Microscopic approach to irreversible thermodynamics. II. An example from semiconductor physics

Aurea R. Vasconcellos and Roberto Luzzi

Departamento de Física do Estado Sólido e Ciência de Materiais

Instituto de Física, Universidade Estadual de Campinas (UNICAMP), Caixa Postal 6165, 13081 Campinas São Paulo, Brazil

Leopoldo S. García-Colin

Departamento de Física, Universidad Autónoma Metropolitana, Apartado Postal 55-543, 09340 México, Distrito Federal, Mexico and El Colegio Nacional, Luiz Gonzalez Obregón 23, 06240 México, Distrito Federal, Mexico (Received 29 January 1990; revised manuscript received 31 July 1990)

The general theory described in the preceding article [Phys. Rev. A 43, 6622 (1991)] based on the nonequilibrium-statistical-operator method, which provides mechano-statistical foundations for phenomenological irreversible thermodynamics, is applied to a specific problem. This is the case of a highly excited plasma in a semiconductor, where fluxes of mass and energy naturally appear, as well as other higher-order fluxes, as basic variables necessary for the description of the macroscopic state of the system. A criterion for the truncation of the basic set of variables is presented. The equations of motion for the macrovariables are derived for the case of a simple model. They have the structure of nonlinear and nonlocal transport equations, which fit into a natural extension of those of linear irreversible thermodynamics. In particular, Maxwell-Cattaneo-Vernotte-type equations of extended irreversible thermodynamics are recovered, having relaxation times and transport coefficients that may be calculated from the microscopic dynamics of the system composed of averages over the nonequilibrium ensemble.

I. INTRODUCTION

In the preceding paper,¹ hereafter referred to as I, we presented a general theory, based on the nonequilibriumstatistical-operator method (NSOM), which provides mechano-statistical foundations for phenomenological extended irreversible thermodynamics (EIT). This paper is devoted to the presentation of a specific example that clarifies the general theory illustrating how it works in practice.

We briefly recall the main points of the theory that we are putting to work in the present paper. The nonequilibrium statistical operator (NSO) $\rho(t)$ is derived by means of Jaynes's maximum-entropy principle. This NSO is a functional of a basic set of dynamical variables, say, P_i , $j = 1, 2, \ldots, n$, whose average values with the NSO define the macrovariables $Q_i(t) = \text{Tr}[P_i\rho(t)]$ that are interpreted as those composing the Gibbs space of variables that describe the macroscopic state of the system. The choice of this basic set is up to now not founded on any satisfactory approach,² including the particular selection of the generalized fluxes as basic variables as is done in EIT. We have discussed in I a plausible criterion for the determination of the basic set of dynamical variables and, thus, of the G space of macrovariables, appropriate for a large class of experimental situations. In Sec. III this criterion is applied to the case of a highly photoexcited plasma in semiconductors (HEPS).

For that purpose, the total Hamiltonian H is split into two parts H_0 and H'. The first one contains the kinetic energies of the subsystems that compose the whole system and the strong interactions that produce very fast relaxations, that is, in time lapses smaller than the characteristic resolution time of the experiment. On the other hand, H' contains the weak interactions that produce slow relaxation processes. Next, the basic variables are chosen in such a way to satisfy, in an appropriate quantum representation, the closure condition, which we call the Peletminskii-Zubarev symmetry condition,

$$[P_j, H_0] = \sum_k \Omega_{jk} P_k , \qquad (1)$$

where Ω_{jk} are c numbers. Thus the quantities P_j form a Hilbert subspace on which they are kept precessing because of the action of H_0 and from where they are projected out by the action of H', the interaction which, as shown in I, is responsible for the relaxation effects in Q variables.

In the case of the HEPS dealt with in Sec. II, H_0 is composed of the carrier's kinetic energy plus the (fast) Coulomb interaction (we recall that it produces internal thermalization of carriers in the few hundreds of femtoseconds time scale).³ We start the construction of the space of basic dynamical variables beginning with the density and density of energy in the reciprocal space. Commutation of them with H_0 produces a relation of the type of Eq. (1) once the dynamical quantities for the fluxes of matter and energy are incorporated into the basic variables. We see then the fluxes naturally arising into the mesoscopic description of the system as proposed by EIT. The commutation procedure with H_0 is repeated now using the explicit expressions for the fluxes to obtain once more an equation such as (1), that is to say, expressions involving quantities representing higher-order fluxes to be added to the basic variables and so on. In our example the procedure should continue indefinitely. This fact calls for the introduction of a truncation procedure: This is done in the way described in Sec. II and the approximation involved is discussed. Such a truncation procedure appears to be in wide use in problems in hydrodynamics.

Finally, as shown in I, the NSOM provides a nonlinear quantum theory of transport that in the limit of small fluxes leads to equations of motion for the basic variables that are of the Maxwell-Cattaneo-Vernotte (MCV) type of EIT. In Sec. III we explicitly illustrate these results, resorting to a very simple model where we include only the kinetic energy, the density of energy, and the energy flux of a fermion fluid interacting with a boson gas taken as a heat bath. As expected, we obtain MCV-like equations with explicit expressions, on the microscopic level, for the transport coefficients, particularly Maxwell's relaxation time that appears in the equation of evolution for the flux of energy. In the quasistatic regime and hydrodynamic limit, we recover Fourier's constitutive equation and an expression for the thermal conductivity that takes the form of that provided by the kinetic theory of gases, where the place of the mean collision time τ is taken by Maxwell's relaxation time. These results follow in the hydrodynamic limit of the very large wavelengths (very short wave numbers) where the equations become local in space; we recall that because of the use of the NSOM-linear theory of relaxation to approximate the NSOM-generalized transport equations, the results are memoryless. The extension of the theory to include nonlinearity in the fluxes and memory effects are planned to be reported in a future paper.

II. HYDRODYNAMIC APPROACH TO PLASMA IN SEMICONDUCTORS

Let us consider now the application of the ideas developed in I to the particular case of a highly excited plasma in semiconductors. In earlier publications two of us with collaborators have used Zubarev's NSOM to study ultrafast relaxation phenomena and transient transport in uniform HEPS.⁴ For the case of the HEPS, we take for H_0 the Hamiltonian of the subsystems of electrons, composed of Bloch band states plus Coulomb interactions, and that of the free phonons. The energy operator H' contains the electron-phonon, electronradiation, and phonon-phonon interactions. The semiconductor sample is in contact with a thermal bath, and both, together with the laser radiation field, are taken as an isolated system to which the NSOM applies. The thermal bath and laser source are considered as ideal reservoirs, namely, as constantly in a stationary condition characterized by a temperature T_0 and a classic radiation field of given intensity and spectral composition, respectively. The complete NSO is then the product of the steady-state distribution of the reservoirs times the NSO of the open semiconductor system. The HEPS Hamiltonian reads as,

$$H = H_0 + H' , \qquad (2)$$

where

$$H_{0} = \sum_{\mathbf{k},a} \varepsilon_{\mathbf{k}a} C_{\mathbf{k}a}^{\dagger} C_{\mathbf{k}a}$$
$$+ \sum_{\mathbf{k},\mathbf{k}'} \sum_{\mathbf{q},a,b} V(\mathbf{q}) C_{\mathbf{k}+\mathbf{q},a}^{\dagger} C_{\mathbf{k}a} C_{\mathbf{k}'b}^{\dagger} C_{\mathbf{k}'-\mathbf{q}b} + H_{\mathrm{ph}} .$$
(3)

 $H_{\rm ph}$ is the Hamiltonian of the free phonons; $V(q) = 4\pi e^2/\epsilon_0 q^2$ is the matrix element of Coulomb interaction; $\epsilon_{\rm ka}$ are Bloch electron energies that are taken in the effective mass approximation, namely, for electrons $(a=e) \ \epsilon_{\rm ke} = E_G + \hbar^2 k^2 / 2m_e$ and for holes $(a=h) \ \epsilon_{\rm kh} = \hbar^2 k^2 / 2m_h$; m_e and m_h are the effective masses; E_G is the energy gap in this inverted band semiconductor; and ϵ_0 is the static dielectric constant. Coulomb interaction among carriers, the second term on the right-hand side of Eq. (3), will be treated in the random-phase approximation.⁵ Finally, H' contains the energy operators for the interaction of carriers and phonons and carriers with the radiation fields.

In the aforementioned references,⁴ the description of the nonequilibrium thermodynamic evolution and optical responses of HEPS is done for constant T_0 , given laser intensity I_L photon frequency ω_L , neglecting selfabsorption and induced recombination (thus eliminating the radiation fields other than those of the laser and spontaneous recombination), and in conditions of homogeneous spatial distribution. Six dynamical quantities are deemed to be appropriate for such description, namely, the energy of carriers, H_c , the energies of the different phonon (acoustic and transverse- and longitudinaloptical) branches, H_A , $H_{\rm TO}$, $H_{\rm LO}$, and the numbers operators for electrons, N_e , and for holes, N_h . The NSOM-nonequilibrium thermodynamically conjugate variables $F_i(t)$ (cf. Sec. III in I) are in this case referred to as the quasitemperatures of electrons, $\beta_c(t) = 1/kT_c^*(t)$, of phonons, $\beta_A(t) \equiv 1/kT_A^*(t)$, $\beta_{\text{TO}}(t) = 1/kT_{\text{TO}}^*(t), \ \beta_{\text{LO}}(t) = 1/kT_{\text{LO}}^*(t), \ \text{and the quasi-}$ chemical potentials $\mu_e(t)$ and $\mu_h(t)$.

The six quantities $\{H_c, H_A, H_{\text{TO}}, H_{\text{LO}}, N_e, N_h\}$ commute with H_0 , thus verifying the symmetry condition of Eq. (1) [see also Eq. (29) in I] with $\Omega_{jk} = 0$ and also among themselves. The Gibbs space G is composed of the average values $\{E_c(t), E_A(t), E_{\text{TO}}(t), E_{\text{LO}}(t), n(t)\}$ (the concentration of electrons and holes is the same since they are produced in pairs; however, the quasichemical potentials are unequal because of their different effective masses).

Resorting to the linear theory of relaxation (LTR),⁶ the coupled set of nonlinear integro-differential equations of evolution for the basic set of macrovariables is derived and solved for different initial conditions, and comparison with experimental observations based on ultrafast laser spectroscopy was made.⁴

Let us next broaden the analysis of the HEPS, allowing now for the presence of spatial inhomogeneities in the carrier system. For that purpose we add to space G the carrier Q Fourier amplitudes for density, $n(\mathbf{Q}, t)$, and energy density $h_a(\mathbf{Q}, t)$, whose dynamical operators are

$$N_a(\mathbf{Q}) = \sum_{k} C^{\dagger}_{\mathbf{k}+\mathbf{Q},a} C_{\mathbf{k},a}$$
(4a)

and

$$H_a(\mathbf{Q}) = \sum_{\mathbf{k}} \frac{\hbar^2}{2m_a} \mathbf{k} \cdot (\mathbf{k} + \mathbf{Q}) C^{\dagger}_{\mathbf{k} + \mathbf{Q}, a} C_{\mathbf{k}, a} . \qquad (4b)$$

We have taken the effective-mass approximation for the energy dispersion relations, and planes waves instead of Bloch band wave functions with $C^{\dagger}(C)$ being creation (annihilation) operators in such states. Further, as noted, the subscript *a* stands as a = e for electrons and a = h for holes, and \mathbf{Q} ($\neq 0$) runs over all reciprocal space.

Consequently, the two transport equations associated with these quantities must be added to the previous set of six generalized transport equations. Such equations are

$$\begin{split} \frac{d}{dt}n_{a}(\mathbf{Q},t) &= \mathrm{Tr}\left[\frac{1}{i\hslash}[N_{a}(\mathbf{Q}),H_{0}+H']\rho_{w}(t)\right] \\ &= \mathrm{Tr}\left[\frac{1}{i\hslash}[N_{a}(\mathbf{Q}),H_{0}]\rho_{w}(t)\right] + \Lambda_{1a}[H'], \quad (5a) \\ \frac{d}{dt}h_{a}(\mathbf{Q},t) &= \mathrm{Tr}\left[\frac{1}{i\hslash}[H_{a}(\mathbf{Q}),H_{0}+H']\rho_{w}(t)\right] \\ &= \mathrm{Tr}\left[\frac{1}{i\hslash}[H_{a}(\mathbf{Q}),H]\rho_{w}(t)\right] + \Lambda_{2a}[H'], \quad (5b) \end{split}$$

ſ

where we have separated out the rate of change due to H_0 and that due to H', the latter one contained in the terms denoted by Λ . Further, $\rho_w(t)$ is the NSO constructed according to the procedure described in I.

The commutation of $N(\mathbf{Q})$ and $H_a(\mathbf{Q})$ with H_0 yields (for the sake of simplicity, hereafter we use $\hbar = 1$)

 $[N_a(\mathbf{Q}), H_0] = (\mathbf{Q}/m_a) \cdot \mathbf{P}_a(\mathbf{Q}) ,$ (6a) $[H_a(\mathbf{Q}), H_b] = (\mathbf{Q}/m_a) \cdot \mathbf{P}_a(\mathbf{Q}) .$ (6b)

$$[H_a(\mathbf{Q}), H_0] = (\mathbf{Q}/m_a) \cdot \mathbf{I}_a(\mathbf{Q}) - V(\mathbf{Q}) \mathbf{Q} \cdot \sum_k (\mathbf{k}/m_a) f_a(\mathbf{k}, t) N(\mathbf{Q}) , \qquad (6b)$$

where

$$\mathbf{P}_{a}(\mathbf{Q}) = \sum_{\mathbf{k}} \left(\mathbf{k} + \frac{1}{2}\mathbf{Q}\right) C_{\mathbf{k}+\mathbf{Q},a}^{\dagger} C_{\mathbf{k},a} , \qquad (7)$$

$$\mathbf{I}_{a}(\mathbf{Q}) = \frac{1}{2m_{a}}\sum_{\mathbf{k}} \left[\mathbf{k} \cdot \left[\mathbf{k} + \frac{\mathbf{Q}}{2}\right]\right] \left[\mathbf{k} + \frac{1}{2}\mathbf{Q}\right] C_{\mathbf{k}+\mathbf{Q},a}^{\dagger} C_{\mathbf{k},a} , \qquad (8)$$

which are the Fourier amplitudes of the density of the linear momentum and the density of kinetic energy flux in the Bloch band (parabolic band in our model). The last term in Eq. (6b) is the contribution resulting from the Coulomb interaction, which, as mentioned before, has been dealt with in the time-dependent random-phase approximation.⁵ Further, we have introduced

$$f_a(\mathbf{k};t) = \operatorname{Tr}[C_{\mathbf{k},a} C_{\mathbf{k},a} \rho_{\mathrm{CG}}(t,0)], \qquad (9)$$

where $\rho_{CG}(t,0)$ is the auxiliary coarse-grained (CG) operator associated with $\rho_w(t)$ as described in I, and

$$N(\mathbf{Q}) = N_e(\mathbf{Q}) - N_h(\mathbf{Q}) . \tag{10}$$

Equations (6) tell us that H_0 relates $N_a(\mathbf{Q})$ and $H_a(\mathbf{Q})$ with the quantities $\mathbf{P}_a(\mathbf{Q})$ and $\mathbf{I}_a(\mathbf{Q})$, which according to the basic prescription, i.e., the Zubarev-Peletminskii symmetry condition of Eq. (1), have to be incorporated to the set of variables. Commutations of both with H_0 yield

$$[\mathbf{P}_a(\mathbf{Q}), H_0] = \mathbf{\Phi}_a(\mathbf{Q}) + V(\mathbf{Q})n(t)N(\mathbf{Q})\mathbf{Q} , \qquad (11a)$$

$$\left[\mathbf{I}_{a}(\mathbf{Q}),H_{0}\right] = \Psi_{a}(\mathbf{Q}) - \frac{V(Q)}{2m_{a}}\sum_{\mathbf{k}}\left[\left|k^{2} + \frac{Q^{2}}{2}\right|\mathbf{Q} + 2(\mathbf{k}\cdot\mathbf{Q})\mathbf{k}\right|f_{a}(\mathbf{k};t)N(\mathbf{Q}), \qquad (11b)$$

where

$$\Phi_{a}(\mathbf{Q}) = \frac{1}{m_{a}^{2}} \sum_{\mathbf{k}} \left[(\mathbf{k} \cdot \mathbf{Q}) + \frac{Q^{2}}{2} \right] \left[\mathbf{k} + \frac{1}{2} \mathbf{Q} \right] C_{\mathbf{k}+\mathbf{Q},a}^{\dagger} C_{\mathbf{k},a} , \qquad (12)$$

$$\Psi_{a}(\mathbf{Q}) = \frac{1}{2m_{a}^{2}} \sum_{\mathbf{k}} \left[\mathbf{k}^{2} (\mathbf{k} \cdot \mathbf{Q}) \mathbf{k} + (\mathbf{k} \cdot \mathbf{Q})^{2} \mathbf{k} + k^{2} (\mathbf{k} \cdot \mathbf{Q}) \mathbf{Q} \right] C_{\mathbf{k}+\mathbf{Q},a}^{\dagger} C_{\mathbf{k},\mathbf{a}} , \qquad (13)$$

which we call the second-order flux of density and energy density, respectively.

Again, incorporating Φ and Ψ to the basic set of dynamical variables, we proceed to calculate their commutators with H_0 to obtain

VASCONCELLOS, LUZZI, AND GARCÍA-COLIN

$$[\boldsymbol{\Phi}_{a}(\mathbf{Q}), \boldsymbol{H}_{0}] = \mathbf{U}_{a}(\mathbf{Q}) - \frac{V(Q)}{m_{a}} \sum_{\mathbf{k}} [Q^{2}\mathbf{k} + (\mathbf{k} \cdot \mathbf{Q})\mathbf{Q}]f_{a}(\mathbf{k}; t)N(\mathbf{Q}) , \qquad (14a)$$

$$[\Psi_a(\mathbf{Q}), H_0] = \mathbf{W}_a(\mathbf{Q}) - \frac{V(\mathbf{Q})}{2m_a^2} \sum_{\mathbf{k}} [\mathbf{Q}^2(\mathbf{k} \cdot \mathbf{Q})\mathbf{k} + 2(\mathbf{k} \cdot \mathbf{Q})^2\mathbf{k} + k^2\mathbf{Q}^2\mathbf{k} + (\mathbf{k} \cdot \mathbf{Q})^2\mathbf{Q} + k^2(\mathbf{k} \cdot \mathbf{Q})\mathbf{Q}]f_a(\mathbf{k}; t)N(\mathbf{Q}) , \qquad (14b)$$

where

$$U_a(Q) = \frac{1}{m_a^2} \sum_{\mathbf{k}} \left[\mathbf{k} \cdot \mathbf{Q} + \frac{1}{2} Q^2 \right]^2 \left[\mathbf{k} + \frac{1}{2} \mathbf{Q} \right] C_{\mathbf{k}+\mathbf{Q},a}^{\dagger} C_{\mathbf{k},a} , \qquad (15)$$

$$\mathbf{W}_{a}(\mathbf{Q}) = \frac{1}{2m_{a}^{3}} \sum_{\mathbf{k}} \left(\mathbf{k}^{2} + \mathbf{k} \cdot \mathbf{Q}\right) \left[\mathbf{k} \cdot \mathbf{Q} + \frac{Q^{2}}{2}\right] \left[\mathbf{k} + \frac{1}{2}\mathbf{Q}\right] C_{\mathbf{k}+\mathbf{Q},a}^{\dagger} C_{\mathbf{k},a}$$
(16)

are higher-order fluxes of density and energy density.

The commutators of U and W with H_0 produce new terms to be added to the basic set and so on, producing an, in principle, infinite chain of variables coupled through their commutations with H_0 . One may then look for a truncation procedure; in the present case we note that the commutator of H_0 with U and W leads to terms which are proportional to the fourth power of Q that can be neglected in the limit of small Q, if we assume that only spatial variations associated with long wavelengths are the relevant ones. For the specific case of the carrier system in the HEPS we are considering, it implies, as shown later on, that the quantum of plasma energy $\hbar \omega_p$ is much larger than the average kinetic energy $\hbar v_{th}Q$ (v_{th} is the thermal velocity) involved in the formation of the plasma wave of wavelength $2\pi/Q$ and amplitude n(Q). Hence the choice of H_0 together with Peletminskii-Zubarev symmetry condition and the truncation procedure just stated suggests that the relevant basic set of dynamical quantities to be used are

$$\{H_c, H_{\rm LO}, H_{\rm TO}, H_A, N_a, N_a(\mathbf{Q}), H_a(\mathbf{Q}), \mathbf{P}_a(\mathbf{Q}), \mathbf{I}_a(\mathbf{Q}), \mathbf{\Phi}_a(\mathbf{Q}), \mathbf{\Psi}_a(\mathbf{Q}), \mathbf{U}_a(\mathbf{Q}), \mathbf{W}_a(\mathbf{Q})\},$$
(17)

comprising a total of 46, and we recall that the wave vector **Q** runs over all the reciprocal space, and a = e or h.

The average values of the quantities of Eq. (17) over the nonequilibrium ensemble specified by $\rho_w(t)$ are the set of macroscopic variables, defining a Gibbs space of dimension 46, which characterizes the nonequilibrium thermodynamic state of the system. Such a state may be written in terms of only 22 quantities, which are explicitly given in the Appendix. This contraction is due to the fact that vectorial ones reduce to 12 scalars since only the projection of those quantities in the **Q** direction are relevant; further, $\langle N_e | t \rangle = \langle N_h | t \rangle = n(t)$, because the electrons and holes are produced in pairs.

We look for the undamped oscillatory solutions generated by H_0 —the plasma waves—that result in a steady state for different choices of Gibbs space. This implies that we are considering the case of continuous constant laser illumination of the sample, which leads, after a certain transient, to a steady state (SS) with constant quasitemperature and concentration.^{4(c)} (A description of the calculations is given in the Appendix.)

(i) Following the notation introduced in the Appendix, neglecting Z_{1a} (the local density of energy) and all fluxes, except the linear momentum X_{2a} , we obtain coupled equations for X_{1a} and X_{2a} , which have an oscillatory solution at the plasma frequency

$$\omega_{\rm pl}^2 = 4\pi n e^2 / m_{\rm r} \,, \tag{18}$$

where m_x is the exciton mass, $m_x^{-1} = m_e^{-1} + m_h^{-1}$. Hence, for this particularly contracted Gibbs space used to describe the macroscopic state of the HEPS, we obtain a dispersionless plasma frequency, i.e., the one that corresponds to the infinite-wavelength excitation (uniform polarization).⁵

(ii) Consider now a G space expanded in relation to that of case (i) including Z_{1a} and all the fluxes, namely, X_{2a} , X_{3a} , Z_{2a} , and Z_{5a} . Once this is done and the secular equation solved, we obtain, for the plasma frequency,

$$\omega_{\rm pl}^2(Q) = \omega_{\rm pl}^2 + \frac{3}{2} v_{\rm th}^2 Q^2 .$$
⁽¹⁹⁾

This is the dispersion relation for plasma waves correct up to second order in Q,⁵ where v_{th} is the thermal velocity given by $m_x v_{\text{th}}^2 / 2 = \frac{3}{2} \beta_c^{-1}$.

(iii) When in Gibbs space, besides the ten uniform variables, we incorporate the infinite set of variables

$$n_a(\mathbf{k};\mathbf{Q}) = \operatorname{Tr}(C^{\dagger}_{\mathbf{k}+\mathbf{Q},a}C_{\mathbf{k},a}\rho_w) , \qquad (20)$$

one obtains a secular equation for the plasma-wave dispersion relation that can be reduced to the well-known integral equation⁵

$$1 + V(Q) \sum_{\mathbf{k},a} \frac{f_a^{\rm SS}(\mathbf{k} + \mathbf{Q}) - f_a^{\rm SS}(\mathbf{k})}{\hbar\omega - [\mathbf{k} \cdot (\mathbf{k} + \frac{1}{2}\mathbf{Q})/m_a]} = 0 , \qquad (21)$$

which provides a dispersion relation in all orders of Q. This is equivalent to introducing the infinite set of fluxes of all order which are independent linear combinations of $n_a(\mathbf{k}, \mathbf{Q})$, thus strongly reinforcing, from our statistical point of view, the arguments advanced in favor of EIT for the description of the macrostate of arbitrarily far-from-equilibrium systems. As noted in I, the procedure seems to be a far-reaching generalization, and in the quantum domain, of Grad's 13-moment procedure.

6636

6637

III. EQUATIONS OF EVOLUTION

We have shown in I that the NSOM equations of evolution for the basic set of variables, including the particular case of the fluxes, admit a form which is strictly of the Mori-Langevin-type transport equations. Here we will show how these equations may be brought to a form which resembles more the Maxwell-Cattaneo-Vernotte equation of EIT. This implies the presence of a Maxwell term of the form $\Theta \partial I / \partial t$, where Θ is a relaxation time, besides the terms obtained for the constitutive equation for the energy flux.

It would be natural at this stage to use the system of a HEPS to illustrate this and other of the relevant features of the general transport equations for the macrovariables describing its nonequilibrium states. This, however, stands as a gigantic task since we would have to contend with at least five equations for the fluxes which, as Eq. (18) suggest, would only lead to an approximate picture of the time evolution of the system. Therefore, we will simplify the calculations to a much more manageable system which, although somewhat unrealistic, brings to the fore the main features of the method. Hence we proceed by resorting to a very simple model which consists of a noninteracting Fermi gas with a uniform and constant density n and kinetic energy given by

$$H_0 = \sum_k \varepsilon_k C_k^{\dagger} C_k \quad , \tag{22}$$

where $\varepsilon_k = \hbar^2 k^2 / 2m$, and a system of bosons at constant temperature T_0 and with energy dispersion $\hbar \omega_q$, both systems coupled through the energy interaction operator

$$H' = \sum_{k,q} V_q (b_q^{\dagger} - b_{-q}) C_{k+q}^{\dagger} C_k , \qquad (23)$$

where b (b^{\dagger}) are annihilation (creation) operators in boson states.

We assume that in an EIT approach the macroscopic state of the Fermi gas with constant concentration can be described by the basic set of macrovariables

$$\left\{E_{0}(t), h\left(\mathbf{Q}, t\right), \mathbf{I}(\mathbf{Q}, t)\right\}, \qquad (24)$$

namely, the kinetic energy and Fourier amplitudes of the kinetic energy and its flux, which are the average values over the NSOM ensemble of the quantity of Eq. (22) and those of Eqs. (4b) and (8). This implies that we neglect contributions of all other fluxes that, according to the scheme described in Sec. II, should be included in the equations of evolution. This amounts to a truncation procedure that involves an approximate treatment of the problem.

For this model the auxiliary statistical operator is

$$\rho_{\rm CG}(t,0) = \exp\left[-\phi(t) - \beta(t)H_0 - \sum_{\mathbf{Q}} \left[\beta(\mathbf{Q},t)\hat{h}(\mathbf{Q}) + \alpha(\mathbf{Q},t)\cdot\hat{\mathbf{I}}(\mathbf{Q})\right]\right],\tag{25}$$

where we have introduced the NSOM-intensive variables associated to those of Eq. (24), namely, the reciprocal quasitemperature $\beta(t)$, the Fourier amplitude of the reciprocal of the local temperature $\beta(\mathbf{Q},t)$, and the quantity $\alpha(\mathbf{Q},t)$. Further, $\hat{h}(\mathbf{Q})$ and $\hat{I}(\mathbf{Q})$, with carets, are the dynamical quantities for the Fourier amplitudes of energy and momentum densities.

To calculate the equations of evolution for the variables of Eq. (24), we resort to the NSOM-linear theory of relaxation (LTR) in Zubarev's approach.⁶ We recall that it consists of an approximation in which relaxation processes are accounted for the interactions taken only up to second order in the interaction strengths and the collision operator is Markoffian. If we call Q_i the different variables of the set of Eqs. (24), in their general form these equations are given by

$$\frac{\partial Q_j}{\partial t} = J_j^{(0)}(t) + J_j^{(1)}(t) + J_j^{(2)}(t) , \qquad (26)$$

where

$$J_{j}^{(0)}(t) = \operatorname{Tr}\left[\frac{1}{i\hbar}[P_{j},H_{0}]\rho_{\mathrm{CG}}(t)\right],$$
(27a)

$$J_{j}^{(1)}(t) = \operatorname{Tr}\left[\frac{1}{i\hbar}[P_{j},H']\rho_{\mathrm{CG}}(t)\right],$$
(27b)

$$J_{j}^{(2)}(t) = \left[\frac{1}{i\hbar}\right]^{2} \int_{-\infty}^{0} dt' e^{\epsilon t'} \mathrm{Tr}\{[H'(t'), [H', P_{j}]]\rho_{\mathrm{CG}}(t)\} + \frac{1}{i\hbar} \int_{-\infty}^{0} dt' e^{\epsilon t'} \sum_{k} \frac{\delta J_{j}^{(1)}(t)}{\delta Q_{k}(t)} \mathrm{Tr}\{[H'(t'), P_{k}]\rho_{\mathrm{CG}}(t)\},$$
(27c)

with δ standing for a functional derivative, and the P_j 's are the dynamical quantities associated to the basic variables, i.e., $Q_i(t) = \text{Tr}[P_i\rho(t)]$.

For the particular case of the variables of Eq. (24), the collision integral $J^{(1)}$ vanishes in all three cases and, taking $\hbar = 1$ throughout this section, we obtain

$$\frac{d}{dt}E_{0}(t) = -2\pi \sum_{k,q} \omega_{q} |V_{q}|^{2} [v_{q}f_{k}(1-f_{k+q}) - (v_{q+1})f_{k+q}(1-f_{k})]\delta(\varepsilon_{k+q} - \varepsilon_{k} - \omega_{q}), \qquad (28a)$$

$$\frac{\partial}{\partial t}h(\mathbf{Q},t) = i\mathbf{Q}\cdot\mathbf{I}(\mathbf{Q},t) - \frac{\pi}{m}\sum_{\mathbf{k},\mathbf{q}} \left[\mathbf{q}\cdot(2\mathbf{k}+\mathbf{q}+\mathbf{Q})\right]A(\mathbf{k},\mathbf{q},\mathbf{Q})n_{\mathbf{k}\mathbf{Q}}(t) , \qquad (28b)$$

$$\frac{\partial}{\partial t}\mathbf{I}(\mathbf{Q},t) = \mathbf{J}^{(0)}(\mathbf{Q},t) - \frac{\pi}{2m^2} \sum_{\mathbf{k},\mathbf{q}} \boldsymbol{\xi}(\mathbf{k},\mathbf{q},\mathbf{Q}) A(\mathbf{k},\mathbf{q},\mathbf{Q}) n_{\mathbf{k}\mathbf{Q}}(t) , \qquad (28c)$$

where

$$\xi(\mathbf{k}, \mathbf{q}, \mathbf{Q}) = [\mathbf{k} \cdot (\mathbf{k} + \mathbf{q})] \mathbf{q} + [\mathbf{q} \cdot (\mathbf{k} + \mathbf{q} + \mathbf{Q})] (\mathbf{k} + \mathbf{q}) + [q^{2} + (2\mathbf{k} \cdot \mathbf{Q})] \frac{1}{2} \mathbf{Q} , \qquad (29a)$$

$$A(k, q, Q) = |V_{q}|^{2} \{ [(v_{q} + 1)(1 - f_{k+q}) + v_{q}f_{k+Q}] \delta(\varepsilon_{k+q} - \varepsilon_{k} + \omega_{q}) + [(v_{q} + 1)f_{k+q} + v_{q}(1 - f_{k+q})] \delta(\varepsilon_{k+q} - \varepsilon_{k} - \omega_{q}) \} + \cdots , \qquad (29b)$$

where the ellipsis represents the same term with $k \rightarrow k + Q$,

$$n_{kQ}(t) = \operatorname{Tr}[C_{k+Q}^{\dagger}C_{k}\rho_{\mathrm{CG}}(t,0)], \qquad (30a)$$

$$f_k(t) = \operatorname{Tr}[C_k^{\dagger} C_k \rho_{\rm CG}(t,0)] , \qquad (30b)$$

$$v_q(t) = \operatorname{Tr}[b_q^{\dagger} b_q \rho_{\mathrm{CG}}(t,0)] , \qquad (30c)$$

and

$$\mathbf{J}^{(0)}(\mathbf{Q},t) = \frac{1}{i} \operatorname{Tr}[\boldsymbol{\Psi}(\mathbf{Q})\boldsymbol{\rho}_{\mathrm{CG}}(t,0)] , \qquad (30d)$$

where Ψ is given by Eq. (13) so that

$$\mathbf{J}^{(0)}(\mathbf{Q},t) = \frac{1}{2im^2} \sum_{\mathbf{k}} \left[k^2 (\mathbf{k} \cdot \mathbf{Q}) (\mathbf{k} + \mathbf{Q}) + (\mathbf{k} \cdot \mathbf{Q})^2 \mathbf{k} \right] n_{\mathbf{k}\mathbf{Q}}(t) .$$
(31)

As indicated at the beginning of this section, we restrict the macroscopic description of the system to that provided by the five variables of Eq. (24), that is to say, that ψ and all other higher-order fluxes (**W**, etc., of Sec. II) are not incorporated as basic variables. This truncation procedure requires that in order to close the system of equations of evolution it becomes necessary to give an expression for the quantity $n_{kQ}(t)$ of Eq. (30a) [it appears in Eqs. (28b) and (28c)] in terms of the basic variables. Assuming a small deviation from the homogeneous state, we separate the statistical operator $\rho_{CG}(t,0)$ into two parts, one depending only on the uniform variables and another depending on the nonuniform (**Q**-dependent) variables. This is done using the operator identity

$$e^{-A+B} = \int_0^1 du \ Y(B|u) e^{-uA} B e^{uA} e^{-A}$$
, (32a)

with

$$Y(B|u) = 1 + \int_0^u dx \ Y(B|x)e^{-xA}Be^{xA} , \qquad (32b)$$

where, for our case,

$$A = \phi_0(t) + \beta(t)H_c ,$$

$$B = -\phi_1(t) - \sum_{\mathbf{Q}} \beta(\mathbf{Q}, t)\hat{h}(\mathbf{Q}) - \sum_{\mathbf{Q}} \alpha(\mathbf{Q}, t) \cdot \hat{\mathbf{I}}(\mathbf{Q}) .$$

Here $\phi(t) = \phi_0(t) + \phi_1(t)$ normalizes ρ_{CG} , and $\phi_0(t)$ normalizes the statistical operator describing the homogeneous state, namely,

$$\overline{\rho}_u(t,0) = \exp\left[-\phi_0(t) - \beta(t)H_c(t)\right] .$$

In the regime of small inhomogeneities, we take the first-order approximation in Eq. (32a); i.e., we put Y = 1. Then

$$n_{\mathbf{k}\mathbf{Q}}(t) = \operatorname{Tr}\{C_{\mathbf{k}+\mathbf{Q}}^{\dagger}C_{\mathbf{k}}[1+K_{1}(t,0)]\overline{\rho}_{u}(t,0)\}$$
$$= \operatorname{Tr}[C_{\mathbf{k}+\mathbf{Q}}^{\dagger}C_{\mathbf{k}}K_{1}(t,0)\overline{\rho}_{u}(t,0)], \qquad (33)$$

where

$$K_{1}(t,0) = -\sum_{\mathbf{Q}}' \left[\beta(\mathbf{Q},t)\Delta\hat{h}(\mathbf{Q}) + \alpha(\mathbf{Q},t)\overline{\Delta}\hat{\mathbf{I}}(\mathbf{Q})\right], \qquad (34)$$

with $\Delta A = A - \text{Tr}[A\bar{\rho}_u(t,0)]$. Finally,

$$n_{\mathbf{kQ}}(t) = a(\mathbf{k}, \mathbf{Q}; t)\beta(\mathbf{Q}; t) + \frac{1}{m}a(\mathbf{k}, \mathbf{Q}; t) \left[\mathbf{k} + \frac{\mathbf{Q}}{2}\right] \cdot \alpha(\mathbf{Q}, t) ,$$
(35)

where

$$a(\mathbf{k},\mathbf{Q};t) = \frac{\mathbf{k} \cdot (\mathbf{k} + \mathbf{Q})}{2m} \frac{1 - e^{\beta(t)\Delta\varepsilon}}{\beta(t)\Delta\varepsilon} f_{\mathbf{k}}^{u}(t) [1 - f_{\mathbf{k}+\mathbf{Q}}^{u}(t)] ,$$
(36a)

$$\Delta \varepsilon = \varepsilon_{\mathbf{k}+\mathbf{Q}} - \varepsilon_{\mathbf{k}} \tag{36b}$$

and

$$f_{\mathbf{k}}^{u}(t) = \operatorname{Tr}[C_{\mathbf{k}}^{\dagger}C_{\mathbf{k}}\overline{\rho}_{u}(t,0)] . \qquad (36c)$$

Replacing Eq. (35) in the expression for the flux [average of Eq. (8)], we obtain

$$\mathbf{I}(\mathbf{Q},t) = \boldsymbol{l}_1(\mathbf{Q},t)\boldsymbol{\beta}(\mathbf{Q},t) + \boldsymbol{l}_2(\mathbf{Q},t)\boldsymbol{\alpha}(\mathbf{Q},t) , \qquad (37)$$

where

$$l_1(\mathbf{Q},t) = \frac{1}{8m^2} \sum_{\mathbf{k}} \left[\mathbf{k} \cdot (2\mathbf{k} + \mathbf{Q}) \right] a(\mathbf{k},\mathbf{Q};t)(2\mathbf{k} + \mathbf{Q}) , \quad (38a)$$

6638

(38b)

$$l_2(\mathbf{Q},t) = \frac{1}{16m^2} \sum_{\mathbf{k}} \left[\mathbf{k} \cdot (2\mathbf{k} + \mathbf{Q}) \right] |2\mathbf{k} + \mathbf{Q}|^2 a(\mathbf{k},\mathbf{Q};t)$$

perature, namely,

$$\boldsymbol{\alpha}(\mathbf{Q},t) = \boldsymbol{l}_2^{-1}(\mathbf{Q},t)\mathbf{I}(\mathbf{Q},t) - \boldsymbol{l}_2^{-1}(\mathbf{Q},t)\boldsymbol{l}_1(\mathbf{Q},t)\boldsymbol{\beta}(\mathbf{Q},t) , \quad (39)$$

and the isotropy of the model makes l_2 a scalar instead of a tensor.

Equation (37) allows us to write the "generalized drift velocity" α in terms of the flux and reciprocal quasitem-

and then

$$n_{\mathbf{k}\mathbf{Q}}(t) = G_1(\mathbf{k},\mathbf{Q};t)\beta(\mathbf{Q},t) + G_2(\mathbf{k},\mathbf{Q};t)\cdot\mathbf{I}(\mathbf{Q},t) , \quad (40)$$

where

$$G_1(\mathbf{k},\mathbf{Q};t) = a(\mathbf{k},\mathbf{Q};t) \left[1 - \frac{1}{2m} l_2^{-1}(\mathbf{Q},t) l_1(\mathbf{Q},t) \cdot (2\mathbf{k} + \mathbf{Q}) \right]$$
(41a)

and

$$\mathbf{G}_{2}(\mathbf{k},\mathbf{Q};t) = \frac{1}{2m} a(\mathbf{k},\mathbf{Q};t) l_{2}^{-1}(\mathbf{Q},t)(2\mathbf{k}+\mathbf{Q}) .$$
(41b)

Replacing the expression for $n_{kQ}(t)$ given by Eq. (40) in the equations of evolution [Eqs. (28b) and (28c)], we find

$$\frac{\partial}{\partial t}h(\mathbf{Q},t) = i\mathbf{Q}\cdot\mathbf{I}(\mathbf{Q},t) - A_{1}(\mathbf{Q},t)\beta(\mathbf{Q},t) - \mathbf{A}_{2}(\mathbf{Q},t)\cdot\mathbf{I}(\mathbf{Q},t) , \qquad (42)$$

$$\frac{\partial}{\partial t}\mathbf{I}(\mathbf{Q},t) = i\mathbf{B}_{1}(\mathbf{Q},t)\beta(\mathbf{Q},t) + iB_{2}(\mathbf{Q},t)\cdot\mathbf{I}(\mathbf{Q},t) - \mathbf{C}(\mathbf{Q},t)\beta(\mathbf{Q},t) - \Theta^{-1}(\mathbf{Q},t)\mathbf{I}(\mathbf{Q},t) , \qquad (43)$$

where

$$A_1(\mathbf{Q},t) = \frac{\pi}{m} \sum_{\mathbf{k},\mathbf{q}} \left[\mathbf{q} \cdot (2\mathbf{k} + \mathbf{q} + \mathbf{Q}) \right] A(\mathbf{k},\mathbf{q},\mathbf{Q}) G_1(\mathbf{k},\mathbf{Q};t) , \qquad (44a)$$

$$\mathbf{A}_{2}(\mathbf{Q},t) = \frac{\pi}{m} \sum_{\mathbf{k},\mathbf{q}} \left[\mathbf{q} \cdot (2\mathbf{k} + \mathbf{q} + \mathbf{Q}) \right] A(\mathbf{k},\mathbf{q},\mathbf{Q}) \mathbf{G}_{2}(\mathbf{k},\mathbf{Q};t) , \qquad (44b)$$

$$\mathbf{B}_{1}(\mathbf{Q},t) = \frac{1}{2m^{3}} \sum_{\mathbf{k}} \left[k^{2}(\mathbf{k} \cdot \mathbf{Q})(\mathbf{k} + \mathbf{Q}) + (\mathbf{k} \cdot \mathbf{Q})^{2} \mathbf{k} \right] G_{1}(\mathbf{k},\mathbf{Q},t) , \qquad (44c)$$

$$B_{2}(\mathbf{Q},t)\cdot\mathbf{I}(\mathbf{Q},t) = \frac{1}{2m^{3}} \sum_{\mathbf{k}} \left[k^{2}(\mathbf{k}\cdot\mathbf{Q})(\mathbf{k}+\mathbf{Q}) + (\mathbf{k}\cdot\mathbf{Q})^{2}\mathbf{k}\right] \left[\mathbf{G}_{2}(\mathbf{k}\cdot\mathbf{Q},t)\cdot\mathbf{I}(\mathbf{Q},t)\right], \qquad (44d)$$

$$\mathbf{C}(\mathbf{Q},t) = \frac{\pi}{2m^2} \sum_{\mathbf{k},\mathbf{q}} \boldsymbol{\xi}(\mathbf{k},\mathbf{q},\mathbf{Q}) A(\mathbf{k},\mathbf{q},\mathbf{Q}) G_1(\mathbf{k},\mathbf{Q};t) , \qquad (44e)$$

$$\widehat{\Theta}^{-1}(\mathbf{Q},t)\mathbf{I}(\mathbf{Q},t) = \frac{\pi}{2m^2} \sum_{\mathbf{k},\mathbf{q}} \xi(\mathbf{k},\mathbf{q},\mathbf{Q}) A(\mathbf{k},\mathbf{q},\mathbf{Q}) [\mathbf{G}_2(\mathbf{k},\mathbf{Q};t) \cdot \mathbf{I}(\mathbf{Q},t)] , \qquad (44f)$$

with ξ and A given by Eqs. (29a) and (29b).

Concerning these two equations, it is worth noticing that they are Markovian in character because of the use of the LTR, given by Eqs. (26). An extension of the theory beyond LTR is possible, as described elsewhere,⁷ so that the equations would also contain information on the past history of the system. However, the formalism of Ref. 7 allows for a transformation of the collision operators that include aftereffects in terms of an infinite series of instantaneous collision integrals, so that the structure of Eqs. (33) is maintained; this is planned to be shown in a future paper. On the other hand, these equations are nonlocal in space, but we recall, in the regime of small inhomogeneities.

Multiplying Eq. (43) by $\Theta(\mathbf{Q}, t)$, neglecting the terms with coefficients B_2 and C, and taking the quasistatic limit $\partial \mathbf{I}/\partial t \simeq 0$, one obtains in configuration space a nonlocal

constitutive equation of the form

$$\mathbf{I}(\mathbf{r},t) = -\int d^{3}r'\kappa(\mathbf{r}-\mathbf{r}';t)\nabla'T(\mathbf{r}',t) , \qquad (45)$$

once we interpret $\beta(\mathbf{Q}, t)$ as the Fourier transform of the reciprocal of a local temperature. Clearly, κ may be here regarded as the nonlocal thermal conductivity. This question, as well as the interpretation of the terms with coefficients C and B are planned to be discussed in detail in a future communication.

So far, given the simplicity of the model, we are still left with rather complicated expressions involving the wave vectors \mathbf{Q} , \mathbf{k} , and \mathbf{q} . We further simplify them by considering the limit of very long wavelengths, i.e., small values of Q. We take the limit of Q going to zero, retaining everywhere only terms up to first order in Q in the expressions for the collision integrals, and, under these conditions, using the fact that for this isotropic model summations over \mathbf{k} and \mathbf{q} containing contributions odd in these vectors vanish, we obtain the equation of evolution for the flux, namely,

$$\frac{\partial}{\partial t}\mathbf{I}(\mathbf{Q},t) = -i\mathbf{Q}A(t)\beta(\mathbf{Q},t) - \Theta^{-1}(t)\mathbf{I}(\mathbf{Q},t) , \qquad (46)$$

where

$$A(t) = \frac{1}{4m^3} \sum_{\mathbf{k}} k^6 f_{\mathbf{k}}^u(t) [1 - f_{\mathbf{k}}^u(t)] , \qquad (47a)$$

$$\Theta^{-1}(t) = \frac{\pi}{12m^3} \sum_{\mathbf{k},\mathbf{q}} A(\mathbf{k},\mathbf{q}) q^2 k^2 f_k^u (1 - f_k^u) , \qquad (47b)$$

which is independent of Q and plays the role of the reciprocal of the relaxation time; coefficients B_2 and C, which are of order Q^2 have been neglected.

Equation (46) can be rewritten as

$$\Theta(t)\frac{\partial}{\partial t}\mathbf{I}(\mathbf{Q},t) = \Lambda(t)[-i\mathbf{Q}\beta(\mathbf{Q},t)] - \mathbf{I}(\mathbf{Q},t) , \qquad (48)$$

where

$$\Lambda(t) = \Theta(t) A(t) . \tag{49}$$

Taking for f^{u} a Maxwell distribution for the fermion system with concentration *n* and reciprocal temperature $\beta(t)$, the coefficient *A* becomes

$$A(t) = 35n / 8m\beta^{3}(t) .$$
 (50)

Inverting Eq. (48) to the direct space, we find that

$$-\Theta(t)\frac{\partial}{\partial t}\mathbf{I}(\mathbf{r},t) = \frac{35n}{8m}k^2\frac{T^3(t)}{T^2(\mathbf{r},t)}\Theta(t)\nabla T(\mathbf{r},t) + \mathbf{I}(\mathbf{r},t)$$
(51)

(k here is the Boltzmann constant).

If, consistently, we consider weak spatial variation, we can make the approximation $T(\mathbf{r}, t) \simeq T(t)$, and then the coefficient in front of the gradient of the temperature becomes

$$\kappa = \frac{35n}{8m} k^2 T(t) \Theta(t) , \qquad (52)$$

which can be identified with the thermal conductivity. It has a form that closely resembles that of kinetic theory, namely,

$$\kappa = \frac{1}{2} C \overline{v}^2 \tau , \qquad (53)$$

where C is the specific heat of the fermions, \overline{v} their average velocity, and τ the average time between collisions with the scattering centers. On the other hand, if we identify Θ with τ —in the classical limit—we find a close identification of Eqs. (52) and (53), except for a numerical factor $\frac{12}{35}$ (near $\frac{1}{3}$). This numerical difference is ascribed to the truncation method and approximations we have introduced in dealing with this model. Further, it ought to be stressed that in our result $\Theta(t)$ is not an undetermined parameter since its explicit value may be computed from Eq. (44f).

We see that Eq. (51) is precisely of the type of the

Maxwell-Cattaneo-Vernotte equations of EIT. In the quasistatic regime we recover from Eq. (51) the constitutive equation of hydrodynamics:

$$\mathbf{I}(\mathbf{r},t) = -\kappa(t) \nabla T(\mathbf{r},t) , \qquad (54)$$

except that it depends on the instantaneous macroscopic state of the system at time t. Finally, it should be noted that the relaxation time for the flux of energy in the Maxwell-Cattaneo-Vernotte-like equation (40) can be identified with the one that appears in the expression for the thermal conductivity.

IV. CONCLUSIONS

We have shown that for the particular case of a highly excited plasma [with a Coulomb interaction dealt with in the random-phase approximation (RPA)], similarly to the case of propagation of sound waves in fluids⁸ treated in the linear irreversible thermodynamics approach, an incorrect dispersion relation for a collective excitation (plasma waves) follows from the incompleteness of the associate Gibbs space. A correct (RPA) dispersion relation, up to second order in the wave vector Q, is obtained [case (ii) in Sec. III] with the quantum-mechanical nonequilibrium equivalent of Grad's 13-moment approach.⁹ The complete (RPA) plasmon dispersion relation is obtained using the infinite set of momenta [case (iii) in Sec. III].

The equations of motion for the macroscopic variables $Q_i(t)$ are derived for the case of a simple model and have the structure of nonlinear and nonlocal transport equations. Their structure is too complicated to be analyzed in general, but for small deviations from the homogeneous state they reduce to those derived by other methods. We also show how these equations fit into a natural extension of linear irreversible thermodynamics as it has been conceived by some authors.^{10,11} In particular, the Maxwell-Cattaneo-Vernotte-type equations are recovered with relaxation times and transport coefficients that may, in principle, be calculated from the microscopic dynamics of the system averaged over the coarse-grained probability density $\rho_{CG}(t)$ of the NSOM. We have explicitly obtained the transport equation for the energy flux to generalize Fourier's well-known constitutive equation for the heat flux, with an explicit value for the thermal conductivity which closely agrees with that computed from the relaxation-time approximation of the kinetic theory of gases.

ACKNOWLEDGMENTS

The authors acknowledge financial support from São Paulo State Research Agency, FAPESP (L.G.C.), and Brasil National Research Council, CNPq (A.R.V., R. L.).

APPENDIX: PLASMA DISPERSION RELATIONS

As noted in the main text, the 46 basic variables of Eq. (17) reduce to 22, for practical purposes, since in the equations of evolution there appear only the projection of the 10 vectorial ones in the **Q** direction. We write for them

$$Q_{1}(t) = \langle H_{c} | t \rangle, \quad Q_{2}(t) = \langle H_{LO} | t \rangle,$$

$$Q_{3}(t) = \langle H_{TO} | t \rangle, \quad Q_{4}(t) = \langle H_{A} | t \rangle,$$

$$Q_{5}(t) = \langle N_{e} | t \rangle, \quad Q_{6}(t) = \langle N_{h} | t \rangle,$$

$$X_{1a}(t) = \langle N_{a}(\mathbf{Q}) | t \rangle,$$

$$X_{2a}(t) = (\mathbf{Q}/m_{a}) \cdot \langle \mathbf{P}_{a}(\mathbf{Q}) | t \rangle,$$

$$Z_{1a}(t) = \langle H_{c}(\mathbf{Q}) | t \rangle,$$

$$Z_{1a}(t) = \langle H_{c}(\mathbf{Q}) | t \rangle,$$

$$Z_{3a}(t) = (\mathbf{Q}/m_{a}) \cdot \langle \mathbf{I}_{a}(\mathbf{Q}) | t \rangle,$$

$$Z_{4a}(t) = (\mathbf{Q}/m_{a}) \cdot \langle \mathbf{W}_{a}(\mathbf{Q}) | t \rangle,$$

$$Z_{5a} = (\mathbf{Q}/m_{a}) \cdot \langle \mathbf{W}_{a}(\mathbf{Q}) | t \rangle.$$
(A1)

(i) Considering only Q_1-Q_6 and the inhomogeneous variables X_{1a} and X_{2a} , we find the evolution equations under H_0 :

$$\frac{d}{dt}X_{1a} = iX_{2a}/m , \qquad (A2a)$$

$$\frac{d}{dt}X_{2a} \simeq iV(\mathbf{Q})nX_{1a} , \qquad (A2b)$$

where $V(Q) = 4\pi e^2 / \epsilon_0 Q^2$. The secular equation for the oscillating solutions is a determinant A of fourth order with ω in each diagonal term and elements

$$A_{13} = A_{14} = A_{23} = A_{24} = A_{31} = A_{32} = A_{41} = A_{42} = 0,$$

and $A_{12} = m_e^{-1}$, $A_{21} = nV(Q)$, $A_{34} = m_h^{-1}$, $A_{43} = nV(Q)$,
 $A_{34} = m_h^{-1}$, and $A_{43} = nV(Q)$, which has the solution

- ¹A. R. Vasconcellos, R. Luzzi, and L. Garcia-Colin, preceding paper, Phys. Rev. A 43, 6622 (1991).
- ²R. Zwanzig, Annu. Rev. Phys. Chem. 16, 67 (1965); Kinam 3, 5 (1981); in *Perspectives in Statistical Physics*, edited by H. J. Ravechè (North-Holland, Amsterdam, 1981).
- ³E.g., A. Elci, M. O. Scully, A. L. Smirl, and J. C. Matter, Phys. Rev. B 16, 191 (1977).
- ⁴R. Luzzi and A. R. Vasconcellos, in Semiconductors Probed by Ultrafast Laser Spectroscopy, edited by R. R. Alfano (Academic, New York, 1984), Vol. I, p. 135; A. C. Algarte and R. Luzzi, Phys. Rev. B 27, 7563 (1983); T. Tomé, A. R. Vasconcellos, and R. Luzzi, Physica B 144, 376 (1987); V. N. Freire, A. R. Vasconcellos, and R. Luzzi, Phys. Rev. B 39, 13264 (1989).
- ⁵D. Pines, Elementary Excitations in Solids (Benjamin, New

 $\omega^2 = \omega_{pl}^2 = 4\pi n e^2 / m_x$, where $m_x^{-1} = m_e^{-1} + m_h^{-1}$, shown in Eq. (18).

(ii) Consider now the 22 quantities of Eq. (A1). The 16 equations of motion for the nonhomogeneous quantities X's and Z's lead to a secular equation in the form of a determinant of that order. To obtain a dispersion relation for plasma waves up to second order in Q, we neglect the equation for Z_{5a} that produces terms of order Q^4 . We omit to write down the extensive expressions for the equations of motion for the 14 remaining variables in the chosen Gibbs space and the accompanying determinant for the secular equation, only noting that straightforward algebra leads to the dispersion relation of Eq. (19).

(iii) The complete dispersion relation for the plasma waves follows by taking quantities $n_a(\mathbf{k}, \mathbf{Q}) = C_{\mathbf{k}+\mathbf{Q}a}^{\dagger} C_{\mathbf{k}a}$ as basic variables, and then their equations of evolution are

$$\frac{d}{dt}n(\mathbf{k},\mathbf{Q}) = i\Delta\varepsilon^{a}_{\mathbf{k}\mathbf{Q}}n_{a}(\mathbf{k},\mathbf{Q}) - iV(\mathbf{Q})$$
$$\times\Delta f_{a}(\mathbf{k},\mathbf{Q})\sum_{\mathbf{k}',b}n_{b}(\mathbf{k}',\mathbf{Q}) , \qquad (A3)$$

where

$$\Delta \varepsilon_{\mathbf{k}\mathbf{Q}}^{a} = \varepsilon_{\mathbf{k}+\mathbf{Q}}^{a} - \varepsilon_{\mathbf{k}}^{a} ,$$

$$\Delta f_{a}(\mathbf{k},\mathbf{Q}) = f_{a}^{SS}(\mathbf{k}+\mathbf{Q}) - f_{a}^{SS}(\mathbf{k})$$

Transforming Fourier in the time variable, we get

$$(\omega - \Delta \varepsilon_{\mathbf{kQ}}^{a}) n_{a}(\mathbf{k}, \mathbf{Q}) = -\Delta f_{\mathbf{kQ}} V(\mathbf{Q}) \sum_{\mathbf{k}, b} n_{b}(\mathbf{k}, \mathbf{Q}) .$$
(A4)

Dividing by $\omega - \Delta E$ and summing over k and a, we obtain the well-known integral equation for the plasma dispersion relation, namely, Eq. (21) in Sec. II.

York, 1964).

- ⁶D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Plenum, New York, 1974).
- ⁷L. Lauck, A. R. Vasconcellos, and R. Luzzi, Physica A 168, 789 (1990).
- ⁸J. D. Foch, Jr., and G. M. Ford, in *Studies in Statistical Mechanics V*, edited by J. de Boer and G. E. Ulhenbeck (North-Holland, Amsterdam, 1970).
- ⁹H. Grad, *Principles of the Kinetic Theory of Gases*, edited by S. Függe, Handbuch der Physik, Vol. XII (Springer, Berlin, 1958).
- ¹⁰D. Jou, J. Casas-Vazquez, and G. Lebon, Rep. Prog. Phys. 51, 1105 (1988).
- ¹¹L. S. Garcia-Colin, Rev. Mex. Fís. 34, 344 (1988).