Order to disorder transformation in an Ohmic resistor: Quantum theory of Joule heating

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Abstract. The Joule–Lenz heating effect in a resistor is a transformation of ordered (electrochemical) into disordered (thermal) energy. The elementary quantitative account rests upon Ohm’s conduction law. The latter continues to be a theoretical challenge in the 21st century, just as the Joule heating effect at the microscopic level. This work first reviews thermodynamical prolegomena to near-equilibrium electrical conduction. The heating effect (under an applied force field) is argued to be a consequence of the thermalisation mechanism (acting under no force) underpinning the Zeroth Law of thermodynamics. The microscopic theory of thermalisation is worked out in a crystalline solid. Static disorder cannot account for thermalisation of the electron gas at the lattice temperature. The necessary dynamical disorder is handled perturbatively within a Wigner-function-like quantum-mechanical framework. Connection is made with the irreversible Boltzmann–Lorentz description of electron transport via a multiple-scale expansion; Fermi’s golden rule is reappraised. Classical disorder fails to account for the thermalisation of electrons at the environmental temperature. Quantum disorder embodied in the quantization of lattice vibrations and the entanglement of electrons and phonons correctly account for the Zeroth Law. The mechanism of internal thermal equilibration of the environment is discussed.

1 Elements of electronic conduction in solids

Joule and Lenz observed that a piece of solid electric conductor traversed by a steady electric current produces heat at a rate quadratic in $I$ [1, 2]. Previously Ohm had discovered that the voltage $U$ needed to pass a current $I$ is proportional to $I$. Hence, the electric power $UI$ released by the battery feeding the conductor accounts for the Joule–Lenz heating. The concept of voltage was devised by Volta [3] who coined the word tension électrique still in use in modern French (elektrische Spannung in German). The concept of voltage was not well understood as both the electrostatics of vacuum and the electrodynamics of material media were then in inchoative stages. In 1980, speaking about Volta’s concept of electromotive force akin to that of voltage, Varney and Fisher remark that ‘the concept of electromotive force as first presented by Volta seems to be all but forgotten. Introduction of the term often occurs without any definition at all and is often confused with electrostatic potential difference. [...] Volta’s use of the term [...] is presented through the introduction of electrostatic and non-electrostatic fields [...]. A failure to note a distinction between these types of electric fields mars some highly important works including J. C. Maxwell’s’ [4, 5]. The point is clarified by Guggenheim: ‘The electrostatic potential difference between two points is admittedly defined in electrostatics, the mathematical theory of an imaginary fluid called electricity, whose equilibrium or motion is determined entirely by the electric field. Electricity of this kind does not exist. Only electrons and ions have physical existence and these differ fundamentally from the hypothetical fluid electricity in that their equilibrium is thermodynamic not electrostatic. Although the above considerations seem almost obvious to anyone who has thought about the matter, there has been in the past considerable confusion’ [6]. Because electrical conduction occurs in a material medium endowed with a well-defined temperature, equilibrium or non-equilibrium has to be contemplated within the frame of thinking of thermodynamics. Equilibrium thermodynamics (thermostatics) is not sufficient when electric and/or heat currents are flowing. We shall be considering near-equilibrium states such that equilibrium is negligibly altered by weak currents, and a continuous medium where near-equilibrium holds locally. The goal of this work is to provide a microscopic insight into the conversion of electric power into heat in a conductor.

Let us first state what is operationally meant by a voltage across two points. It is ‘the cost in energy (work done) required to move a unit of positive electric charge from the more negative point (lower potential) to the more positive point (higher potential). Equivalently, it is the energy released when a unit charge moves “downhill” from the higher potential to the lower’ [7]. Now the charge moves in a material medium whose temperature $T$ is set by a thermostat which performs its function by bringing or removing energy in the form of heat. From
now on we consider an electronic conductor. Since the gas of \( N \) movable electrons is not isolated, the relevant energy is not the internal energy \( U \) of the gas, but —holding volume constant— its Helmholtz energy \( A = U - TS \), where \( S \) is the entropy of the gas. Besides, the external energy \( \mathcal{N} \mathcal{E} \) of the gas in the applied electric potential \( V \) should be included, where \( \mathcal{E} = e \) denotes the signed electron charge. In thermodynamics, \( \mathcal{d}A = -S \mathcal{d}T + g \mathcal{d}N \), where \( g \) is the chemical potential or Gibbs energy per electron [6, 8]. Therefore, \( \mathcal{d}(A + \mathcal{N} \mathcal{E}) = -S \mathcal{d}T + \bar{g} \mathcal{d}N \) where \( \bar{g} = g + eV \) is the electrochemical potential. The isoenthalpic energy change associated with \( N \rightarrow N + dN \) is \( \bar{g} \mathcal{d}N \); i.e. the change is \( \bar{g} \) per electron. We are concerned with unbinding an electron at a point and binding it at another point in the solid. Since the energy cost per carrier of charge \( \mathcal{E} \) is \( \bar{g} \), the voltage across the two points is the difference between the values of \( \bar{g}/e = V + e\bar{V} \). Consequently, even under ‘direct-current’ (steady) conditions, electrical conduction is not a purely electrostatic affair as is often, either avowedly or implicitly, meant in popular accounts of electricity. (It is not a purely electrodynamic affair either when an additional magnetic field is present [9].)

Local departure from equilibrium is embodied in the gradient \( \nabla \bar{g} \). The response is taken to be linear in \( \nabla(-\bar{g}) \); i.e. current is driven by the electrochemical field \( \mathcal{V}(-\bar{g}/e) \) instead of the electric field \( \mathcal{V}(-V) \). The local version of Ohm’s conduction law is written \( \mathcal{J}_k = \gamma \mathcal{V}(-\bar{g}/e) \), where \( \mathcal{J}_k \) denotes the electron current density, \( \mathcal{J}_k \) is the electric current density reckoned in amperc per square-metre in SI unit, and \( \gamma \) is called the electrical conductivity of the medium. A weak current negligibly altering equilibrium presupposes a weak electrochemical gradient. The law holds in an isothermal medium. A temperature gradient brings in an additional contribution linear in \( \mathcal{V}T \) known as a thermoelectric current; this is excluded in this paper.

The paper is structured as follows. In section 2 the role of the Zeroth Law of thermodynamics is brought out. Section 3 shows that the microphysics of ohmic conduction and heating is not yet settled; the essential role of dynamical disorder is demonstrated. Section 4 expounds a simple model of environmental disorder based upon Debye’s modelling of acoustic vibrations. Section 5 takes up the quantum description of electron transport in this dynamically disordered environment. On that basis, section 6 concludes that a classical disorder is unable to account for thermalisation. A description based upon quantum disorder is put forth in section 7. The thermal equilibration of the environment is discussed in section 8. The paper is closed in section 9.

2 Near-equilibrium conduction and the Zeroth Law of thermodynamics

This paper focusses on the nexus between electronic conduction in a solid and thermodynamics. The nexus is obvious when current is flowing, for then heat is produced. The fact that the loss of electrochemical work is balanced by the production of heat is rooted in the First Law of thermodynamics; this is dealt with in appendix A. The paper is closed when no current is flowing, for then electrons have a well-defined temperature which is set by the host lattice acting as a thermostat of the electron gas. In the present issue the thermostat is superimposed in space on the gas of electrons. This has to do with the Zeroth Law of thermodynamics: ‘Two objects are in thermal equilibrium if heat can pass between them but no heat is actually doing so. [...] The Zeroth Law of thermodynamics says that if two objects are in thermal equilibrium with a third, then they are in thermal equilibrium with each other’ [10]. Macrophysically speaking, the electron gas is endowed with a temperature because heat can pass between it and a lattice which is in equilibrium. Now the production of heat, by a current, and the thermalisation of the electron gas, without a current, are two sides of the same coin. The connection between thermalisation and heating arises because

(i) as electrons drift under an applied force, they have their average energy raised above equilibrium;
(ii) the excess energy gained from the force is released to the lattice, in the disorderly form of heat, because the lattice acts to thermalise the electron gas at the ambient temperature.

In view of this connection, the challenge of this paper is to theoretically address the microphysics underlying the Zeroth Law of thermodynamics. Taking the lattice as a set of atomic oscillators in thermal equilibrium, our task will be to investigate how the host lattice sets the temperature of the guest electrons, or nearly so when equilibrium is slightly upset by the passage of a current. Unlike the lattice, in this paper the electron gas is not supposed to have a temperature while this gas is being thermalised by the lattice. The special case of electrons having a temperature of their own not equal to that of the lattice (similar to a nuclear-spin temperature not equal to that of the lattice vibrations) is dealt with in appendix B. The next section very briefly reviews previous accounts of the microphysics of Ohm’s law and the heating effect, and concludes that the present-day state of understanding is not satisfactory.

3 Questionings about the microscopic interpretation

When accounting for electronic conduction in a metal at the microscopic level, textbooks often refer to Drude’s 1900–02 papers [11]. In the proposed scenario, charge carriers, possibly electrons whose existence in vacuum had been disclosed in 1897, collide on static obstacles which at that time were believed to be atoms. As far as carrier velocities are concerned, Drude did not make use of the statistical model of Maxwell and Boltzmann, but of the older model of Krönig considering a single speed [12]. As a result, in Drude’s picture a carrier-obstacle collision is elastic. While Drude recovered Ohm’s local
law together with that of Wiedemann and Franz regarding heat conduction, he did not address the Joule–Lenz heating effect. Correspondingly the mechanism of carrier thermalisation was unspoken. Carriers were merely assumed to have a speed associated with a kinetic energy $3kT/2$ in modern notation, where the Boltzmann constant $k$ is the ideal-gas constant divided by the Avogadro–Loschmidt number. In 1905 Lorentz replaced the single-speed model with the statistical one of Maxwell and Boltzmann [13]; yet the Lorentz theory [...] gives no account of the Joulian heat, since only elastic collisions between the electrons and immovable ions are considered’ [14].

Elastic collisions produce orientational disorder—momenta are scattered in a chance-like manner—but no heat and thus no entropy production. For heat to be interchanged between the carriers and the host lattice, inelastic collisions on moving obstacles are necessary. In other words one should consider an agitated lattice i.e. ‘thermal vibrations’. A parenthetical remark is due to dispel a possible misunderstanding as we are associating electrical resistance with a production of heat. Students are often taught that free electrons in e.g. commonly grown Cu are principally scattered by static lattice imperfections such as structural defects and/or unintentional impurities, which at a low temperature dominate the electrical resistance. Yet those scattering events are elastic and, unlike the lattice vibrations, do not allow for energy interchange with the host medium. This apparent paradox is cleared up by noting that, for a given length directed along the applied force, additional scattering by static imperfections increases the undirected total path length of one electron. Thereby, for given wire length and applied force, the time spent by a free electron to cross the wire from entrance to exit is enhanced, and so too is the number of inelastic scatterings by lattice vibrations. As a collateral effect the electrical resistance is enhanced by elastic scatterings although they do not produce heat. Mechanisms of elastic scattering are not considered in this paper.

The advent of quantum theory in the first decades of the 20th century opened the way to a microscopic explanation of electronic conduction. First, a free electron moves through a crystal lattice in a wave-like manner according to quantum dynamics. The matter-wave is scattered by any deviation from perfect periodicity. Secondly, when the number of free electrons approaches the number of available quantum states, quantum statistics (Pauli exclusion) restricts the possible scatterings [15–18]. Later on, the development of semiconductor physics [19] improved our understanding of conduction, not only in the ohmic, near-equilibrium range but also under a strong applied force causing non-ohmic response and significant departure from the thermal-equilibrium state in which the distribution of electron energies is controlled by the lattice acting as a thermostat of the electron gas [20, 21]. In 1983, however, Leggett expressed his dissatisfaction [22]: ‘even in those cases where there is a widespread belief that [...] solid-state physics can be reduced to atomic theory and electromagnetism, this is a complete illusion. For example, I would challenge every one in this room to prove Ohm’s law rigorously, for a real sample, from the laws of atomic theory and electromagnetism’.

In 2012, experiments performed on well-controlled Si nanowires revealed that Ohm’s local law can retain its validity at the atomic scale [25], even at very low temperatures where, on theoretical grounds, quantum features are expected to profoundly alter ohmic behaviour [26].

We have argued that Ohm’s law and the Joule–Lenz heating effect are closely linked to one another. From 2004 to 2020 this effect has been theoretically investigated by Horsfield, Todorov and co-workers who were motivated by nanoscale conductors. In 2004 they state that ‘modelling Joule heating is a difficult problem’ [27]. In 2020 they conclude that ‘the quantum-mechanical description of Joule heating is a challenging endeavor that has been the focus of continuous research extending over decades [...]’. The emerging approach, denoted as Driven Liouville–von-Neumann + Kinetic Equation, reproduces qualitatively the Joule heating. [...] the predicted trends are consistent with the microscopic Ohm’s law, although the numerical results do not fully agree, in this case, with those calculated via Fermi’s golden rule’ [28]. This concurs with Leggett’s arguing that the existing theory of ohmic conduction is not satisfactory. This paper aims at working out the theory. Section 4 describes a simple model of dynamical disorder whose effect on the electron dynamics will be investigated in section 5.

### 4 The disordered environment

In the previous section it was remarked that a dynamically disordered environment is mandatory to account for the Joule heating and/or the zero-field thermalisation of the electron gas. To this end, a
simplified description of the lattice dynamics is introduced in this section. Let \( \mathbf{a}(\mathbf{r}, \omega) \) denote the displacement, at time \( \omega \), of an atom off its equilibrium position \( \mathbf{r} \). In a regular lattice of \( N_\text{s} \) atoms occupying a volume \( \Omega \), \( \mathbf{a}(\mathbf{r}, \omega) \) is the sum of contributions from \( N_\text{s} \) wave-vectors \( \mathbf{q} \).

\[
\mathbf{a}(\mathbf{r}, \omega) = \text{Re}\left\{ \sum_\mathbf{q} A_\mathbf{q} \exp(i(\mathbf{q} \cdot \mathbf{r} - \omega \mathbf{q})) \right\} \mathbf{u}_\mathbf{q}, \quad (1)
\]

where \( \text{Re}\{z\} \) means the real part of complex number \( z \), \( A_\mathbf{q} \) is a complex amplitude and \( \mathbf{u}_\mathbf{q} = \mathbf{q}/|\mathbf{q}| \) is the longitudinal unit vector. We are considering travelling waves with cyclic (Born–von Kármán) boundary conditions so that \( q_x \), \( q_y \), and \( q_z \) have discrete allowed values separated by a multiple of \( 2\pi/L \) where \( L^3 = \Omega \) is the volume of the solid taken as a cubic box [29]. Only longitudinally polarized acoustic (LA) modes are of interest for the purposes of this paper, because transversely polarized modes play no role in the electron-lattice interaction to be described shortly. In a simplified Debye modelling of the acoustic vibrational modes, the angular frequency \( \omega_\mathbf{q} \) is \( c_s(|\mathbf{q}|) \), the longitudinal sound speed, and \( |\mathbf{q}| \) is restricted to the Debye sphere, \( |\mathbf{q}| \leq q_\text{D} \); see figure 1. This sphere supersedes the fundamental Brillouin zone (BZ) of an arbitrary crystal lattice. In many calculations the discrete sum over the \( N_\text{s} \) allowed wave-vectors in the BZ may be replaced by an integral,

\[
\sum_\mathbf{q} \approx \int d^3\mathbf{q}/(2\pi)^3 \quad (2)
\]

On taking the volume per mode \((2\pi/L)^3\) as the summand on the left-hand side, it is calculated that \( q_\text{D} = (6\pi^2 N_\text{s}/\Omega)^{1/3} \). In Si, \( N_\text{s}/\Omega = 5 \times 10^{26} \text{ m}^{-3} \) gives \( q_\text{D} = 0.74\times10^{13} \text{ rad s}^{-1} \). The cut-off frequency \( \omega_\text{D} \equiv c_s q_\text{D} \) is \( 3.1\times10^{13} \text{ rad s}^{-1} \).

**Fig. 1.** A longitudinal acoustic wave travelling in a box of finite volume \( \Omega \) is specified by a discrete allowed wave-vector \( \mathbf{q} \) in the reciprocal space. The volume per allowed wave-vector, shown in red, is \((2\pi)^3/\Omega\). The \( N_\text{s} \) modes are located in the fundamental Brillouin zone which is replaced by the Debye sphere \( q \leq q_\text{D} \). Its surface and the boundaries of the positive octant \((q_x, q_y, q_z \geq 0) \) are shown in yellow. The scaled wave-vector \( \mathbf{q} \) is defined as \( \mathbf{q} L/2\pi \) where \( L^3 = \Omega \).

An LA mode is specified by its complex amplitude \( A_\mathbf{q} = |A_\mathbf{q}| \exp(iq_x) \), or equivalently its phase \( \phi_\mathbf{q} \) lying between \(-\pi\) and \(+\pi\) together with its (kinetic + elastic) energy \( E_\mathbf{q} = 2\pi^2 N_\text{Mo}_\mathbf{q}/|\mathbf{q}|^2 \), where \( M \) is the mass of one atom. In mechanics, \( E_\mathbf{q} \) and \( \phi_\mathbf{q} \) have determined values. In statistical mechanics, for a canonical ensemble \( E_\mathbf{q} \) and \( \phi_\mathbf{q} \) are random variables specified by their probability distributions, namely

\[
\rho_\phi(E_\mathbf{q}) \, dE_\mathbf{q} = \exp\left(-\frac{E_\mathbf{q}}{kT}\right) \frac{dE_\mathbf{q}}{kT}, \quad (3)
\]

\[
\rho_\phi(\phi_\mathbf{q}) \, d\phi_\mathbf{q} = \frac{d\phi_\mathbf{q}}{2\pi}, \quad (4)
\]

where \( T \) is the environmental temperature. Then, if \( \langle \cdot \rangle \) and \( \Delta \) respectively denote the average and the root-mean-square deviation in a statistical ensemble,

\[
\langle E_\mathbf{q} \rangle = kT \text{ and } \Delta E_\mathbf{q} = kT, \quad (5)
\]

\[
\langle A_\mathbf{q} \rangle = 0 \text{ and } \Delta|A_\mathbf{q}| = \left(\frac{2kT}{N_\text{s}M_\mathbf{q}}\right)^{1/2}, \quad (6)
\]

\[
\langle \phi_\mathbf{q} \rangle = 0. \quad (7)
\]

This is the equipartition regime such that all modes have the same mean energy. As shown in section 7, this regime holds when the energy-level spacing of quantized oscillations is negligible compared to \( kT \).

We now turn to the electron-lattice interaction. The symmetric part of the differential displacement tensor \( \partial\mathbf{u}/\partial\mathbf{x} \) is the strain tensor composed of dilatation (fractional volume change) \( \Sigma \partial a_i/\partial x = \text{div} \mathbf{a} \), and shear. Only the former plays a role in a simple modelling of the electron-lattice interaction: the conduction-band bottom is shifted by \( \Xi \text{div} \mathbf{a} \) and the change in band curvature (‘effective masses’) is neglected [30]. The coefficient \( \Xi \) is called the deformation-potential constant; its value in Si at 300 K is \( \sim 6 \text{ eV} \) for dilatation. As a result of the environmental strain locally shifting the energies, a conduction electron senses the deformation-potential energy

\[
U_\mathbf{q}(\mathbf{r}, \omega) = \Xi \text{Re} \left\{ \sum_\mathbf{q} A_\mathbf{q}(\omega) \exp(iq_\mathbf{r}) \right\}, \quad (8)
\]

where \( A_\mathbf{q}(\omega) = A_\mathbf{q} \exp(-i\omega \mathbf{q}) \). The transverse modes are not involved as they cause no dilatation. This holds for an elastically isotropic crystal; an exhaustive account of the electron-lattice interaction is given by Sham and Ziman [31].

One realisation of the random function \( U_\mathbf{q} \), associated with a given set of complex amplitudes \( A_\mathbf{q} \) for each wave-vector \( \mathbf{q} \), can be visualized in figure 2. In it the function almost looks periodic because it is drawn at moderate values of \( |q_\mathbf{D}| \) and not many terms are included in the sum (8). Owing to the thermal agitation of the lattice, the energiescape \( U_\mathbf{q} \) is a homogeneous (stationary)
random function of position (time) characterized by its mean and its spatiotemporal covariance,
\[ \langle U_d(r, t) \rangle = 0, \]
\[ C_l(s, \tau) = \langle u(r + s, t + \tau) u(r, t) \rangle \]
where \( u = U_d - \langle U_d \rangle \).
(10)

In equipartition the covariance is calculated from (8) to be
\[ C_l(s, \tau) = \frac{kT \Xi^2}{N_0 M c_s^2} \sum_q \cos(qs - \omega_q \tau). \]
(11)
It obeys the wave equation of d’Alembert, namely \( \Delta C_l - c_s^2(\partial^2 C_l / \partial \tau^2) = 0 \), so that \( C_l(s, \tau) \) propagates at speed \( c_s \), just as displacement \( a(r, t) \) in electrodynamics the thermal ‘black-body’ radiation in an empty cavity behaves similarly [32].

From (2) and (11) the spatial covariance \( C_l(s, \tau = 0) \) of the energyscape is calculated to be
\[ C_l(s, \tau = 0) = \frac{kT \Xi^2}{M c_s^2} F(\tilde{s}) \] where \( \tilde{s} = q_D s \)
and \[ F(\tilde{s}) = \frac{3}{2} \frac{\sin \tilde{s} - \tilde{s} \cos \tilde{s}}{\tilde{s}^3}. \]
(12)
The function is graphed in figure 3. It exhibits a nonmonotonous, algebraic decay over a characteristic separation distance,
\[ l_c = \frac{1}{q_D} \int_0^{\infty} F(\tilde{s}) d\tilde{s} = \frac{3\pi}{4q_D^2}. \]
(13)
called the correlation length. In our numerical example \( l_c = 1.65 \times 10^{-10} \) m. This definition of \( l_c \) coincides with the one used when the covariance decays exponentially, as happens in [33, 34]. In figure 2 the space average of \( U_d \) over an area exceeding \( l_c^2 \) is seen to coincide with the ensemble average \( \langle U_d \rangle = 0 \). This evinces the notion of ergodicity: a random field is ergodic if all information about its statistics can be obtained from a single realisation of the field [35, 36]. Thereby an ensemble enabling calculation of the average consists, in three dimensions, of a large number of correlation volumes \( l_c^3 \). The ensemble average \( \langle \rangle \) can be obtained from a space average over one element of the ensemble if \( \Omega \gg l_c^3 \).

![Fig. 2](image-url) - One realisation of the random function \( U_d(r, t) \) is shown in two dimensions \( x \) and \( y \) at a given time \( t \). The realisation is associated with one set of complex amplitudes \( A_q \) for all wave-vectors \( q \) in the Brillouin zone.

From (2) and (11) the time covariance \( C_l(s = 0, \tau) \) of the energyscape is calculated to be
\[ C_l(s = 0, \tau) = \frac{kT \Xi^2}{M c_s^2} G(\bar{\tau}) \] where \( \bar{\tau} = \omega_D \tau \)
and \[ G(\bar{\tau}) = 3 \frac{(\bar{\tau}^2 - 2) \sin \bar{\tau} + 2 \bar{\tau} \cos \bar{\tau}}{\bar{\tau}^3}. \]
(14)
The function is graphed in figure 4. It exhibits a nonmonotonous, algebraic decay over a characteristic time lag \( \tau_c \), called the correlation time. This time cannot be defined in the same way as the correlation length because the integral of \( G(\bar{\tau}) \) vanishes. Using the speed of sound \( c_s \), we take \( \tau_c = l_c/c_s \); numerically, \( \tau_c = 0.75 \times 10^{-13} \) s.

![Fig. 3](image-url) - Spatial covariance \( C_l(s, \tau = 0) \) of random energyscape \( U_d(r, t) \) at a given time \( t \), as a function of the separation distance \( |s| \).

From (2) and (11) the time covariance \( C_l(s = 0, \tau) \) of the energyscape is calculated to be
\[ C_l(s = 0, \tau) = \frac{kT \Xi^2}{M c_s^2} G(\bar{\tau}) \] where \( \bar{\tau} = \omega_D \tau \)
and \[ G(\bar{\tau}) = 3 \frac{(\bar{\tau}^2 - 2) \sin \bar{\tau} + 2 \bar{\tau} \cos \bar{\tau}}{\bar{\tau}^3}. \]
(14)
The function is graphed in figure 4. It exhibits a nonmonotonous, algebraic decay over a characteristic time lag \( \tau_c \), called the correlation time. This time cannot be defined in the same way as the correlation length because the integral of \( G(\bar{\tau}) \) vanishes. Using the speed of sound \( c_s \), we take \( \tau_c = l_c/c_s \); numerically, \( \tau_c = 0.75 \times 10^{-13} \) s.

![Fig. 4](image-url) - Time covariance \( C_l(s = 0, \tau) \) of random energyscape \( U_d(r, t) \) at a given position \( r \), as a function of the time lag \( \tau \).
The random potential energy gives rise to a 
Zitterkraft (stochastic force) \( \mathbf{Z} = -\nabla(U_\text{eff}) \) characterized by a 
vanishing mean, \( \langle \mathbf{Z}(\mathbf{r}, t) \rangle = 0 \), and a covariance matrix 
\[
\langle Z_{ij}(r+s,t+\tau)Z_{ij}(r,t) \rangle = -\left( \frac{\partial^2 U_{\text{eff}}}{\partial s_i \partial s_j} \right)_{s=0,\tau=0}.
\]
where \( i, j = x, y, z \). (15)

For an isotropic function \( C_{ij}(s, \tau) = C_{i}(s, \tau) \), the 
calculated root-mean-square force sensed by the electron from the 
strained environment is 
\[
\sqrt{\langle Z(\mathbf{r}, t)^2 \rangle} = \sqrt{-\frac{\partial^2 C_i}{\partial s^2}} \bigg|_{s=0,\tau=0} = \sqrt{\frac{kT}{5M}} c_s \zeta_d.
\]
We now turn to the quantum dynamics of an electron in 
such a stochastic environment.

5 Stochastic quantum dynamics 
of electron transport

5.1 Statement of the issue
The one-electron self-consistent quantum dynamics is 
ruled by Schrödinger’s equation on the wave function 
\( \psi(\mathbf{r}, t) \),
\[
\frac{i\hbar}{\partial t} \frac{\partial \psi}{\partial t} = \left[ \frac{-i\hbar \nabla^2}{2m_0} + U_0(\mathbf{r}) + U_1(\mathbf{r}) + U_2(\mathbf{r}, t) \right] \psi,
\]
where \( \hbar = h/2\pi \) is the reduced Planck constant, \( m_0 \) is 
the electron mass, \( U_0(\mathbf{r}) \) is the periodic potential energy of 
the atomic lattice, \( U_1(\mathbf{r}) = -\nabla V(\mathbf{r}) \) is the energy of the 
applied electrostatic field, and \( U_2(\mathbf{r}, t) \) is the 
time-dependent random energy gauge embodying the 
dynamical environmental disorder. The potential energy \( U_0 \) 
is self-consistent in Hartree’s sense, that is to say an 
electron feels an effective potential lumping together the 
Coulomb attraction of the nuclei and the average 
repulsion of the other electrons. To solve for the 
dynamics, we have to scale the various forces:

(i) \( \nabla U_0 \approx (\text{Hartree energy})/(\text{Bohr radius}) \approx 8 \times 10^{-8} \text{ J/m} \);

(ii) \( \nabla U_1 \approx 10^{-13} \text{ J/m} \) for a large applied electric field 
causing saturation of the drift-velocity response;

(iii) \( \nabla U_2 \approx 2 \times 10^{-9} \text{ J/m} \) in Si where \( \Xi = -6 \text{ eV} \) at 
\( T = 300 \text{ K} \); see (16).

The strongest term \( U_2 \) has to be handled exactly while 
the weaker terms \( U_1 \) and \( U_0 \) will be accounted for 
perturbatively. The periodic potential energy of 
the lattice is handled exactly by means of Bloch’s theory of 
the energy-band structure providing an approximate 
continuum representation of the medium which takes 
\( U_0(\mathbf{r}) \) into account without knowing it explicitly. The 
unknown energy \( U_0(\mathbf{r}) \) is traded for the experimentally 
accessible dispersion relation of each energy band \( \nu \),
\[
E_{\nu}(\mathbf{p}) = E_{\nu}(\mathbf{p}_{0\nu}) + \frac{\mathbf{p} \cdot \mathbf{p}}{2m_{\nu}} + \ldots
\]
where the pseudomomentum \( \mathbf{p} \) is \( \hbar \) times the pseudo-wave-vector in the fundamental Brillouin zone of 
reciprocal space and \( \mathbf{p}_{0\nu} \) denotes the bottom of band \( \nu \),
while the wave function \( \psi \) is traded for an envelope 
function \( \psi' \) [33, 37]. The latter is defined on \( \Omega \) with 
Born–von Kármán cyclic boundary conditions and it 
varies little over one lattice spacing. In the absence of \( U_1 + U_2 \), the envelope satisfies
\[
\frac{i\hbar}{\partial t} \frac{\partial \psi'}{\partial t} = E_s(-i\hbar \nabla)\psi'.
\]
Under the extra potential energy \( U_1 + U_2 \), the effective 
wave-function \( \psi' \) is governed by
\[
\frac{i\hbar}{\partial t} \frac{\partial \psi'}{\partial t} = [E_s(-i\hbar \nabla) + U_1(\mathbf{r}) + U_2(\mathbf{r}, t)]\psi'.
\]
The spatial Fourier transform, denoted by an over hat, is defined as
\[
\hat{\psi}''(\mathbf{p}, t) = \int \Omega \hat{\psi}''(\mathbf{p}, t) \exp(-i\mathbf{p} \cdot \mathbf{r})
\]
\[
\hat{\psi}''(\mathbf{q}, t) = \int BZ \hat{\psi}''(\mathbf{p}, t) \exp(+i\mathbf{p} \cdot \mathbf{r})
\]
and \( \hat{\psi}'' \) has the same physical dimension as \( \psi' \).

5.2 From the envelope wave function to 
the Wannier–Bloch quasi-distribution
The effective wave-function \( \psi'(\mathbf{r}) \) governed by the 
dynamical equation (20) is now traded for its 
Wannier–Bloch transform \( f_{WB}(\mathbf{r}, \mathbf{p}) \) defined in figure 5.

Fig. 5. Definition of the Wannier–Bloch transform 
\( f_{WB}(\mathbf{r}, \mathbf{p}) \) from the effective wave-function \( \psi'(\mathbf{r}) \) or \( \psi'(\mathbf{q}) \) 
at the same time (the time variable \( t \) is omitted for a 
simpler notation).

Function \( f_{WB} \) is the solid-state crystal implementation 
of the Wigner transform defined in a vacuum where \( U_0 \) is 
absent [33, 38]. The localized Wannier functions of the 
crystal supersede the delta functions of position in 
vacuum; the delocalized Bloch functions supersede the 
plane waves. In trading \( \psi'(\mathbf{r}) \) for \( f_{WB}(\mathbf{r}, \mathbf{p}) \) a complex-valued 
probability amplitude is exchanged for a real-valued 
quasi-probability density which has some, but not 
all, attributes of a probability distribution in the phase 
space \( \Omega \times BZ \). The new function provides the marginal 
distributions in position and pseudomomentum, namely
\[
\int_{BZ} f_{WB}(\mathbf{r}, \mathbf{p}) \frac{d^3 \mathbf{p}}{h^3} = |\psi(\mathbf{r})|^2, \tag{23}
\]
\[
\int_{V} f_{WB}(\mathbf{r}, \mathbf{p}) \, d^3 \mathbf{r} = |\Omega \psi(\mathbf{p})|^2, \tag{24}
\]
whence
\[
\int_{\Omega_{BZ}} f_{WB}(\mathbf{r}, \mathbf{p}) \, d^3 \mathbf{r} \frac{d^3 \mathbf{p}}{h^3} = \frac{1}{h^3}. \tag{25}
\]

Owing to (23) and (24) the resolutions in the marginal distributions are mutually restricted by Heisenberg's inequality. Despite those attributes, \(f_{WB}(\mathbf{r}, \mathbf{p}) \, d^3 \mathbf{r} \frac{d^3 \mathbf{p}}{h^3}\) cannot be thought of as the probability of finding the electron in the phase-space volume \(d^3 \mathbf{r} \, d^3 \mathbf{p} / h^3\). For example, at a position \(\mathbf{r}\) where \(\psi(\mathbf{r})\) vanishes so that no particle can be detected, \(f_{WB}(\mathbf{r}, \mathbf{p})\) usually takes non-vanishing values, either positive or negative, such that the integral over \(\mathbf{p}\) vanishes [39]. Thus, \(f_{WB}(\mathbf{r}, \mathbf{p})\) is not a momentum-resolved density in position space or a position-resolved density in momentum space. Accordingly, given a phase-space subvolume \(\Omega\), the integral
\[
\int_{\Omega} f_{WB}(\mathbf{r}, \mathbf{p}) \, d^3 \mathbf{r} \frac{d^3 \mathbf{p}}{h^3} \tag{26}
\]
may lie outside the range 0–1. The Wannier–Bloch or Wigner function is just a mathematical tool enabling calculation of expectation values of observables. Although this function was introduced by Wigner in 1932 and later advertised by Moyal, it was slow in gaining acceptance: 'In his correspondence with Moyal, Dirac was suspicious of the phase-space formulation of quantum mechanics. He believed that the uncertainty principle made it impossible to talk about functions that were well defined for position and momentum simultaneously' [40].

The dynamical equation governing \(\psi'\) is transformed into a dynamical equation on the Wannier–Bloch transform: \(\partial \psi_{WB}/\partial t\) is, just as \(\partial \psi'/\partial t\), the sum of three contributions associated with the pseudo-kinetic energy \(E_{p}(\mathbf{x} + i\hbar \mathbf{v})\) [41, 42]², the smooth potential energy \(U_{i}(\mathbf{r})\) and the arbitrarily-varying energy \(U_{1}(\mathbf{r}, t)\), namely
\[
\frac{\partial \psi_{WB}}{\partial t} = \left(\frac{\partial E_{p}}{\partial \mathbf{p}} \right) \left(\frac{\partial \psi_{WB}}{\partial \mathbf{r}}\right) + O(\hbar^2) + \frac{i}{\hbar} \sum_{\mathbf{q}} \hat{U}_{2}(\mathbf{q}, t) \left[ f_{WB}(\mathbf{r}, \mathbf{p} + \mathbf{q}/2) - f_{WB}(\mathbf{r}, \mathbf{p} - \mathbf{q}/2) \right] e^{i \mathbf{q} \cdot \mathbf{r}}, \tag{27}
\]
where the spatial Fourier transform of \(U_{2}(\mathbf{r}, t)\) is calculated from (8) and (21) as
\[
\hat{U}_{2}(\mathbf{q}, t) = -\frac{\hbar^2}{24} \left[ \left(\frac{\partial^2 E_{p}}{\partial \mathbf{p}^2}\right) \left(\frac{\partial^2 f_{WB}}{\partial \mathbf{r}^2}\right) + 3 \left(\frac{\partial E_{p}}{\partial \mathbf{p}}\right) \left(\frac{\partial^2 f_{WB}}{\partial \mathbf{r} \partial \mathbf{p}}\right) + \left(\frac{\partial^2 E_{p}}{\partial \mathbf{r}^2}\right) \left(\frac{\partial^2 f_{WB}}{\partial \mathbf{r}^2}\right) - \left(\frac{\partial^2 E_{p}}{\partial \mathbf{r} \partial \mathbf{p}}\right) \left(\frac{\partial^2 f_{WB}}{\partial \mathbf{r} \partial \mathbf{p}}\right) \right] + O(\hbar^2).
\]

In our problem \(\partial E_{p}/\partial \mathbf{r} = 0\) as the energy-band structure does not depend on position.

\[\hat{U}_{2}(\mathbf{q}, t) = \frac{\hbar}{2} \left[ i \mathbf{q} \cdot \left( \frac{\partial A_{q}(t)}{\partial \mathbf{r}} - \frac{\partial A_{-q}(t)}{\partial \mathbf{r}} \right) + \iota (\mathbf{q} \cdot \mathbf{r}) \right]. \tag{28}\]

The first contribution to the right-hand side of (27) is an expansion in increasing orders of the dispersion relation and/or the space derivatives of the Wannier–Bloch function. The lowest-order term involves the group velocity \(v_{g}(\mathbf{p}) = \partial E_{p}/\partial \mathbf{p}\) of a Bloch electron in band \(\nu\).

The second contribution to the right-hand side of (27) mimics the force term in the Liouville equation of classical statistical physics. It amounts to shifting \(\mathbf{p}\) at a time rate \(\mathbf{V}(\mathbf{x}(\mathbf{p}))\) in reflection of Newton's second law. If the integral (26) lies in the range 0–1 at zero time, it keeps so at later times so that \(f_{WB}(\mathbf{r}, \mathbf{p})\) continues to look classical [34]. This is conditional upon a smooth variation of \(U_{1}\). Otherwise the \(U_{1}\) contribution to the dynamical equation is non-local in \(\mathbf{p}\), like the \(U_{2}\) term, and it is able to turn a classical-looking distribution at zero time into a non-classical quasi-distribution such that (26) exits the 0–1 range at \(t > 0\) [43].

### 5.3 From the Wigner dynamical equation to the Boltzmann kinetic equation

A typical \(f_{WB}\) due to the energyscape \(U_{1} + U_{2}\) is shown in one space dimension in figure 6 at given \(t\) and \(\mathbf{p}\).

![Fig. 6. Graph of typical Wannier–Bloch transform \(f_{WB}\) of an electron in the energyscape \(U_{1} + U_{2}\), as a function of position, at given pseudomomentum and time, in one dimension. There are two position variables: the slow one \(x\) is \(\varepsilon\) times the fast one \(x'\); in the figure \(\varepsilon = 0.01\). The effect of \(U_{2}(x)\) on \(f_{WB}\) is manifested both in an irregular behaviour over the small scale \(l_{e}\) and in the slowly-varying base line \(f_{0} = \langle f_{WB}\rangle\) which also depends on \(U_{1}(x)\).](image-url)
Owing to $U_r$, an irregular variation over the small scale $l_c$ superimposes upon a smooth variation over a larger scale. Such irregularity is what information scientists usually call noise: it makes no sense and conveys no useful information. We wish to eliminate the noise and retain the 'signal'. To this end, we generalize a method successfully used to handle a static disorder $U_s(r)$ [33, 34]. The random energy landscape has a small correlation length $l_c = l_c L$, with $\epsilon \ll 1$ and $L$ (unrelated to the box side $\Omega^{1/2}$ of section 4) denoting a macroscopic length scale, and a small correlation time $\tau_c = l_c / \epsilon - \epsilon$. In such issues it is convenient to consider that $f_{\omega}$ is a function of two formally independent position (time) variables:

(i) the microscale variable $r^* = \epsilon^{-1} r$ ($t^* = \epsilon^{-1} t$) present in $U_s(r^*, t^*)$;

(ii) the macroscopic variable $r (t)$.

That is to say, $f_{\omega} = f_{\omega}(r, r^*, t, t^*)$ where variable $p$ is omitted to alleviate the notation. The procedure is an instantiation of the multiple-scale expansion method [44, 45], which here is limited to two scales. The same method underlies the replacement, in section 5.1, of $\psi$ by its envelope $\psi^*$ in which the periodic-atomic-scale variation is waived [33, 37]. On calculating a space or time rate of change we shall be faced with terms of disparate order,

$$\frac{\partial}{\partial r^*} \sim \epsilon^{-1} \left( \frac{\partial}{\partial r} \right) \quad \text{and} \quad \frac{\partial}{\partial t^*} \sim \epsilon^{-1} \left( \frac{\partial}{\partial t} \right).$$

(29)

Next, $f_{\omega}$ is expanded in powers of $\epsilon^{1/2}$, namely

$$f_{\omega} = f_0(r, r^*, t, t^*) + \epsilon^{1/2} f_1(r, r^*, t, t^*) + \epsilon f_2(r, r^*, t, t^*) + O(\epsilon^{3/2}).$$

(30)

The justification relies on a random-walk argument [33, 34, 46]. At any time $t$, over a length $l_c$ energy $U_s$ typically varies by $+u_0$ or $-u_0$ with equal probabilities, where $u_0 = (kT/Mc^2)^{1/2} \Xi$. Over a length $L \gg l_c$ consisting of $L/l_c$ segments $l_c$, the root-mean-square variation of $U_s$ is $u_0(L/l_c)^{1/2}$. A significant variation will arise in $f_0$ if $u_0(L/l_c)^{1/2}$ is on a par with the typical energy range $E_{\text{wp}}$ spanned by $f_{\omega}$. Thereby the typical scale $L$ over which the smoothest-out description is valid is obtained by equating $E_{\text{wp}}$ with $u_0(L/l_c)^{1/2}$. This is tantamount to taking $\epsilon^{1/2} = (kT/Mc^2)^{1/2} \Xi/E_{\text{wp}}$, so that (30) is an expansion in integer powers of the perturbation $U_s$.

From now on, the $U_s$ contribution is dropped as no electric field is applied. From (27) the dynamical equation is

$$\left[ -\frac{\partial}{\partial t} + v_0(p) \left( \frac{\partial}{\partial r} + \frac{\partial}{\partial t} \right) \right] \omega = \left( \frac{\partial f_{\omega}}{\partial r} \right)_u,$$

(31)

where we have introduced the short-hand notation,

$$\left( \frac{\partial f}{\partial t} \right)_u = \frac{1}{\hbar} \sum_q \dot{u}(q) \left[ f(r, r^*, p + \hbar \frac{q}{2}) - f(r, r^*, p - \hbar \frac{q}{2}) \right] e^{iqr^*},$$

(32)

to denote the rate of change of a function $f$ due to the fluctuating potential energy $u$, with $\dot{u}(q)$ given by (28). In (32) the dependencies on $t$ and $t^*$ in $f$ and $u$ have been omitted to alleviate the notation. Expansion (30) is now plugged into equations (31),(32), where $\dot{u}(q) \sim \epsilon^{1/2}$. Collecting terms of like powers in $\epsilon$, we obtain a chain of coupled equations,

$$O(\epsilon^{-1}) \left[ \frac{\partial}{\partial r^*} + v_0(p) \frac{\partial}{\partial r} \right] \omega_0 = 0,$$

(33)

$$O(\epsilon^{-1/2}) \left[ \frac{\partial}{\partial r^*} + v_0(p) \frac{\partial}{\partial r} \right] \omega_1 = \left( \frac{\partial f_0}{\partial t} \right)_u,$$

(34)

$$O(\epsilon^0) \left[ \frac{\partial}{\partial r^*} + v_0(p) \frac{\partial}{\partial r} \right] \omega_0 + \left[ \frac{\partial}{\partial r^*} + v_0(p) \frac{\partial}{\partial r} \right] \omega_1 = \left( \frac{\partial f_0}{\partial t} \right)_u,$$

(35)

We examine each equation of the chain in turn. The $O(\epsilon^{-1})$ equation is satisfied whatever $p$ if $f_0(r, r^*, t, t^*)$ is to be taken as a function of $f_0(r, t)$ of the macroscopic variables $r$ and $t$ only besides $p$. That is to say, small-scale details over $l_c$ and $\tau_c$ are absent in the zero-order function $f_0$; one speaks of the elimination of the fast variables $r^*$ and $t^*$ [45].

The $O(\epsilon^{-1/2})$ equation can be solved by using the Fourier transform $\mathcal{F}(q', \omega')$ of $f_1$ with respect to the variables $r^*$ and $t^*$,

$$f_1(r^*, t^*) = \frac{2}{B_z} e^{-i \omega' t^*} \int_{-\infty}^{\infty} \text{d}\omega e^{-i \omega' \omega} \mathcal{F}(q', \omega'),$$

(36)

$$\mathcal{F}(q', \omega') = \int_{\Omega} \frac{d^3r'}{2\pi} e^{-i q'r'} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} e^{-i \omega' \omega} \mathcal{F}(r', \omega'),$$

(37)

with the other variables treated as parameters. The $O(\epsilon^{-1/2})$ equation becomes

$$\int_{B_z} \frac{2}{(2\pi)^3} e^{-i q'r'} \int_{-\infty}^{\infty} \text{d}\omega e^{-i \omega' \omega} [f_0(r, p + h q/2) - f_0(r, p - h q/2)] e^{i \omega' \omega},$$

(38)

The solution is

$$f_1(r^*, t^*) = \frac{2}{B_z} e^{-i \omega' t^*} \int_{-\infty}^{\infty} \text{d}\omega e^{-i \omega' \omega} \mathcal{F}(q', \omega'),$$

$$\mathcal{F}(q', \omega') = \frac{\hat{u}(q', \omega') f_0(r, p + h q/2) - f_0(r, p - h q/2)}{h} - i \chi + q' \mathcal{F}(q', \omega')$$

(39)

where $\eta$ is a small regularization parameter to be set to zero at the end of the calculation. Thereupon $f_1$ is plugged into the right-hand side of the $O(\epsilon^0)$ equation.

Lastly, we perform ensemble averaging in the $O(\epsilon^0)$ equation. On the one hand, $f_{\omega}$ is identical with $f_0$ as $(\langle \rangle$) amounts to a local space-averaging owing to ergodicity, and $f_0$ does not vary over the small scale. On the other hand, the small-scale behaviour of $f_0$ is governed by the stochastic potential $U_s$ which fluctuates over the scales $\tau_c$ and $l_c$ with a covariance governed by the equation of d'Alembert. An order-of-magnitude connection ensues,

$$\tau_c \left| \frac{\partial f_0}{\partial t} \right| \sim l_c \left| \frac{\partial f_0}{\partial t} \right|.$$
It is seen that from past to future.

If should be dropped just as $W$ stems from averaging over realisations of the disorder in the spatial covariance of environmental noise. With a static disorder involving a rate involves the spatiotemporal covariance of the

The right-hand side of (41) is a scattering term whose

It is seen that

(i) $W_{pp'}$ is real-valued because $C_L(s, \tau)$ is even in $s$ and $\tau$;

(ii) $f_0$ satisfies a Boltzmann kinetic equation of the linear type first used by Lorentz in his theory of electronic conduction in a solid [13].

The right-hand side of (41) is a scattering term whose rate involves the spatiotemporal covariance of the environmental noise. With a static disorder involving a spatial covariance $C_L(s)$, we recover the formula of [34],

If $W_{pp'}$ is thought of in terms of the scattering cross section of an electron, this formula means that the ensemble-average scattering cross section is proportional to the Fourier transform of the spatial covariance. The notion of a cross section, however, is not quite appropriate for the energyscape shown in figure 2, and we shall rather make use of the notion of a scattering rate defined below.

The Wigner dynamical equation (27) exhibits invariance under time reversal $t \rightarrow -t$ insofar as $U_d(r, -t) = U_d(r, t)$. This invariance is broken by the scattering term (42) in the kinetic equation (41). Irreversibility stems from averaging over realisations of the disorder in which the fine-grained $f_0$ is replaced by the coarse-grained $\langle f_0 \rangle$. Owing to ergodicity, space-averaging over a sample of volume exceeding $l_2^3$ coincides with ensemble-averaging. Upon zooming out to larger spatial scales, information present in $f_0$ gets lost in $\langle f_0 \rangle$. The loss of information is irretrievable, which entails an irreversible evolution of $f_0$, i.e. a one-way arrow of time from past to future.

The meaning of the scattering term is brought out by rewriting $C_L(s, \tau)$ given by (11) as a sum of plane-wave terms, namely

$$k = \frac{2\pi}{\Omega x^2} \sum \{ \exp[i(qs - q_0)] + \exp[-i(qs - q_0)] \} .$$

Then, integration over time in (42) provides a selection rule on energy, i.e.

$$\int_{-\infty}^{\infty} \exp[i(\pm \omega q - \omega^2)] d\tau = h \delta(\pm \omega q + E(p') - E(p)) .$$

The energy variation of an electron, $E(p') - E(p)$, is thought of as due to absorption (−) or emission (+) of a vibrational quantum $\hbar \omega q$ of the lattice, called a phonon. Integration over positions in the crystal volume yields

$$\int \exp[\pm \hbar \omega q(p' - p)/\hbar] d\Omega = \delta(\pm \hbar \omega q(p' - p)/\hbar) ,$$

where $\delta$ is the Kronecker symbol and $K$ is a reciprocal lattice vector. If $(p' - p)/\hbar$ lies within the Brillouin zone, then a wave-vector $q$ of the emitted (+) or absorbed (−) phonon such that $p' - p = \pm \hbar q$ is selected; this is called a normal process. Otherwise $K = 0$ is needed to obtain a non-vanishing integral; this is called an umklapp process. Emission and absorption processes are pictorially shown as Feynman diagrams in figure 7.

Three remarks are in order.

(i) Vibrational quanta (phonons) show up although the deformation-potential energy $U_d$ causing the scatterings has been regarded as a classical field.

(ii) $W_{pp'}$ is given by Fermi’s golden rule of first-order perturbation theory [49]. This is consistent with our assumption that the perturbation $u$ be small, that is to say a random kick undergone by an electron in a scattering event changes its energy by (typically) $\pm \epsilon^{1/2} E_{\text{typ}}$ or less, where $E_{\text{typ}}$ is the typical energy range spanned by the electron.

(iii) In the present derivation of the golden rule, no energy indeterminacy $\hbar/\tau(p)$ ever appears, where

$$\frac{1}{\tau(p)} = \int_{BZ} W_{pp'} d^3p' \quad \text{(47)}$$

is the electron-lattice scattering rate, i.e. $\tau(p)$ is the lifetime of the Bloch eigenstate $p$. This is at variance...
with textbook derivations, in which the state of the particle at \( t < t_0 \) is taken to be an eigenstate of the free Hamiltonian, and the interaction is switched on at \( t = t_0 \). In contradistinction, our rate-equation description does not select a specific instant \( t_0 \) inasmuch as the interaction is switched on at \( t = -\infty \). Therefore, the validity of the golden rule only rests on the smallness of \( u \), and no collisional broadening \( h/\tau(p) \), or collision duration, smearing out the delta function of energy arises. This conclusion had previously been reached in other ways [50].

For comparison with the calculation of section 7, and disregarding umklapp processes for the sake of notational simplicity, we write the scattering term of the Boltzmann kinetic equation in a different guise, namely

\[
\frac{2\pi kT^2}{\hbar^2} \int_{BZ} \Omega d\mathbf{q} \times \left\{ \left[ f_0(r, p + \mathbf{q}) - f_0(r, p) \right] \delta(-\hbar\omega_q + E(p + \mathbf{q}) - E(p)) + \left[ f_0(r, p - \mathbf{q}) - f_0(r, p) \right] \delta(\hbar\omega_q + E(p - \mathbf{q}) - E(p)) \right\}.
\]

(48)

While in (41) the scattering operator was written on the pattern ‘usual in master equations, in integrations of time’ — which is why the semi-classical treatment, in which the state of the pseudomomentum \( \mathbf{q} \), the evolution ends \( \mathbf{p}' \) — is replaced by the operator \( a_q(a_q^\dagger) \), and the Hamiltonian is [49]

\[
H_q = \frac{\hbar^2}{2} \left( a_q^\dagger a_q + \frac{1}{2} \right) \hbar\omega_q = \left( a_q^\dagger a_q + \frac{1}{2} \right) \hbar\omega_q.
\]

(52)

The latter equality stems from the fact that \( [a_q, a_q^\dagger] = 1 \). The eigenvalues of \( H_q \) are \( (\hbar\omega_q + \frac{1}{2} \hbar\omega) \), where the discrete index \( n_q \), called the occupation number of mode \( q \), has an enumerable infinity of possible values \( 0, 1, 2, \ldots \). The eigenvectors of \( H_q \) are \( \gamma_{n_q} = (X_q)^{-1} \exp[-i(n_q + \frac{1}{2})\hbar\omega_q] \), where \( X_q \) is the coordinate of the LA mode \( q \). We have

\[
a_q^\dagger \gamma_{n_q} = \sqrt{n_q} \gamma_{n_q-1}, \quad a_q \gamma_{n_q} = \sqrt{n_q + 1} \gamma_{n_q+1},
\]

(52)

which is why \( a_q\gamma_{n_q} \) is called the annihilation (creation) operator of one vibrational quantum, or phonon, of wave-vector \( q \) [49].
An arbitrary state-vector of mode \( q \) is, in the energy eigenbasis,

\[ \chi_q = \sum_{n_\phi \geq 0} \alpha_{n_\phi, q} \chi_{n_\phi, q} \]  

where \( \sum_{n_\phi \geq 0} |\alpha_{n_\phi, q}|^2 = 1 \). (53)

The matrix of the projector \( |\chi_q\rangle \langle \chi_q| \) in the energy eigenbasis has populations \( |\alpha_{n_\phi, q}|^2 \) as diagonal elements, and coherences \( \alpha_{n_\phi, q=n_q, \phi} / m_q \) as off-diagonal elements. The quantum and classical mind-sets are contrasted in Table 1. The table also compares the mechanical and statistical-mechanical definitions of a state.

**Table 1.** The state of an LA mode, \( \chi_q(r, t) = \text{Re} \{ A_q \exp[i(q \cdot r - \omega_q t)] \} \), where \( A_q = |A_q| \exp(i\varphi_q) \) and \( |A_q|^2 \propto E_q \), can be defined in several ways depending on the context.

<table>
<thead>
<tr>
<th>Mechanics</th>
<th>Statistical mechanics (canonical ensemble)</th>
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<tbody>
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<td>classical</td>
<td>(</td>
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</table>
| quantum | \( \chi_q = \sum_{n_\phi \geq 0} \alpha_{n_\phi, q} \chi_{n_\phi, q} \) eigenstate \( \chi_{n_\phi, q} \) of \( H_q \) eigenvalue \( (n_\phi + \frac{1}{2})\hbar \omega_q \) \! 
| \( \Sigma_{n_\phi \geq 0} |\alpha_{n_\phi, q}|^2 = 1 \) | \( \langle H_q \rangle = \frac{(n_\phi + \frac{1}{2})\hbar \omega_q}{2} \) mean energy \( \langle h\omega_q / kT \rangle \) diagonal matrix in energy eigenbasis |

The Hilbert space of the lattice vibrational states is the Kronecker (tensor) product of \( N_q \) Hilbert spaces of simple harmonic oscillators indexed by \( q \) running in the Brillouin zone. To a large extent, quantum elasto-dynamics, which deals with a real-valued massless Klein–Gordon field \cite{49}, can be paralleled with quantum electrodynamics. The energy of the ground state \( (n_\phi = 0 \text{ whatever } q, \text{ called the phonon vacuum}), \)

\[ \sum_{q} \frac{1}{2} \hbar \omega_q \int \frac{1}{4\pi} \hbar \omega_q (\Omega d^3q) = \frac{3}{4} N_q \hbar \omega_q c, \]  

is finite. This zero-point energy depends on temperature via \( c \), and the thermal expansion of the lattice affecting \( \eta_D \).

### 7.2 Quantum statistical elasto-dynamics

In thermal equilibrium, the oscillator indexed by \( q \) does not have a determined state vector \( \chi_q \). Instead, the state of the oscillator is specified by a set of realisations \( \chi_q^{(i)} \) of weights \( w_i \geq 0 \) such that \( \sum_i w_i = 1 \). The statistical operator \( \rho_q \) which is the repository of the available information about the oscillator, is the mixture \( \sum_i w_i |\chi_q^{(i)} \rangle \langle \chi_q^{(i)}| \). For a canonical ensemble,

\[ \rho_q = \frac{1}{Z_q} \exp(-\frac{H_q}{kT}), \]  

where \( T \) is the temperature of the heat bath and \( Z_q = \text{tr}[\exp(-H_q/kT)] \) is called the partition function. In the energy eigenbasis, the matrix elements are

\[ \rho_{q,m_q} = \left[ 1 - \exp(-\frac{\hbar \omega_q}{kT}) \right] \exp(-\frac{\hbar \omega_q}{kT}) \delta_{m_q} \]  

where \( n_q, m_q \geq 0 \). (56)

The diagonality of the matrix reflects the quantum incoherence of the thermalised oscillator in this basis. It is the quantum counterpart of the classical condition that \( \varphi_q \) be distributed evenly between \( -\pi \) and \( +\pi \), as shown in Table 1. The diagonal elements are the quantum counterpart of the continuous distribution of \( E_q \) relevant when the energy-level spacings \( \hbar \omega_q \) are much smaller than the thermal energy \( kT \).

From the statistical operator, the mean energy and the indetermination in energy, defined as the root-mean-square deviation, are calculated as

\[ \langle H_q \rangle = \langle n_\phi + \frac{1}{2} \rangle \hbar \omega_q \]  

\[ \Delta H_q = \sqrt{\langle (n_\phi + 1) \rangle \hbar \omega_q} \]  

where

\[ \langle n_\phi \rangle = \left[ \exp(\hbar \omega_q / kT) - 1 \right]^{-1} \]  

is the thermal occupancy of mode \( q \). The mean energy and the indetermination in energy are shown in figure 8. The equipartition regime (5) is recovered as \( \langle n_\phi \rangle \gg 1 \).

![Fig. 8. Energy of a harmonic oscillator in quantum mechanics (in \( \hbar \omega_q \) unit) as a function of the number \( n_\phi \) of quanta. In quantum mechanics \( n_\phi = 0, 1, 2 \ldots \) is a discrete variable defined in an energy eigenstate. In quantum statistical mechanics \( \langle n_\phi \rangle \) is a continuous variable (Bose occupancy at temperature \( T \)). Shown are the mean value \( \langle H_q \rangle \) together with \( \langle H_q \rangle \pm \Delta H_q \) where \( \Delta H_q \) is the standard deviation about the mean in the canonical ensemble.](https://via.placeholder.com/150)

### 7.3 The joint electron-phonon dynamics

An electron interacting with the quantized environment cannot be assigned a wave function \( \psi \) in its own right. The description of the composite \{electron + environment\} system must now be through a state vector.
Ψ involving both electron and environment (phonon) variables. This has been called \textit{Verschränkung}/entanglement (Schrödinger) or non-separability (d’Espaghan) \cite{39, 52}. We begin with non-interacting electron and phonons. The dynamics of the joint state-vector \(\Psi\) is governed by
\[i\hbar \frac{\partial \Psi}{\partial t} = \left[\hat{H} - i\hbar \nabla\right] \Psi,\] (60)
where \(\hat{H} - i\hbar \nabla\) is the effective electron Hamiltonian whose eigenstates are envelope functions where the cell-periodic variation of the wave function has been dismissed (section 5.1) and \(\Sigma \hat{H}_q\) is the Hamiltonian of the phonons. The state vector \(\Psi\) is a function \(\Psi(\mathbf{r}, \{X_q\}^N_t, t)\) of the electron position \(\mathbf{r}\) and the coordinates \(X_q\) of the vibrational modes. The state vectors make up a Hilbert space which is the tensor product of \(1 + N_c\) Hilbert spaces:

(i) the first space is spanned by the basis \(\{b^\dagger_n\}\)

(ii) every other space as indexed by \(q\) is spanned by a basis set \(\{\gamma_{q, n} \}\)

On the right-hand side of (60) we now introduce the deformation-potential interaction coupling the dynamics of the electron and the phonons,
\[H_{el-ph} = \sum_q i q C_q \left( a_q e^{i q \cdot r} - a^\dagger_q e^{-i q \cdot r} \right),\] (61)
where \(C_q = \left( \frac{\hbar}{2 N_c M \omega_q} \right)^{1/2} \). (62)

The operator \(H_{el-ph}\) supersedes the classical electron-lattice interaction energy given by (8) and rewritten as
\[U_2 = \sum_q i q C_q \left[ \hat{A}_q(t) e^{i q \cdot r} - \hat{A}_q^\dagger(t) e^{-i q \cdot r} \right].\] (63)

From now on, the Schrödinger equation accounts for the dynamics of the phonons \textit{together with} that of the electron. This is in contrast to the treatment of section 5 where \(U_2(\mathbf{r}, t)\) or equivalently the set \(\{\hat{A}_q\}\) are pregiven quantities of the host lattice unaffected by the dynamics of a guest electron.

Following Quertioz and Dollfus \cite{53} we take advantage of the fact that the phonon and electron-phonon Hamiltonians are sums over modes to investigate the joint evolution of the electron and \textit{one} mode \(q\). The joint-state vector \(\Psi\) evolves according to
\[i\hbar \frac{\partial \Psi}{\partial t} = \left[\hat{H} - i\hbar \nabla\right] \Psi,\] (60)
In the basis \(\{b^\dagger_n\}^{N_c}\) the state vector may be written as
\[\Psi(\mathbf{r}, X; t) = \sum_n \sum_{n=0} \Psi_n(t) b_n(\mathbf{r}) \gamma_{n, N_c}(X),\] (65)
where \(X\) is the coordinate of the given mode \(n\). On letting \(\sum_n \Psi_n(t) b_n(\mathbf{r}) = \Psi_{el-ph}(\mathbf{r}, t)\), we have
\[\Psi(\mathbf{r}, X; t) = \sum_n \Psi_{n, N_c}(\mathbf{r}, t) \gamma_{n, N_c}(X).\] (66)
The evolution equation (60) yields
\[i\hbar \frac{\partial \Psi}{\partial t} = \left[\hat{H} - i\hbar \nabla\right] \Psi,\] (60)
\[i\hbar \frac{\partial \Psi}{\partial t} = \left[\hat{H} - i\hbar \nabla\right] \Psi + i q C_q \left( e^{i q \cdot r} \cdot \nabla_n \Psi_{n+1} - e^{-i q \cdot r} \cdot \nabla_n \Psi_n \right).\] (67)

We define a generalized Wigner transform —actually, a matrix— of the state-vector \(\Psi\) with respect to the electron variables as
\[\tilde{f}_W(\mathbf{r}, \mathbf{p})|_{n, m} = \int_{-\infty}^{\infty} \Psi_n(\mathbf{r} + \frac{s}{2}) \Psi^*_m(\mathbf{r} - \frac{s}{2}) \exp\left(-\frac{i \mathbf{p} \cdot \mathbf{s}}{\hbar}\right) ds,\] (68)
where the time dependence is omitted to alleviate the notation. The matrix is Hermitian in that \(\tilde{f}_W(\mathbf{r}, \mathbf{p})|_{n, m} = \tilde{f}_W(\mathbf{r}, \mathbf{p})|_{m, n}\). Just as \(\partial \Psi/\partial t\) is a sum of three terms, \(f_W\) evolves according to
\[\frac{\partial f_W}{\partial t} = \left( \frac{\partial f_W}{\partial t} \right)_{el-ph} + \left( \frac{\partial f_W}{\partial t} \right)_{el-ph} + \left( \frac{\partial f_W}{\partial t} \right)_{el-ph} + \left( \frac{\partial f_W}{\partial t} \right)_{el-ph},\] (69)
where
\[\left( \frac{\partial f_W}{\partial t} \right)_{el-ph} = -\nu_{p q}(\mathbf{p}) \tilde{f}_W,\] (70)
\[\left( \frac{\partial f_W}{\partial t} \right)_{el-ph} = -\nu_q(\mathbf{p}) \tilde{f}_W|_{n, m},\] (71)
\[\left( \frac{\partial f_W}{\partial t} \right)_{el-ph} = \frac{q C_q}{\hbar} \left[ \sqrt{n + 1} e^{i q \cdot r} f_{n+1, m}(\mathbf{p}, \mathbf{r}, \mathbf{p} + \frac{\mathbf{q}}{2})_{n+1, m} + \sqrt{n} e^{-i q \cdot r} f_{n, m+1, m}(\mathbf{p}, \mathbf{r}, \mathbf{p} - \frac{\mathbf{q}}{2})_{n-1, m} - \sqrt{n} e^{i q \cdot r} f_{n, m+1, m}(\mathbf{p}, \mathbf{r}, \mathbf{p} + \frac{\mathbf{q}}{2})_{n-1, m} - \sqrt{n+1} e^{-i q \cdot r} f_{n+1, m}(\mathbf{p}, \mathbf{r}, \mathbf{p} - \frac{\mathbf{q}}{2})_{n+1, m} \right].\] (72)

\textbf{7.4 From the Wigner dynamical equation to the Boltzmann kinetic equation}

We introduce a new Hermitian matrix \(F_{el-ph}\) by letting
\[\tilde{f}_W(\mathbf{r}, \mathbf{p})|_{n, m} = \exp[-i \omega_q(\mathbf{p}) \cdot (m-n)] \tilde{f}_W(\mathbf{r}, \mathbf{p})|_{n, m},\] (73)
Its dynamics is governed by
\[\frac{\partial f_W}{\partial t} + \nabla \cdot (\mathbf{v}_W(\mathbf{p}) \tilde{f}_W) = \frac{\partial F_{el-ph}}{\partial t},\] (74)
This is akin to the dynamics of the scalar Wigner function of section 5. To solve for equation (74) we shall use the same method, namely a multiple-scale expansion in powers of \(\varepsilon \sim \varepsilon^{1/2}\) involving fast (\(t', t\)) and slow (\(t = t', t = t'\)) variables. In the present issue, the expansion
\[F_{el-ph} = F_{el-ph}(\mathbf{r}, t', t) + \varepsilon^{1/2} F_{el-ph}(\mathbf{r}, t', t') + \varepsilon F_{el-ph}(\mathbf{r}, t', t') + O(\varepsilon^2)\] (75)
is to be understood matrixwise. Plugging (75) into the dynamical equation (74) and collecting terms of like powers of \(\varepsilon\) throw up a chain of equations,
\[O(\varepsilon^{-1})\] (76)
\[O(\varepsilon^{1/2})\] (77)
\[O(\varepsilon^0)\] (78)
where we use a short-hand notation reminiscent of (32),
\[\frac{\partial F}{\partial t} |_{el-ph, \mathbf{p}, \mathbf{r}, N_c} = \frac{q C_q}{\hbar} \left[ \sqrt{n+1} e^{i q \cdot r'} F(\mathbf{r}, t', \mathbf{p} - \frac{\mathbf{q}}{2})_{n+1, m} + \sqrt{n} e^{-i q \cdot r'} F(\mathbf{r}, t', \mathbf{p} - \frac{\mathbf{q}}{2})_{n-1, m} \right].\] (72)
\[
-\sqrt{n} e^{-iq\cdot r} F(r, r', p + \hbar \frac{q}{2})_{n,m-1} \\
-\sqrt{m} e^{-iq\cdot r'} F(r, r', p + \hbar \frac{q}{2})_{n,m-1}.
\]

To solve for these equations, we follow the train of logic used to solve for (31)–(32) in section 5.3. First, the O(e\(^{-1}\)) equation is satisfied whenever \( p \) if \( F_0(r, r', t, t')_{n,m} \) is taken as a matrix \( F_0(t, i)_{n,m} \) dependent on the macro-scale variables \( t \) and \( t' \) only besides \( p \); that is to say, microscale details over \( t \) and \( t' \) are absent in respect to matrix \( F_0 \).

Next, the \( O(e^{-\frac{1}{2}}) \) equation is solved by means of the Fourier transform of matrix \( F_0 \) with respect to the variables \( r' \) and \( t' \), with variables \( r, t \) and \( p \) treated as parameters. Just like in section 5.3, in order to invert the \( F_0 \) equation, \( \omega' \) is replaced by \( \omega + i\eta \; \text{where} \; \eta \; \text{is a small regularization parameter to be set to zero at the end of the calculation.}

We obtain
\[
F_1(r', t') = e^{-iq\cdot r'} \int_{-\infty}^{\infty} \frac{2\pi}{\omega' + i\eta - \hbar \frac{q}{2}} e^{iq\cdot \hat{\varphi}(p)} \left( \frac{\delta F_1}{\partial \omega'} \right)_{\Delta t, \Delta \Phi}.
\]

This equation relates the matrix element \( F_1(r, r', t, t')_{n,m} \) at pseudomomentum \( p \) to matrix elements \( F_0(r, i)_{n,m,1} \) and \( F_0(r, t)_{n,m,1} \) at pseudomomenta \( p \pm i\hbar q/2 \). Thereupon \( F_1 \) as given by (80) is plugged into the right-hand side of the \( O(e^0) \) equation. The matrix element \( \frac{\delta F_1}{\partial \omega'} \) is then further integrated into matrix elements \( F_0(r, i)_{n,m,1} \), \( F_0(r, t)_{n,m,1} \), \( F_0(t, t')_{n,m,2} \), and \( F_0(t, i)_{n,m,2} \) at pseudomomenta \( p, p \pm i\hbar q/2 \) and \( p \pm i\hbar q \). Off-diagonal elements \( F_0(r, i)_{n,m,2} \) and \( F_0(t, i)_{n,m,2} \) involving a two-phonon interaction will be dropped, besides,
\[
-\frac{1}{\omega' - q\varphi(p)} + i\eta \rightarrow 0
\]

where \( \varphi \) denotes the Cauchy principal value. Upon integrating the delta-functions combine and the principal values drop out. Heretofore we have been considering one given mode \( q \), but summation over all modes is to be performed in (80).

Lastly, ensemble averaging is performed in the \( O(e^0) \) equation. Dropping \( \langle \delta \partial / \partial t' \rangle + \hat{\varphi}(p) \langle \delta \partial / \partial r' \rangle \rangle \rangle \) is justified on the same grounds as in obtaining (41), whence
\[
\left[ \frac{\delta}{\partial t' + \hat{\varphi}(p)} \right]_{\Delta t, \Delta \Phi} F_0 = \left( \frac{\delta F_1}{\partial \omega'} \right)_{\Delta t, \Delta \Phi}.
\]

When obtaining (41), ensemble averaging was performed over the realisations of the dynamical state of the lattice classically defined through the set of complex amplitudes \( \{ A_q \} \). Owing to quantum entanglement we do not have a separable dynamical state of the lattice. From the state operator \( \hat{\rho} = \| \Psi \rangle \langle \Psi \| \) of the composite system, we can derive a reduced electron operator as the partial trace \( \rho_{el} \) of the full operator \( \hat{\rho} \), and a reduced phonon operator as the partial trace \( \rho_{ph} \) of \( \hat{\rho} \). If the dynamics of the phonons and the electron were not entangled, \( \rho \) would just be the tensor product of the two reduced operators. Because entanglement is due to \( \Xi \) and we are considering \( \Xi \rightarrow 0 \), we expect
\[
\rho = \rho_{el} \otimes \rho_{ph} + O(\Xi).
\]

The reduced operator \( \rho_{ph} \) for the phonon system is henceforth taken to be the time-independent canonical-equilibrium \( \rho_{ph} \) of section 7.2 once canonical ensemble averaging is performed. We therefore expect, for one mode \( q \),
\[
\langle \rho \rangle = \rho_{el} \otimes \rho_{ph} + O(\Xi),
\]

where \( \rho_{el} \) is the electron operator to be determined. Actually the statistical operator of the harmonic lattice is the tensor product of the operators of all modes. In terms of the Wigner transform with respect to the electron variables, (84) entails
\[
\langle f_0(q, p) \rangle_{\rho_{ph}} = \langle f_0(q, p) \rangle_{\rho_{el} \otimes \rho_{ph}} + O(\Xi),
\]

where \( f_0(q, p) \) is the Wigner function derived from \( \rho_{el} \). Because the matrix of \( f_0 \) in the energy basis is diagonal, we have \( \langle f_0(q, p) \rangle_{\rho_{ph}} = \langle f_0(q, p) \rangle_{\rho_{el} \otimes \rho_{ph}} \) where \( \rho_{el} \) is the canonical population \( \rho_{el,n} \). Consequently, to order \( \omega' \), the electron Wigner function is
\[
f_0(q, p) = \sum_{n \geq 0} \langle f_0(q, p) \rangle_{\rho_{ph}} = \sum_{n \geq 0} \langle f_0(q, p) \rangle_{\rho_{el} \otimes \rho_{ph}}.
\]

To the same order, we can replace \( \langle F_0(r, p) \rangle_{\rho_{ph}} \) with its zero-order approximant \( \langle F_0(r, p) \rangle_{\rho_{el}} \) which is governed by (82). We get
\[
\left[ \frac{\partial}{\partial t'} + \hat{\varphi}(p) \right] \rho_{el} = \frac{2\pi}{\hbar} (q C_q)^2 \times
\]
\[
\sum_{n \geq 0} \left\{ (n+1) f_{el}(r, p - \hbar q) \right\}_{p-1} \times
\]
\[
\begin{align*}
- & f_{el}(r, p) \delta (E(p - \hbar q) - E(p) - \hbar \omega_q) \\
+ & n f_{el}(r, p + \hbar q) \delta (E(p + \hbar q) - E(p) - \hbar \omega_q) \\
- & f_{el}(r, p) \delta (E(p + \hbar q) - E(p) - \hbar \omega_q),
\end{align*}
\]

where for simplicity unclapped processes \( K \neq 0 \) have not been considered. From (87), on using identities \( \sum_{n \geq 0} n \rho_{el,n} \rho_{el} = \sum_{n \geq 0} n \rho_{el,n} = (n+1) \rho_{el} \) and \( \sum_{n \geq 0} (n+1) \rho_{el} = \sum_{n \geq 0} n \rho_{el} = (n+1) \rho_{el} \), and on accounting for all phonon modes, a closed equation on the electron Wigner function ensues,
\[
\left[ \frac{\partial}{\partial t'} + \hat{\varphi}(p) \right] \rho_{el} = \sum_{n \geq 0} \frac{2\pi}{\hbar} q C_q(n+1)^2 \times
\]
\[
\left\{ \left( n \rho_{el} - (n+1) \rho_{el} \right) \times
\begin{align*}
\delta (E(p - \hbar q) - E(p) - \hbar \omega_q) \\
+ & (n+1) \rho_{el} \delta (E(p + \hbar q) - E(p) - \hbar \omega_q) \\
- & \rho_{el} \delta (E(p + \hbar q) - E(p) - \hbar \omega_q),
\end{align*}
\right.
\]

Thereby \( f_{el}(r, p, t) \) is governed by a kinetic equation of the Boltzmann–Lorentz type whose scattering term is similar to, but different from, (48). Integrating out positions yields the Pauli master equation governing the evolution of the distribution of pseudomomenta, \( f_{el}(r, p, t) \). The environmental scattering term is found to vanish for a Maxwell–Boltzmann function at the lattice temperature
\[
f_0(p) = \exp(\frac{E(p)}{kT}),
\]

because \( \langle n_q \rangle / (n_q + 1) = \exp(\hbar \omega_q / kT) \). Therefore \( f_{el}(r, p, t) \) relaxes to the thermodynamically expected distribution. Two points are worth noting.
(i) Not only the scattering integral but also the integrand vanishes at any energy; this is the principle of detailed balancing.

(ii) The scattering term \( \sum_{p',p} |W_{p',p}f_{e}(r, p') - W_{p,p}f_{e}(r, p)|^2 \Delta \) of the semiclassical kinetic equation contains an exclusion factor \( 1 - f_{b}(r, p) \) factoring \( f_{b}(r, p') \) [respectively, \( 1 - f_{b}(r, p') \) factoring \( f_{b}(r, p) \)] \([15, 54–56]\). This scattering term vanishes for a Fermi–Dirac, instead of Maxwell–Boltzmann, function. Exclusion factors cannot arise in the present work dealing with a single-particle effective wavefunction \( \psi'(r) \) unless the matter-wave field be quantized. In other words, electrons have been described here in first quantization where no distinction is made between a fermion and a boson. To obtain exclusion factors in the scattering term, the scalar field \( \psi' \) has to be replaced with an operator obeying an anti-commutation relation \([57]\). This is called second quantization; see Table 2.

<table>
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7.5 Classical versus quantum elastodynamics

To get a better insight into the change brought about by quantizing the elastic deformation field, compare the treatment of the disorder in classical elastodynamics, reflected in the interaction term (for one mode)

\[
\left( \frac{\partial}{\partial t} \right)_u \sqrt{\frac{C_{\alpha \alpha}}{\hbar}} \left[ \tilde{A}_q(t) + \tilde{A}_q^*(t) \right] \left[ (r, r', p - \hbar \frac{q}{2}) - (r, r', p + \hbar \frac{q}{2}) \right] e^{\pm i q \cdot r'}
\]

(90)

[see (28) and (32)], with the treatment in quantum elastodynamics, reflected in \( (\partial F/\partial x)_{\alpha \beta} \). In the latter, the contributions associated with matrix elements of \( F(r, r', p - \hbar q/2) \) have a weight \((n_q + 1)^{1/2} \) greater than \( n_q^{1/2} \) associated with \( F(r, r', p + \hbar q/2) \). This imbalance does not arise in (90) where the scalars \( \tilde{A}_q \) and \( \tilde{A}_q^* \) have the same modulus \((E_q^{\alpha \beta}h \hbar q)^{1/2} \). This contrast is reminiscent of classical as opposed to quantum electrodynamics. There also exists a stochastic electrodynamics where the fields are scalars and \( E_q^{\alpha \beta}h \hbar q_0 \) with \( q_0 \) denoting the photon number. In the ground state (photonic vacuum, \( n_q = 0 \)), the electromagnetic field is a non-zero stochastic quantity of zero mean \([58, 59]\). In this way, stochastic electrodynamics includes the zero-point or vacuum fluctuations of the field. In a similar way, a stochastic elastodynamics may be devised in which \( \langle \tilde{A}_q \rangle = 0 \) in the phonon vacuum while \( \langle \tilde{A}_q^2 \rangle = n_q + \frac{1}{2} \neq 0 \). In this framework also, no imbalance between \( (n_q + 1)^{1/2} \) and \( n_q^{1/2} \) arises as \( \langle \tilde{A}_q^* \rangle \) and \( \langle \tilde{A}_q \rangle \) are equal to one another. The imbalance is specific to quantum elastodynamics involving non-commuting operators (\( q \)-numbers). The imbalance is reflected in spontaneous emission of phonons occurring when the mode is empty, \( n_q = 0 \), whereas spontaneous absorption is forbidden by the First Law of thermodynamics.

One of the questions Abragam asked Haroche at the latter’s Ph. D. thesis defence was: ‘Why make use of the full mathematical apparatus of quantum theory to account for effects explainable within the classical treatment of the electromagnetic field? Is it possible to think of new effects for which a quantum-field-theoretic description is not only a useful device but a genuine necessity?’ In other words, are there inherently quantum phenomena such that the graininess of radiation quanta comes in a way that a classical-field-theoretic description would be unable to explain? ’ [60]. The obvious way to address Abragam’s question is to contemplate the case of a mode containing few quanta, i.e. \( n_q \) is hardly larger than unity, and this was the path followed by Haroche. But there exists another case in which the graininess of quanta plays an essential role even though \( n_q \) largely exceeds unity, namely the thermal equilibration of a system at the temperature of its environment. Thermal equilibration and the Zeroth Law are rooted in the difference between \( n_q \) and \( n_q^{+1} \), however large \( n_q \). The next section deals with the thermal equilibration of the environment, and the paper is concluded in section 9.

8 On the thermal equilibration of the environment

8.1 Electron thermalization under no electric field

If the phonons are in thermal equilibrium at time \( t = 0 \), their equilibrium can be significantly disturbed at \( t > 0 \) if the guest electrons are initially far from equilibrium and are numerous. This is why a closer scrutiny at the thermal equilibration of the phonon bath is in order.

Remember first a molecular gas. When isolated, such a gas equilibrates by itself at a definite temperature owing to the intermolecular collisions exchanging energy, with no need of an external thermostat setting the gas temperature. The rate of self-equilibration depends on the number density of the gas; that rate is usually very fast, except in a rarefied (Knudsen) gas where collisions are infrequent. Quotation from Khinchin [61]: ‘statistical mechanics bases its method precisely on a possibility of such an exchange of energy between various particles constituting the matter. [...] The energy of the system must contain also terms which depend simultaneously on the energy of several particles (mutual potentials of particles), and which assure the possibility of an energetical interaction between the particles. [...] In the majority of computations in statistical mechanics we will be able to neglect such terms, and, to a good approximation, assume that the energy of the system is equal to the sum of the energies of constituent particles [...]’. However, these mixed terms which are neglected,
from the point of principle play a very important role, since it is precisely their presence that assures the possibility of an exchange of energy between the particles, on which is based the whole method of the statistical mechanics’.

Consider now the photon gas called the black-body radiation in electrodynamics. The state of affairs is described in a dual language based either on the corpuscle or the wave picture. In the latter we have to do with an assembly of electromagnetic waves enclosed in a cavity whose walls have a well-defined temperature and are black. Unlike a white wall which fully reflects any incoming monochromatic wave without changing its frequency, a black wall fully absorbs the waves and re-emits the absorbed energy with a spectrum set by the temperature of the wall. In the corpuscle picture, the conveyors of radiation are photons moving at the speed of light in vacuum. No photon-photon scattering or interaction enables the thermalisation of the photon gas in contradistinction to a molecular gas. In the words of Landau and Lifshitz, ‘it should be remembered that at least a small amount of matter must be present if thermal equilibrium is to be reached in the radiation, since the interaction between the photons themselves may be regarded as completely absent. The mechanism by which equilibrium can be established consists in the absorption and emission of photons by matter’ [62]. The fact that the temperature of photons is set by the walls of the black cavity acting as a thermostat is in line with the Zeroth Law of thermodynamics as stated in section 1.

The electrical conductor dealt with in this paper hosts the assembly of elastic waves of the lattice atoms. To describe these waves, just like in the photon gas we are free to use a dual language based either on the wave or the corpuscle picture. In the latter a gas of quasi-particles called phonons pervades the lattice. Unlike photons, phonons can thermalise by themselves because of the phonon-phonon scattering events caused by the slight anharmonicity of the lattice vibrations. In the 1910s, prior to the completion of quantum physics, Debye devised a kinetic theory of thermal equilibration in a solid based on the wave picture, i.e. from the point of view of the propagation of elastic waves in a continuous medium [63]. He remarked that, were the vibrations of the medium strictly harmonic, the various waves would move independently, wherefore any arbitrary distribution of energy among them would be permanent. The lattice waves might then be paralleled with the electromagnetic waves enclosed in a cavity made up of white walls. For both kinds of waves, there is no mechanism whereby a condition of thermal equilibrium can be set up. This is why Debye included in the equation of motion non-linear terms in the displacement in order that these permitted exchange of energy between the different waves and subsequent establishment of thermal equilibrium, that is to say a well-defined temperature.

Debye’s model was put on a firmer quantum foundation by Peierls [64, 65]. The anharmonicity of the interatomic potential brings a new contribution to the Hamiltonian of the \{electron + phonons\} system:

\[
H_{el} + H_{ph} + H_{el-ph} + H_{ph-ph}
\]

where \(H_{el} = E_{l}(\mathbf{g} - i \mathbf{V})\) is the energy of a Bloch electron, \(H_{ph} = \sum_{q} H_{q}\) for non-interacting phonons, and lastly a phonon-phonon Hamiltonian \(H_{ph-ph}\) operates on phonon states. As discussed by Peierls, \(H_{ph-ph}\) tends to drive the phonon assembly to thermal equilibrium and set a definite temperature. The stronger the phonon-phonon interaction, the faster the equilibration rate of the phonon assembly. For one guest electron in the host lattice, the phonon bath acts as a thermostat imposing its temperature if the bath is huge \(\left(N_{a} \gg 1\right)\) and the phonon-phonon interaction exists\(^3\). The self-equilibration of the phonon bath is then hardly disturbed by electron relaxation to equilibrium. In section 7 no phonon-phonon interaction Hamiltonian appeared in (64); this interaction was effectively taken into account by considering that it enforces a canonical statistical operator of the phonon assembly. Thereby closure of the description is achieved.

### 8.2 Electron thermalization under an electric field

Under a smoothly-varying electrostatic potential \(V(\mathbf{r})\), an energy \(U_{C}(\mathbf{r}) = eV(\mathbf{r})\) contributes to the electron dynamics in (27) and formally acts via the electrical force \(\mathbf{V}(\mathbf{r} - U_{L})\).

In section 1 we remarked that the electron is actually acted upon by the electrochemical force \(\mathbf{V}(\mathbf{r} - \mathbf{g})\) where \(\mathbf{g} = U_{C} + g\). It is shown elsewhere [56] how the Boltzmann kinetic equation derived from the Wigner dynamical equation can be transformed so as to make the electrochemical force appear explicitly. Under that force and if the geometry allows for the passage of a current, Joule–Lenz heating occurs because the electron-phonon interaction keeps the energy distribution of the electrons close to thermal equilibrium at the bath temperature, and the electric power transferred to the electrons gives rise to heat production in the bulk. The heating can be sensed upon touching a commercial resistor in an electronic circuit made up of discrete components under operation; one can feel that the resistor is warmer than the surrounding atmosphere. Although the phonon gas removes the heat produced by the electron current, it does not exactly impose the ambient temperature to the electron gas. The discrepancy of the resistor and ambient temperatures is observed to depend on the wattage rating of the resistor; the larger the rating, the smaller the

\(^3\) The mutual scattering of conduction electrons in a solid could, just like in a molecular gas, entail the equilibration of the electron gas at a temperature \(T_{e}\) unrelated to that of the solid host \(T\). In transferred electron devices where a strong electric field raises the conduction electrons to an average energy lying well above the thermal-equilibrium value as determined by the lattice host, one often speaks of ‘hot electrons’ [66]. Calculations show that those ‘hot electrons’ often do not have a temperature in the thermodynamic sense [67]. The possible existence of a true electronic temperature is examined in appendix B.

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difference. To make the resistor temperature closer to the ambient one, besides choosing a larger wattage rating one will mount the resistor on a heat sink. In a steady state the sink lowers the lattice temperature in the resistor despite continual heat production. In so doing the thermostat (the phonon assembly) itself is thermalized, but a fully quantum description is hardly tractable at all. As remarked by Landauer, ‘if energy is to be dissipated, e.g. through a conductance, where does it go? Physicists have developed remarkable cleverness in starting from conservative Hamiltonian dynamics, which is easiest to treat, and using it to predict dissipative behavior, which is prevalent. Much of this, however, is based on cheating. A Hamiltonian system with a limited number of degrees of freedom is, of course, just that. It can store energy, it cannot dissipate it’ [68]. In section 7, the quantum treatment of the [electron + phonons] system was through a composite state-vector \( \Psi \) entangling the electron and phonon variables. Now to sustain thermal equilibrium the phonons will themselves be interacting with their own environment, and so on. The iteration continues indefinitely, until we are forced to contemplate a state vector of the Universe. In practice, one resorts to a semiclassical description in which the environment of the conductor is handled classically.

**9 Closing summary**

We now sum up the results reached in this paper. The goal was to understand how, at the microscopic level, the electrochemical (ordered) energy of a battery is converted into thermal (disordered) energy in an electronic conductor. The starting point was the recognition that, in a medium in thermal equilibrium, the voltage is not an electrical but a thermodynamical (electrochemical) quantity. The conduction electrons do not behave in isolation of the environment which sets their temperature. Accordingly, electron thermalisation (under no applied field) and Joule–Lenz heating (under an applied field) are two aspects of the energy interchange between the electrons and the host lattice. Attention was fastened on microscopically understanding the former phenomenon. In Hartree’s self-consistent one-electron picture, energy interchange is possible with moving obstacles whereas a static lattice only affects the dispersion relation of the electron envisioned as a matter wave. Moving obstacles occurring in all solids are the thermal deviations of the atoms off their equilibrium positions; the deviations are viewed as a random superposition of acoustic waves. Each wave causes a mechanical strain which alters the electronic band structure of the crystal in a time-dependent manner. Whereas in the perfectly periodic crystal the electron is in a stationary state of motion, it suffers transitions to other states because of the extra potential energy due to the strain. The dynamical disorder of the thermally agitated lattice was first treated classically as a time-dependent stochastic energyscape plugged into the one-electron effective Schrödinger equation including the electronic band structure of the crystal. This dynamical equation was replaced with one governing the electron’s Wannier–Bloch quasi-distribution superseding the Wigner function relevant in vacuum. The disordered energyscape was dealt with perturbatively within a multiple-scale expansion. Upon averaging over all realisations of the energyscape, an irreversible kinetic equation of the Boltzmann–Lorentz type was found to govern an approximate quasi-distribution relevant on length (time) scales exceeding the correlation length (time) of the disordered environment. Often an irreversible evolution equation is derived on assuming a covariance that decays in *time*. Such a derivation is consistent but circular as it presupposes an arrow of time. Contrariwise our derivation rests upon the *spatial* behaviour of a covariance combined with an ergodicity property; the loss of order is accounted for without assuming irreversibility in a different guise.

The kinetic equation allows for inelastic scatterings; to the first order, a wave of angular frequency \( \omega \) shifts the electron’s energy by \( -\hbar \omega q \) or \( +\hbar \omega q \); one speaks of the emission or absorption of a phonon. However, the steady-state solution of the kinetic equation fails to account for electron thermalisation at the lattice temperature. In keeping with Abragam’s remark on spin systems, a second approach was devised in which the electron is taken to interact with a quantized deformation field. In this quantum elastodynamic treatment, the electron’s dynamics is entangled with that of the phonons. Taking the latter to stay in thermal equilibrium as a phenomenological closure of the description, the ratio of transition rates \( p \to p' \) and \( p' \to p \) is a Boltzmann factor of the electron energy difference \( E(p') - E(p) \) at the lattice temperature; whereby thermal equilibration is ensured. While phonon absorption only occurs with a populated phonon mode, emission also occurs with an empty phonon mode, when the temperature vanishes and the lattice is frozen according to classical physics. Therefore, zero-field thermalisation and Joule heating are basically quantum phenomena — like superconductivity. Each phenomenon requires quantum dynamics and quantum statistics for its explanation.

Our treatment agrees with that of Erdös who similarly zooms out to larger space and time scales while taking an electron-lattice coupling strength scaling as \( e^{1/2} \) [69]. In our approach emphasis is put on disorder (dynamical versus static, quantum versus classical); it is a disorder with minimal complexity in that only the two-point distribution of the disorder is involved in the limit of a weak coupling strength [35, 70].

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Appendix A
The First and Second Laws in near-equilibrium thermodynamics

The First Law of thermodynamics states the balance of energy; energy cannot be produced or destroyed. The law holds in any volume of the electric conductor. Interchange of energy assumes three forms: electrical work done by the external electric field, heat and ‘chemical energy’ associated with the entrance (exit) of electrons into (out of) the given volume and manifested in a contribution $gdN$ to $dU$. In the notations of section 1
\[ d\bar{U} = Td\bar{S} + \bar{g}dN, \quad (A.1) \]
where the total energy $\bar{U} = U + Ne^2V$ lumps together the internal and external energies of the electron gas. In the near-equilibrium states considered in this paper, currents of extensive quantities are flowing. The current density of an extensive quantity $E$ is denoted by $j_E$. From (A.1) in an infinitesimal volume we infer $j_E = Tj_S + \bar{g}j_N$. The overall balance of energy is implemented locally as
\[ \text{div} j_E = 0. \quad (A.2) \]

The production of heat per unit volume is $\text{div}(Tj_S)$; see below. The First Law (A.2) entails that the heat production is $\text{div}(-\bar{g}j_N)$ per unit volume of conductor; it is also $\nabla(-\bar{g})j_N$ since electrons are conserved locally so that $\text{div}j_N = 0$. Depending on the frame of thinking, there are two ways of interpreting the implementation of the First Law; they are contrasted in figures 9 and 10.

The internal energy $U'$ of the lattice has not been accounted for in this energy balance. The fundamental thermodynamic relation of the lattice is $dU' = TS'$; in corpuscular language, there is no chemical potential for the phonons since their number is not conserved, just like in the photon gas [71, 72]. At fixed volume the entropy of the lattice is a function $S'(T)$. If temperature is homogeneous, there is no energy flow associated with the lattice, $0 = j_{E'} = Tj_{S'}$; conduction electrons are the only carriers of heat in the solid. But a temperature gradient entails a flow $j_{E'}$ of heat mediated by the lattice vibrations. The energy balance expressed above is thus restricted to a uniform temperature field. Otherwise the balance has to account not only for $j_{E'}$ but also for thermolectric effects of a kinetic, i.e. non-thermostatic, nature, not dealt with in this paper.

The Second Law of thermodynamics states that entropy can be produced but not destroyed in any volume of conductor. In a near-equilibrium state, the current density of entropy is defined on Clausius’ pattern $dS = \delta Q/T$, as $J_S = J_{S'}/T$ where the electron-gas ($j_E$) and lattice ($j_{E'}$) contributions are lumped together in $J_S$, and $J_{S'}$ is the total heat-current density. According to the Second Law, the entropy production rate (per unit volume) is non-negative,
\[ \text{div} J_S \geq 0. \quad (A.3) \]
This local statement is called the Clausius–Duhem inequality. The macroscopic interpretation is as a principle of degradation of energy [73], to which we return below. The microscopic interpretation is often in terms of generation of disorder; but Bridgman’s warning should not be overlooked: “disorder” is not a thermodynamic concept at all, but is a concept of the kinetic-statistical domain. [...] There is a fuzziness about the common-sense notion of “disorder” which makes it not always altogether suited as an intuitive tool in discussing the Second Law” [74]. In the present issue, moving the free electrons along the electrochemical force gives rise to an ordered transfer of energy (work)\(^4\); by scattering the electrons drifting along the force, the lattice vibrations give rise to a disordered transfer of energy (heat).

The entropy production rate per unit volume may be written as a sum of two terms,

\[
\text{div} \mathbf{J}_S = \frac{\text{div} \mathbf{J}_{Q \text{, } g}}{T} + \mathbf{J}_{Q} \cdot \nabla (-T) \frac{1}{T^2}.
\]  

(A.4)

The first contribution in (A.4) is due to the production of heat per unit volume, \(\text{div} \mathbf{J}_{Q \text{, } g}\). It is \(\nabla (-T) \mathbf{J}_{Q} \) under a uniform temperature, as argued above. Then, one may say that electrochemical work is degraded into heat while electrons are flowing down the electrochemical force. The second contribution to \(\text{div} \mathbf{J}_S\) is due to the flow of heat towards lower temperatures. It is not a degradation in the usual sense, which is why the term ‘dissipation’ is preferred to designate the total production of entropy (A.4).

**Appendix B**

**On the electronic temperature**

The body of the paper deals with the thermalisation of an electron gas by a host lattice endowed with a well-defined temperature, which in addition is static and homogeneous. Starting out with an arbitrary initial distribution of pseudomomenta, the electrons eventually reach a Maxwell–Boltzmann distribution at the lattice temperature. A Fermi–Dirac distribution would be reached were the Schrödinger matter-wave field quantized. In the transient regime the electrons generally do not have a well-defined temperature. In the physics of ionised gases out of equilibrium a well-defined electron temperature is the exception rather than the rule [76]. It may occur, however, if a significant electron-electron interaction, of the bare or screened Coulomb type, exists. Based on mathematical works [77, 78] this appendix sketches how the electron gas may have a temperature of its own distinct from that of the lattice vibrations. Instead of a full quantum description based on a Wigner function, a semi-classical approach is used based on an occupation function \(f(\mathbf{r}, \mathbf{p}, t)\) obeying a Boltzmann kinetic equation including the electron-electron interaction,

\[
\frac{\partial f}{\partial t} + \mathbf{v}(p) \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F}(r) \frac{\partial f}{\partial \mathbf{p}} = \frac{\partial}{\partial \mathbf{p}} \left( \frac{1}{2m} \nabla f + \frac{m}{2} \mathbf{J}_S \right) + \frac{1}{2m} \nabla f - \frac{m}{2} \mathbf{J}_S.
\]

(B.1)

where \(\mathbf{F}(\mathbf{r})\) is the electric force. In (B.1) the elastic scattering operator \(\mathbf{S}_{\text{el}}\), which often is approximated owing to the smallness of inelasticity. The electron-electron scattering operator \(\mathbf{S}_{\text{ee}}\) is bilinear in \(f\) if Pauli exclusion is disregarded, and contains fourth-order terms otherwise [54]. The scatterings governed by the electronic transport are such that

(i) elastic scattering tends to randomize the pseudomomentum distribution over a constant-energy surface;

(ii) inter-electronic scattering does not change the total pseudomomentum nor does it change the total energy of the electron gas, but it redistributes energy among the electrons whereby this scattering tendentially gives rise to a temperature \(T_0\) of the electron gas, in a way similar to intermolecular collisions in a molecular gas [61];

(iii) inelastic scattering causes exchange of energy with the lattice, which tends to thermalise the electrons at the temperature of the lattice vibrations. Issues exist in which the following ordering holds: \(\mathbf{S}_{\text{el}} \gg \mathbf{S}_{\text{ee}} \gg \mathbf{S}_{\text{in}}\). This ordering is underpinned by a ladder of scales: elastic-scattering time \(\ll\) inter-electronic scattering time \(\ll\) electron-phonon energy-exchange time. As a result of the inequality elastic-scattering time \(\ll\) phonon-energy-exchange time, the limiting model derived from the kinetic equation (B.1) is a drift-diffusion (Fokker–Planck) equation in an augmented energy-position space. The equation governs the spectral carrier density \(n(\mathbf{r}, E, t)\) instead of the occupancy \(f(\mathbf{r}, \mathbf{p}, t)\) of phase space; \(g\, dE\) is the contribution of energy range \([E, E + dE]\) to the carrier density \(n\). The Fokker–Planck equation is a continuity equation whose conserving current density involves a diffusivity tensor in energy-position space. Its components in position space are constant-energy averages of the tensor product of the group velocity and the vector mean-free-path. For one space dimension \(x\), the diffusivity tensor is specified by four components \(D_{xx}(E, x), D_{xy}(E, x), D_{yx}(E, x)\) and \(D_{yy}(E, x)\); see [79] for an application. The usual (Fick) diffusion coefficient in position space may not coincide with the energy-averaged \(D_{xy}(E, x)\) [20]. In the Fokker–Planck view, the electron gas interchanges energy with a finite-temperature system, namely the phonon bath, and an infinite-temperature system, namely the force field; yet the electrons generally do not have a canonical distribution of energies at a definite temperature [80, 81].

\(^4\)While \(g\, dN\) is generically designated as an energy, Kittel and Kroemer [75] refer to it as ‘chemical work’ on a par with the mechanical work of pressure forces in a fluid. Likewise, Horowitz and Hill’s definition of voltage [7] qualifies \(g\, dN\) as a work.
approximately reach a thermal energy distribution. Then, \( g(\mathbf{r}, E, t) \) is specified by carrier-density and carrier-temperature functions, \( n(\mathbf{r}, t) \) and \( T_e(\mathbf{r}, t) \). They evolve over a longer time scale owing to the small inelastic interaction with the host lattice embodied in \( S_{\text{cin}} \), which tends to equalize \( T_e \) with \( T \). In the absence of an electric force the electrons are gradually cooled down to the lattice temperature if \( T_e > T \), whereas they are heated up if \( T_e < T \). A positive \( T_e - T \) is sustained under a constant applied force. The descriptions of transport are shown in figure 11.

**Boltzmann**

\( \dot{f}(\mathbf{r}, \mathbf{p}, t) \) in phase space

\[
\frac{\partial f}{\partial t} + \mathbf{v}(\mathbf{p}) \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F}(\mathbf{r}) \frac{\partial f}{\partial \mathbf{p}} = S_{\text{ce}}[f] + S_{\text{ce}}[f] + S_{\text{cin}}[f]
\]

**Fokker–Planck**

\( n(\mathbf{r}, E, t) \) in energy-position space

\[
\frac{\partial n}{\partial t} + \frac{\partial}{\partial E} \left( E \frac{\partial n}{\partial E} \right) + \text{div} \mathbf{J} = 0
\]

with spectral current density \( J_E, \mathbf{J} \)

of drift-diffusion type

**Energy balance**

\( n(\mathbf{r}, t) \) and \( T_e(\mathbf{r}, t) \) in position space

\[
\frac{\partial n}{\partial t} + \text{div} j_N = 0,
\]

\[
\frac{\partial}{\partial t} \left( \frac{n(E)}{E} \right) + \text{div} j_U = \mathbf{F} j_N + \int_{E_c}^{+\infty} W_{\text{pd}}(E) n(\mathbf{r}, E, t) dE
\]

**Fig. 11.** The array of transport descriptions. An arrow points to a level of description of lesser accuracy; a coarser description is sufficient over a larger scale. Over time scales exceeding the velocity-correlation time, the instantaneous velocity \( \mathbf{v}(\mathbf{p}) \) is averaged out so that energy \( E \) and position \( \mathbf{r} \) suffice to specify the particle’s state. Over time scales exceeding the inter-electronic scattering time, the energy dependence of the spectral particle density \( n(\mathbf{r}, E, t) \) becomes approximately canonical at a local temperature \( T_e(\mathbf{r}, t) \); a description in position space becomes sufficient with an electronic temperature supplementing the particle density. The temperature \( T_e \) is a variable in the internal-energy-density function \( n(E) \) of the electron gas. After [82] or [83].
which is the heat capacity of the electron gas at constant volume used in the the two-temperature model of [86]. That model is manufactured in a phenomenological manner without being derived from a higher level of description and without allowing for inhomogeneities and non-local effects.

Lastly, for deformation-potential scattering with acoustic phonons at equipartition, in a dilute gas the average energy gain of an electron from the phonon bath, \( W_{\text{ph}}(E) = \alpha E^{1/2}(2kT - E) \), is generalized according to [55, 83]. In (B.7) energy is reckoned with respect to the conduction-band bottom. In a degenerate gas where the occupancy \( f_\Omega(E, \mathbf{r}, t) = n(E, \mathbf{r}, t)/N(E) \) is significant, the electron-phonon energy-interchange term is generalized according to [55, 83]

\[
\begin{align*}
\left. \left( \frac{\partial n(E)}{\partial T} \right)_n \right|_\Omega & = \frac{1}{\Omega} \left( \frac{\partial U}{\partial T} \right)_n, \quad (\text{B.6})
\end{align*}
\]

The rate is

\[
\begin{align*}
& \int_{E_c}^{+\infty} N(E) W_{\text{ph}}(E) f_\Omega(E) dE \\
& - \int_{E_c}^{+\infty} N(E) \partial \Omega f_\Omega \left( \frac{\partial f_\Omega}{\partial E} + \frac{f_\Omega(1 - f_\Omega)}{kT} \right) dE, \quad (\text{B.8})
\end{align*}
\]

where \( \partial \Omega f_\Omega = kT \alpha (E - E_c)^{3/2} \) in a parabolic band. If electrons have a temperature \( T_c \), then \( \partial f_\Omega / \partial E = -f_\Omega(1 - f_\Omega)/kT \). From (B.8) electrons and phonons do not interchange energy if their temperatures coincide.

Whether or not an electronic temperature is relevant in a given issue depends on the strength of the inter-electronic interaction. Since the total energy and total momentum are conserved in a two-body encounter, the physically relevant rate assessing the strength of the inter-electronic interaction is that for relaxing relative momentum [87]. In a dilute electron gas, that rate is well defined for a fast electron whose energy \( E_c \) reckoned with respect to the conduction-band bottom largely exceeds the average energy. The rate is

\[
\begin{align*}
\frac{1}{\tau_{ee}} & = \frac{n \epsilon^4}{\pi \hbar^2 m^{7/2} (2E)^{1/2} \times L(E), \quad (\text{B.9})
\end{align*}
\]

where \( \epsilon \) is the static permittivity and \( L(E) \) is a numerical factor given in [87]. The rate for relaxing energy in a two-body encounter is \( 1/2\tau_{ee} \). Taking \( E = 0.1 \text{ eV} \) and \( L(E) \approx 1 \), one obtains, roughly,

\[
\begin{align*}
\frac{1}{\tau_{ee}} & \approx 10^{-5} n, \quad (\text{B.10})
\end{align*}
\]

with \( \tau_{ee} \) reckoned in \( s \) (cm\(^{-3}\)) unit. In an undoped or weakly doped semiconductor, inter-electronic scattering is negligible compared to other scatterings. It is significant in a strongly doped semiconductor at the onset of degeneracy, that is to say the Fermi level reaches the conduction-band bottom \( (E_F = g - E_c) \). For strong degeneracy \( (E_F \gg kT) \) as occurs in a metal, the scattering rate of an electron whose energy is close to the Fermi level is reduced by a phase-space factor \( \approx (kT/E_F)^3 \) owing to Pauli exclusion [88–90].

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