning of the last term is apparent if we calculate the entropy current density,

$$\mathbf{j}_{\mathcal{S}}=\int\int\int \mathcal{S}\{f(\mathbf{p})\}\mathbf{v}_g(\mathbf{p})\frac{d^3\mathbf{p}}{h^3}, \tag{41}$$

in the same way as **j** [1]. To first order in $f_1/f_0$,

$$\begin{aligned}-\mathcal{S}\{f(\mathbf{p})\}=&f_0(E)\ln f_0(E)\mp[1\pm f_0(E)]\ln[1\pm f_0(E)]\\ &+f_1(\mathbf{p})\ln\left(\frac{f_0(E)}{1\pm f_0(E)}\right),\end{aligned} \tag{42}$$

so that

$$\mathbf{j}_{\mathcal{S}}(\mathbf{r},t)=-\int_0^{+\infty}\ln\left(\frac{f_0}{1\pm f_0}\right)\mathbf{J}(E,\mathbf{r},t)dE, \tag{43}$$

and Eq. (40) reads

$$\frac{\partial \mathcal{S}}{\partial t}+\mathrm{div}\mathbf{j}_{\mathcal{S}}=-\int_0^{+\infty}\frac{J^\alpha}{f_0(E)[1\pm f_0(E)]}\frac{\partial f_0}{\partial x^\alpha}dE. \tag{44}$$

To calculate the integrand, we rewrite Eq. (3) as

$$J^i=-N(E)D^{ij}(E)\left(\frac{\partial f_0}{\partial x^j}+qF_j\frac{\partial f_0}{\partial x^0}\right), \tag{45}$$

and introduce $D^{i0}(E)=D^{0i}(E)=qF_jD^{ij}(E)$ and $D^{00}(E)=qF_iqF_jD^{ij}(E)$ [1]. Given that $J^0=q\mathbf{F}\cdot\mathbf{J}+J_m(E)$, one obtains

$$\frac{\partial \mathcal{S}}{\partial t}+\mathrm{div}\mathbf{j}_{\mathcal{S}}=\int_0^{+\infty}\frac{N(E)dE}{f_0(E)[1\pm f_0(E)]}D^{\alpha\beta}(E)\frac{\partial f_0}{\partial x^\alpha}\frac{\partial f_0}{\partial x^\beta}-\int_0^{+\infty}\frac{J_m(E)dE}{f_0(E)[1\pm f_0(E)]}\frac{\partial f_0}{\partial x^0}. \tag{46}$$

The last term involves the exchange of energy with the medium, of which the rate of change of entropy

$$\frac{\partial \mathcal{S}_m}{\partial t}=-\int_0^{+\infty}\frac{J_m(E)dE}{kT} \tag{47}$$

should also be taken into account, whence

$$\frac{\partial \mathcal{S}}{\partial t}+\mathrm{div}\mathbf{j}_{\mathcal{S}}+\frac{\partial \mathcal{S}_m}{\partial t}\equiv\dot{\mathcal{S}}, \tag{48a}$$

$$\dot{\mathcal{S}}=\int_0^{+\infty}\frac{N(E)dE}{f_0(E)[1\pm f_0(E)]}\left\{D^{\alpha\beta}(E)\frac{\partial f_0}{\partial x^\alpha}\frac{\partial f_0}{\partial x^\beta}+\mathcal{D}_m(E)\left[\frac{\partial f_0}{\partial x^0}+\frac{f_0(1\pm f_0)}{kT}\right]^2\right\}. \tag{48b}$$

The rate of entropy creation $\dot{\mathcal{S}}$ is *positive*, as expected from thermodynamics. In this framework it stems from the positivity of diffusion tensors ($D^{\alpha\beta}$ and scalar $D_m$). The second term in $\dot{\mathcal{S}}$ vanishes if and only if $f_0$ is the equilibrium occupancy at the temperature $T$ of the medium. The first term in $\dot{\mathcal{S}}$ is the drift-diffusion contribution to entropy creation. If the force $q\mathbf{F}$ is switched off, only the spatial components of $D^{\alpha\beta}$ and **grad** $f_0$ contribute, meaning that *diffusion* increases $\mathcal{S}$ until the occupation is uniform in space. *Drift* in the force field involves the energetic components of $D^{\alpha\beta}$ and $\partial f_0/\partial x^0$. If spatial uniformity is reached, and if the field is so weak that $f_0$ nears the equilibrium occupancy, $\partial f_0/\partial E\approx -f_0(1\pm f_0)/kT\approx-\delta(E-E_F)$ for degenerate fermions, and

$$\dot{\mathcal{S}}=N(E_F)qF_iqF_jD^{ij}(E_F)/kT=q\mathbf{F}\cdot\mathbf{j}/kT, \tag{49}$$

according to Sec. II A. In plain language, entropy is created owing to work in the electric force being converted to heat. Finally, the absence of a field contribution $(\partial\mathcal{S}_F/\partial t)$ stems from the entropiless nature of a force field [4].

If the particle exchanges energy with other systems, other contributions to the four-current $J^\alpha$ should be added in Eq. (44), and other terms in $\dot{\mathcal{S}}$ will arise. If energy exchange with the medium is *not* of the thermalizing type, the second term in $\dot{\mathcal{S}}$ is

$$\int_0^{+\infty}f_0(E)[1\pm f_0(E)]N(E)\mathcal{D}_m(E)dE\times\left[\frac{1}{f_0(1\pm f_0)}\frac{\partial f_0}{\partial x^0}+\frac{1}{kT}\right]\times\left[\frac{1}{f_0(1\pm f_0)}\frac{\partial f_0}{\partial x^0}+\frac{\partial\ln N\mathcal{D}_m}{\partial E}-\frac{\mathcal{W}_m}{\mathcal{D}_m}\right],$$

and the positivity is not obvious. In the case of hot electrons emitting hard phonons of energy $\hbar\omega$, the characteristic energy $E_W$ of the distribution [2] is large, and

$$\frac{1}{f_0(1-f_0)}\frac{\partial f_0}{\partial x^0}\approx-\frac{1}{E_W}$$

is negligibly negative compared to $1/kT$ and $-(\mathcal{W}_m/\mathcal{D}_m)\approx1/\hbar\omega$. Consequently $\dot{\mathcal{S}}>0$.

### C. Minimal entropy production

It is usually contended that, not far from equilibrium, the stationary state coincides with the state of minimal entropy production. This can be straightforwardly checked within the present formalism. Take a homogeneous system interacting with a force field and an energy reservoir, so that the energy distribution is independent of position. Stationarity is attained if $J_F+J_m=0$, corresponding to the minimum of

$$D^{00}(E)\left(\frac{\partial f_0}{\partial x^0}\right)^2+\mathcal{D}_m(E)\left[\frac{\partial f_0}{\partial x^0}+\frac{f_0(1\pm f_0)}{kT}\right]^2$$

with respect to variations of the energy gradient $\partial f_0/\partial x^0$. This minimizes the bracketed term in Eq. (48b), but not $\dot{\mathcal{S}}$ itself with respect to all distributions $f_0$. For definiteness, consider again nearly free electrons isotropically exchanging acoustic phonons with the lattice at a rate $1/\tau$ independent of momentum. The diffusion coefficients are given by Eqs. (33a)–(33b), and the stationary distribution given by Eq. (33c) is $f_0\propto\exp(-E/kT_e)$, where $T_e=(\gamma+1)T$, in the nondegenerate limit. Now if we seek for a Gibbs-like distribution $f_0=\exp(-(E-E_0')/kT')$ minimizing $\dot{\mathcal{S}}$ under the condition that the total number of fermions per unit volume $n$ are conserved, namely

$$\int_0^{+\infty}N(E)f_0(E)dE=n, \tag{50}$$

we find $T'=(\gamma+1)^{1/2}T$ instead of $T_e$. Therefore there exist states of lesser entropy production than the steady state. The states are arbitrarily close to equilibrium as $\gamma\to0$ for a vanishing applied force. The example shows that the connection between minimal entropy production and stationarity invoked in near-equilibrium irreversible thermodynamics is not of a general nature.

## V. CONCLUSIONS

This paper has set up a framework for dealing with nonequilibrium one-particle distributions. Specifying nonequilibrium statistics in terms of an *energy* distribution function is possible only if the transport processes involved occur by drift, that is, the phase–space occupation function is almost the same over a given energy shell. Then, given the energy distribution, a general formula for the spectral particle-current density exists regardless of the quantum nature of the drifting particle. It is the sum of a drift term and a diffusion term in the energy-position manifold. If the energy distribution is a local-equilibrium one, the linear response theory is recovered. In the opposite case, the energy distribution can be determined from two functions embodying the mean and variance of the instantaneous energy change of the particle interacting with the surrounding medium. The functions depend on the Fermi or Bose nature of the particle. In the case where the coupling with the medium is able to thermalize the particle, analytical expressions are obtained for the homogeneous, steady-state nonequilibrium occupancy, and a first-order ordinary differential equation has to be solved in the time-dependent case. A spatio-temporally varying distribution is the solution to a (possibly augmented) Fokker–Planck equation in $E$-$\mathbf{r}$ space.

The rate of change of entropy associated with energy exchange with the surrounding is given by a generalization of the second law of thermodynamics. If the exchange is of the thermalizing type, the total entropy production is a positive-definite quadratic form in $\mathbf{grad}\, f_0$ and $\partial f_0/\partial E$. However, the distribution minimizing entropy production is not, in general, the steady-state one.

[1] E. Bringuier, Phys. Rev. B **57**, 2280 (1998).

[2] E. Bringuier, Am. J. Phys. **66**, 995 (1998) [where Eq. (24b) should be corrected into $D_{\mathrm{ph}}(E)=\frac{1}{2}(\hbar\omega)^2(v(E)/\lambda)$, $\lambda$ being the mean free path at the temperature of interest].

[3] E. Bringuier, J. Appl. Phys. **86**, 6847 (1999).

[4] E. Bringuier, Philos. Mag. B **77**, 959 (1998).

[5] P. Degond and C. Schmeiser, Transp. Theory Stat. Phys. **28**, 31 (1999).

[6] B. K. Ridley, J. Phys. C **16**, 3373 (1983).

[7] M. G. Burt, J. Phys. C **18**, L477 (1985).

[8] B. K. Ridley, Semicond. Sci. Technol. **2**, 116 (1987).

[9] W. Shockley, *Electrons and Holes in Semiconductors* (Van Nostrand, New York, 1950), p. 256.

[10] A. Vassiliev, *Introduction à la Physique Statistique* (Mir, Moscow, 1985; original Russian edition, 1980), Chap. 12.

[11] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1995), Chap. 1.

[12] J. Tavernier and D. Calecki, *Introduction aux Phénomènes de Transport Linéaires dans les Semi-Conducteurs* (Masson, Paris, 1970).

[13] W. Jones and N. H. March, *Theoretical Solid-State Physics*, Nonequilibrium and Disorder Vol. 2 (Wiley-Interscience, New York, 1973), Chap. 6.

[14] Esther M. Conwell, *High-Field Transport in Semiconductors* (Academic, New York, 1967).

[15] E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, Oxford, 1981), Chap. 11.

[16] A. Ishimaru, *Wave Propagation and Scattering in Random Media* (Academic, New York, 1978), Vol. 2.

[17] Zhao-Qing Zhang and Ping Sheng, in *Scattering and Localization of Classical Waves in Random Media*, edited by Ping Sheng (World Scientific, Singapore, 1990), pp. 137–177.

[18] J. H. Page, H. P. Schriemer, A. E. Bailey, and D. A. Weitz, Phys. Rev. E **52**, 3106 (1995).

[19] Gregory Ryskin, Phys. Rev. E **56**, 5123 (1997).

[20] A. Majorana, Transp. Theory Stat. Phys. **20**, 261 (1991).

[21] F. Fuchs and F. Poupaud, Transp. Theory Stat. Phys. **28**, 629 (1999).

[22] E. Bringuier, Phys. Rev. B **58**, 4543 (1998).

[23] E. Bringuier, Philos. Mag. B **79**, 1659 (1999).

[24] B. K. Ridley, *Quantum Processes in Semiconductors*, 2nd ed. (Clarendon, Oxford, 1988), Chap. 8.