Hot-electron relaxation in dense ‘two-temperature’ hydrogen.

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Recent theories of hot-electron relaxation in dense hydrogen or deuterium are examined in the light of recent molecular-dynamics simulations as well as various theoretical developments within the two-temperature model. The theoretical work since 1998 has led to the formulation of the f-sum version of the Fermi Golden rule formula as the most convenient method for the calculation of the rate of energy loss. The attempt to include relaxation via the ion-acoustic modes of the two coupled subsystems, i.e., electrons and ions has led to a coupled-mode formulation which has been established by a variety of formal methods. However, various simplified calculational models of the system with coupled-modes, as well as sophisticated molecular dynamics simulations seem to disagree. It is expected that coupled-mode calculations which use the simple Coulomb potential $V_{ei}(r) = -|e|Z/r$ for the electron-ion interaction within RPA will greatly over-estimate the coupled-mode contribution. A weak pseudopotential $U_{ei}(r)$ would probably bring the estimated coupled-mode contribution to agree with that obtained by simulations. It is also suggested that the available ‘reduced models’ have been constructed without much attention to the satisfaction of important sum rules, Kramers-Kröning relations etc. We also deal with the question of how strongly coupled ion-ion systems can be addressed by an extension of the second-order linear response theory which is the basis of current formulations of energy relaxation in warm-dense matter systems. These are of interest in a variety of fields including hot-electron semi-conductor devices, inertial-fusion studies of hot compressed hydrogen, as well as in astrophysical applications.

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INTRODUCTION

Deuterium and tritium mixtures are used in the inertial-confinement approach to fusion where energy is deposited into an imploding capsule creating a system of hot electrons and relatively cold ions [1]. The same issues arise in semiconductor- or solid-state plasmas created using short-pulse lasers [2]. If a two-temperature (2T) quasi-equilibrium model can be used, an electron temperature $T_e$ and an ion temperature $T_i$ are specified where the temperatures are effectively Lagrange multipliers associated with the conservation of energy in the two subsystems (electrons and ions) over the relevant time scales; the timescale is set by the energy-relaxation time $\tau_{ei}(E)$. At sufficiently high temperatures $T_e$ (i.e., compared to the electron Fermi energy $E_F$), the energy-relaxation time is proportional to the temperature relaxation time $\tau_{ei}(T_e)$ and hence the discussion is couched approximately in terms of temperature relaxation rates $dT_e/dt$, where we assume that the cooler system, (viz., the ions) to be attached to a heat bath held at the temperature $T_i$. Alternative assumptions can be made, including the use of two heat baths for the two subsystems, when the physics becomes substantially different.

The fusion capsules are made up of an outer ablation layer containing an admixture of substances that produce high-$Z$ ions, where $Z$ is the mean ionization (the number of free electrons per ion). For instance, plastic ablation layers produce $Z \geq 4$ carbon ions at the compressions and temperatures encountered in the problem. Thus the simulation of these systems brings us to the complex question of energy relaxation of ions of arbitrary charge $Z$ at temperatures $T_i$ interacting with electrons at an elevated temperature $T_e$. The traditional approach to this problem, stemming from the days of Landau, is to use a classical-trajectory approach treating binary collisions among particles, and allowing for the Coulomb interaction by a ‘cutoff’, leading to the so-called Coulomb Logarithm (e.g., see Chapter 4, Ref. [3]). This approach to energy relaxation (ER) is implemented in the MD-simulations of Hanson and McDonald [4], while a more extended theoretical analysis (which essentially supported the standard results) was given by Boereker and More in 1986 [5] and was reviewed in the appendix to Ref. [6].

However, the usual classical trajectory approach is rather limited. Since the particles interact via potentials whose long-range part is Coulomb-like, the essential excitation modes of the system contain not only particle-particle ‘binary’ interactions, but mostly interactions via their collective modes, i.e., plasmons. The plasmon modes essentially saturate the $f$-sum rule (which totals up the number of modes), and hence the particle character is subsumed under the collective modes which dominate the physics. Furthermore, the collective modes themselves interact and produce hybrid modes. In the case of electron-ion systems, the large mass difference ($M_i \gg m_e$) implies that electrons follow the ions essentially ‘instantly’, and screen their charge-density fluctuations to create ion-acoustic modes that are well known in solids, liquid metals and in semi-conductor plasmas. They were also recognized in plasmas already in the 1930s.
in the work of Silin et al. [7]. Unlike in electron-hole plasmas or in semiconductors, the electron-like excitations and ion-like excitations remain well separated since the ion mass $M_i \gg m_e$. Nevertheless, a complete theory of energy-relaxation in these systems should take account of collective modes as well as their coupled modes in a self-consistent manner. Furthermore, experiments in semiconductor plasmas had clearly shown that ER-rates of hot-electron cooling were significantly slower than those predicted by the simple Fermi Golden rule (FGR) based on the energy transfer from hot-electron plasmons to cold-ion phonons (ion-density fluctuations). Similar, but less clear evidence existed for slower energy relaxation in plasmas as well [8].

As even the FGR calculation had not been used in ER calculations for dense plasmas, the present author attempted to publish such a theory entirely within a quantum approach in 1996, using the two-particle nonequilibrium Green’s functions to formulate a consistent theory; but this was rejected by journal referees who held that a two-particle theory to be inconsistent with the well-established trajectory approach which (they claimed) clearly implied a ‘one-particle’ approach for ER in dense plasmas. However, two years later a longer paper was published jointly with Perrot [9] presenting the FGR as well as the coupled-mode expressions for ER. The present-day reader of that the paper may note a (seemingly irrelevant) running discussion about the inapplicability of the one-body propagator to energy relaxation problems, due to the earlier abortive debate with journal referees well anchored in classical trajectory calculations. Today most workers accept that the excitation modes of the two-particle propagator and their damping hold the key to ER rates.

The analysis of Ref. [6] suggested that simple estimates based on binary-collisions with Coulomb cutoffs, or more systematic treatments using the Fermi golden rule, but neglecting the screening of the ion excitations by the electron excitations (i.e., coupled modes, $cm$) would predict ER-rates larger than what is physically correct. In effect, the ‘neutral-pseudo atoms’ (NPA) formed by the ions screened by the hot electrons were objects intermediate in temperature to $T_i, T_e$ and hence the ER-rate is significantly slowed down. The hybrid plasmons made up of electron-density excitations as well as ion-density excitations are the coupled modes. The effective coupled-mode temperatures $T_{cm}(\omega)$ are also dependent on the mode energy $\omega$: thus for instance, when $\omega \to \omega_c$, where $\omega_c$ is the electron plasma frequency, then $T_{cm} \to T_e$. However, unlike with room temperature materials, obtaining accurate ER-rates for warm-dense matter (WDM) systems is even more difficult than obtaining accurate electrical conductivity data for WDMs. Calculating reliable conductivities themselves for WDM, e.g., via density-functional theory (DFT), molecular dynamics (MD) and the Kubo-Greenwood formula requires, even for a simple metal like sodium, a simulation involving over a 1000 atoms and many $k$-points, of the order of 50-60 points [9]. Hence the challenge for carrying out reliable simulations of energy relaxation is even greater.

Meanwhile, plasma kinetic-theory methods that are more familiar to the WDM community were deployed to study the ER-rates in $2T$ quasi-equilibrium systems. Unlike the Lenard-Balescu method, the Klimontovich approach pays attention to both kinetic and potential energy terms in the dynamics. Rosenfeld had derived the coupled-mode equations of ER using Klimontovich’s methods [10] and found its numerical implementation quite demanding. At the time, the present author was looking into implementation of the $f$-sum rule and other sum rules in ER-calculations. Hence we began to examine them as a means of simplifying the FGR and the $cm$-formulations. Not surprisingly, it was not possible to apply the $f$-sum rule to the coupled-mode problem but the FGR calculations were greatly simplified [11]. Some time later the Lenard-Balescu (LB) equations were used by Gericke et al. [12, 13] who also arrived at coupled-mode effects within an LB formulation. In such kinetic theories, and in Zubarev’s real-time green’s function method, since the intermediate frequency integrations are ‘already done’, vertex corrections and self-energies are partitioned in a different way and it is not easy to bring in our experience from standard many-body theory to the kinetic-theory methods. On the other hand, since we are dealing with nonequilibrium systems where many things are unclear, the reexamination of the problem via a variety of methods is necessary.

Nevertheless, at the level of coupled modes (but without vertex corrections, LFCs etc.), the various theories are in agreement. The disagreement seems to reside in the question of when $cm$ become relevant and possible differences in various different theories themselves, e.g., as discussed in Daligault et al. [14]. Usually, in a many-body theory, whether $cm$ is important or not is taken care of by the theory itself thorough the interplay between the real and imaginary parts of the excitation modes. But it is relevant in computations for avoiding the heavy cost of implementing the full theory. Given the difficulty of obtaining experimental ER-rates, theorists have turned to non-equilibrium molecular dynamics (MD) simulations to determine ER-rates for comparing theory with numerical ‘experiments’ [1, 4, 14, 16]. This is non-trivial since the usual Born-Oppenheimer approximation is no longer available to simplify the simulations. The simulation results regarding coupled modes seem to lead to contradictory conclusions. Furthermore, some kinetic-theory analyses have given ER-rates larger than from FGR, while most theorists agree with our earlier analysis [6] that the presence of coupled modes reduces the rate of energy relaxation, using quite improved numerical computations.

The objective of this review is to examine these con-
clusions and shed some light on the implementation of coupled modes in ER rate calculations. The work of Daligault et al. is interesting since the simulation of ER in a plasma of like charges (‘repulsive hydrogen’) removes the many uncertainties associated with using the so-called quantum statistical potentials (QSP), e.g., as used by Hansen and McDonald in Ref. 4, to control attractive electron-ion interactions. It will be shown that the equations used by Daligault and Dimonte (DD) are in agreement with the equations given by the author and Perrot in Ref. 6, although DD have claimed it to be otherwise. This agreement holds both in the quantum regime, and in the classical regime. The contrary conclusion of DD is partly due to shortcomings in our proof reading, although the information is clear from a number of explanatory subsections and an appendix. Furthermore, their different point of view regarding the description of two-temperature ultra-fast matter has led to their ‘self-consistent’ formulation which seems to us to be inappropriate unless a two-thermostat 2T system is envisaged, as will be discussed below.

ENERGY RELAXATION BY PLASMON MODES.

A Coulomb system with free electrons and ions can have electron plasmons and ion plasmons, and their coupled modes. The ion-electron coupled mode manifests as the ion-acoustic modes of the plasma. Some authors have used Gordeev’s criterion 17 for the existence of well-defined propagating ion-acoustic waves ($T_e \gg T_i$) for determining the relevance of coupled modes (ion-acoustic waves) to ER. Vorberger et al. 18 have suggested more specific limits ($T_i \leq 0.27ZT_e$) involving the mean ionization $Z$ of the ions. The mean ionization is simply the number of free electrons per ion, and is a well-defined physical quantity although some authors have (incorrectly) questioned the very concept of a mean ionization 19. The criteria of Gordeev, or Vorberger et al. attempts to minimize the damping of the ion-acoustic mode, i.e., to have minimal overlap between the phase velocities of the ion-acoustic waves and the particles, ensuring that a minimally damped ion-acoustic wave propagates in the plasma. However, in our view these are precisely the conditions where the ion-acoustic waves do not participate significantly in energy relaxation. Hence MD-simulations which focus on this regime should show negligible contributions to the ER rate from coupled modes. In fact, when ion-acoustic modes participate in ER, then they are likely to be damped by the very relaxation process which is due fundamentally to the electron-ion interaction which also causes the coupled mode.

The Gordeev criterion $T_e \gg T_i$, with $\Delta T = T_e - T_i$ large attempts to reduce the damping of the ion-acoustic modes, but its action is somewhat like throwing the baby out with the bath water. While the damping in the ion-acoustic mode decreases as $T_e$ is increased, the ion contribution to the coupled mode also decreases rapidly, and the coupled mode simply becomes a product of two independent modes at higher $T_e$. Another factor that has to be considered is the energy relaxation time. The relaxation time is proportional to $\Delta T$, and hence, for sufficiently large $T_e$, the relaxation time may be too short for a collective mode to be formed, unless a system with two thermostats is envisaged. That is, the very high $T_e$ limit reduces to the Landau Spitzer limit, as evident from Hazak et al. 11. The relevant regime for ER via coupled modes is the overlap region of the very low-frequency regime of electron excitations and the high-frequency range of ion excitations, together with the need for sufficiently long ER times since coupled modes need a certain amount of time to build up and dissipate. The latter problem does not arise if the system being studied is controlled by two thermostats, where the upper thermostat maintains the electrons at the steady state $T_e$, while the lower thermostat maintains the ions at $T_i$. Such a system can be realized in practice if hot electrons are pulse pumped into the conduction band of a semiconductor, while the ion lattice is coupled to a thermostat. In WDM systems, short-pulsed lasers pulsed at an appropriate rate can raise the electrons to $T_e$, while the ions remain at their initial state for short time scales $t < \tau_{ei}$. Such a 2T ultra-fast matter (FM) can be studied optically with probe lasers deployed immediately after the pump pulse, with a delay exceeding the subsystem equilibration times $\tau_e, \tau_i$ which serve to set up the subsystem temperatures $T_e, T_i$. Only one thermostat (for the ions) is assumed in such studies.

In the following we examine the FGR and coupled mode formulae, keeping in mind the LB-kinetic theory results as well as the MD-simulations results for ER.

A review of ER-models at the Fermi Golden rule level.

In order to compare and contrast the available theoretical models, we summarize the basic theory for our convenience.

Assuming that $T_e > T_i$ to be specific, ER occurs via energy transfer from the excited modes of the electron sub-system to the cold modes in the ion subsystem which may be assumed to be connected to a heat bath without loss of generality. We do not assume a heat bath at the upper temperature, but assume that the experiments are done duing timescales $(\tau_e, \tau_i) \ll t \ll \tau_{ei}$.

The spectral densities of the modes of the species $j = e, i$ are given by the spectral functions $A_j(q, \omega, T_j)$. The spectral functions are essentially the dynamic structure factors $S_j(k, \omega)$ of each subsystem, accessible experimentally using optical experiments. We use only one sub-
script, e.g., $A_j$ when we mean $A_{ij}$, when there is no ambiguity. The spectral functions are given by the imaginary parts of the corresponding dynamic response functions $\chi_j(\vec{k}, \omega)$, e.g., Eq. (16) of Ref. [11]. If the electron-ion interaction $V_{ei}(r)$ is weak, then the Fermi Golden rule and other methods based on linear-response theory can be used. For this purpose the electron-ion interaction $V_{ei}(q)$ cannot be taken as $-\mathcal{Z}V_q$, $V_q = 4\pi/q^2$ except in the Gell-Mann–Brueckner (quantum) limit. Coulomb collisions, be they classical or quantum, require regularization both at short range, and at long range. Hence the use of a pseudopotential $U_{ei}(r)$ which behaves as the Coulomb potential for $r > r_c$, and regularized for $r < r_c$, where $r_c$ is effectively the core radius of the ion is needed. Even with hydrogen, although it has no bound-electron core for the conditions of interest, such a form is needed since the electron pile up very close to the nucleus is highly non-linear. The long-range of the potential will be corrected automatically in the theory by screening effects of other particles. The construction of these pseudopotentials using the NPA-average atom (AA) model was discussed in sec. II of Ref. [3], and will be summarized here for the convenience of the reader (see sec. ). In kinetic-equation methods a short-range local-field-correction (LFC) $G_{ei}$ is invoked via the factor $\{1 - G_{ei}(k, \omega^0)\}$ estimated from HNC equations, to provide some sort of pseudopotential.

Fermi Golden rule results.

The ER rate evaluated within the Fermi golden rule, $R_{fgr}$, can be expressed in terms of the response functions of the plasma as given in Eqs. (4)-(7) of DWP, Ref. [20], and Eq. (12) of Hazak et al., Ref. [11]. The imaginary part of the response function gives the mode spectrum, or spectral function $A_j(k, \omega)$.

$$A_j(q, \omega, T_j) = -2\Im \chi_{jj}(q, \omega, T_j)$$

$$\chi_{jj}(q, \omega, T_j) = \chi_{jj}^0 / (1 - V_{jj}(q)[1 - G_{jj}]\chi_{jj}^0)$$

Furthermore,

$$R_{fgr} = \frac{\delta E}{\delta t} = 2 \int \frac{d^3k}{(2\pi)^3} \frac{\omega d\omega}{2\pi} (\Delta N) F_{ei}$$

$$\Delta N = N(\omega/T_e) - N(\omega/T_i)$$

$$N(\omega/T_j) = 1/\exp^{\omega/T_j} - 1$$

$$\Delta N = (1/2)\{\coth(\omega/2T_e) - \coth(\omega/2T_i)\}$$

$$F_{ei} = \Im (U_{ei}(k))^2 \Im \frac{\chi_e(k, \omega)}{\chi_i(k, \omega)}$$

The plasmons are bosons, and hence Bose factors $N_j(\omega/T_j)$ occur in $\Delta N$, which is the excess-plasmon population which drives the energy flow. In the above $\delta E/\delta t$ is the rate of change of the energy of the system, for time steps $\delta t$ significantly greater than the equilibration times $\tau_e, \tau_i$ which establish $T_e$ and $T_i$ of each sub-system. The relaxation of the whole system is determined by $\tau_{ei}$ such that $\tau_{ei} > \tau_e > \tau_i$. For brevity we write $\delta E/\delta t$ as $dE/dt$. The spherical symmetry of the plasma (i.e., not for solid-state plasmas) is used to write scalars $q, k$ instead of $\vec{q}, \vec{k}$ to simplify the notation. The non-interacting (one-component) response function $\chi^0(q, \omega, T)$ at arbitrary degeneracies was given by Khanna and Glyde [21], and are used here. This reduces to the Lindhard form at low-$T/E_F$ and the Dawson form at high $T/E_F$. The full response function $\chi_j(q, \omega, T)$ with $j = e, i$ uses a $T_j$-dependent local field corrections, e.g., $G_{ei}(k)$ derived from the finite-$T$ electron-electron exchange-correlation (XC) functional of DFT. The full $k$-dependence is given in Ref. [22]. The $\omega$-dependence of the LFC is needed only in the evaluation of coupled modes (see ). If $T_e, T_i$ are both sufficiently large so that $\Delta N \to (T_e - T_i)/\omega$, and if the electron chemical potential $\mu_e \leq 0$, useful analytical approximations become available. The possibility of unequivocally extracting a temperature-relaxation time $\tau_{ei}$ from the relaxation rate exists only in this regime, as was well-known in ER studies in solid-state semiconductors. Neglecting interactions, $E$ becomes the kinetic energy. Using non-interacting classical forms for $3\chi^0_j(k, \omega)$ in Eq. [8] we obtain the well known Landau-Spitzer (L-S) form for the temperature relaxation time $\omega_T$ or $\tau_{ei}$. For the L-S form we set $U_{ei}$ to be the Coulomb interaction $V_{ei}(k)$.

$$1/\tau = \frac{2}{3n} \omega_p^2 \omega_{p_i} \{2\pi T_e/m_e\}^{3/2} L$$

$$L = \log(k_{max}/k_{min})$$

$$T_{ei}/m_e = T_e/m_e + T_i/M_i, \omega_{p_i}^2 = 4\pi n/m_j$$

Here $\omega_{p_j}$ is the plasma frequency of the species $j = e, i$. The effective temperature and the effective mass of the colliding pair are $T_{ei}$ and $m_{ei}$, with $T_j$ in energy units. $L$ is the “Coulomb logarithm”. It depends on $k_{min}$ and $k_{max}$, i.e., momentum cutoffs (or impact parameters) used for modeling the unscreened Coulomb collision. If interacting response functions (e.g., RPA and beyond) are used, single-particle modes become replaced almost completely by plasmon modes, and the interactions become dynamically screened. However, “static screening” emerges when the $f$-sum rule is used to reduce the frequency integrations using the fact that $m_e/M_i$ is very small and hence electrons follow the ions ‘instantly’.

Hence a well-controlled procedure to do the $\omega$-integration is to exploit the $f$-sum rule [11]. Then ion dynamics are automatically preserved. Writing $\Delta = (T_e - T_i)$, Eq. [8] simplifies to:

$$\frac{1}{\Delta} \frac{d\Delta}{dt} = \frac{2}{3n} \omega_p^2 \int_0^\infty \frac{2}{\pi} \left[ \frac{\partial}{\partial \omega} \Im \chi^{ee}(k, \omega) \right] d\omega$$

Hence only the static form of the electron response function is needed, and the calculation is reduced to a simple $k$-integration.
Nearly analytic form for use with systems where the electron chemical potential is less than zero.

If the electron chemical potential \( \mu \sim 0 \), or dips below zero, the degeneracy effects of the plasma can be adequately treated by retaining terms in \( \chi_e(k) \) only up to \( \hbar^{-2} \) In most of the regime of interest to the simulations reported in Ref. [1] and some of the simulations reported in Ref. [14], one can approximate \( \Im \partial \chi^{ee}/\partial \omega \rangle_{\omega=0} \) as:

\[
\Im \partial \chi^{ee}/\partial \omega \rangle_{\omega=0} = \frac{\Im \partial \chi^{ee}_{0}/\partial \omega \rangle_{\omega=0}}{(1+ k_{sc}^{2}/k^{2})^{2}}
\]  
(12)

The \( k \rightarrow 0 \)-local field correction, \( G^{ee}_{0} \) at arbitrary degeneracy \( \sim \) can also be included in \( k_{sc} \) via the following definitions:

\[
(k_{sc}^{0})^{2} = \frac{2}{\pi}(2T^{1/2}) I_{-1/2}(\nu c_{e}/T_{e})
\]  
(13)

\[
I_{\nu}(x) = \int_{0}^{\infty} \frac{dy y^{2}}{e^{y^{2}+1}} \nu \geq -\frac{1}{2}
\]  
(14)

\[
k_{sc} = k_{sc}^{0} [1-G^{ee}_{0}]^{1/2}
\]  
(15)

In approximating \( \Im \partial \chi^{ee}/\partial \omega \) we retain quantum corrections to second order in \( k \), as displayed explicitly below, correcting a typographical error in Ref. 22.

\[
\Im \chi^{ee}_{0} = -\left( \frac{\pi}{2T_{e}} \right)^{3/2} \frac{2m \omega}{\pi k} e^{-\frac{\omega}{T_{e}}(k_{0,sc}^{2}+k^{2})} \frac{\sinh(\hbar \omega/2T_{e})}{\hbar \omega/2T_{e}}
\]  
(16)

Then Eq. (11) can be reduced to the form:

\[
1/\tau = \frac{2}{3n} \frac{\omega^{2}}{p_{e}^{2}} \frac{\omega}{p_{e}} \{2\pi(T_{ei}/m_{ei})\}^{-3/2} Q
\]  
(17)

\[
Q = \frac{1}{2} \left\{ e^{\nu} E_{i}(p_{e}) (p_{e}+1) - 1 \right\}
\]  
(18)

\[
p_{e} = k_{sc}^{2}/(8T_{e})
\]  
(19)

\[
E_{i}(x) = \int_{x}^{\infty} \exp(-t) dt / t
\]  
(20)

The exponential integral [24], \( E_{i}(x) \) of Eq. (17) is evaluated numerically via standard subroutines. Thus we see that the “Coulomb factor” \( Q \) is exactly analogous to the “Coulomb logarithm” of Eq. (10) but without ad hoc cutoffs. \( Q \) contains leading-order quantum corrections, ion-dynamics and electron screening. The expression for \( Q \) should be compared with a similar expression given by Brown et al. [23] which gives nearly equivalent numerical results, and hence reveal the physics content of the Brown et al. result. At high \( T_{e} \), this result approaches the L-S form more rapidly than \( Q \) [22].

It is likely that Eq. (17) should be adequate for evaluating most of the cases of H-plasmas studied in Ref. 1.

**ENERGY RELAXATION VIA COUPLED MODES**

The interactions between the ion modes and electron modes lead to ion-acoustic modes (coupled modes). It is seen in Fig.1(a) of Ref. 6 that electron density fluctuations in the electron density (represented by a shaded loop and denoted by \( \chi_{ee} \)) modify the bare Coulomb interaction \( V_{ee}(q) \) to give a screened interactions obtained by summing a geometric series of such polarization loops. This resummation does not take account of other classes of diagrams (e.g., ladder sums) which may dominate under other conditions of density and temperature. Similar processes arise from the ion density fluctuations \( \chi_{ii} \), modifying the bare ion-ion interaction. Furthermore, processes involving both types of loops occurring arbitrarily become possible, as seen from Fig.2 (c) and Fig.3 (d) of Ref. 6. It is also evident that modifying the ion-ion interaction line \( V_{ii} \) by ‘screening’ it with ions by writing it as \( V_{ii}/\epsilon_{ee}(k, \omega) \) produces no effect as those terms are already included, although some authors have suggested such nonpermitted ‘extensions’ using quantum-kinetic equation methods.

These particle-hole processes modify all interactions including the electron-ion interaction \( U_{ei}(q) \) which determines the relaxation from hot electrons to cold ions. The charge excitations couple together, just as two harmonic oscillators couple together to give combination modes. If the system were in equilibrium \( (T_{e} = T_{i} \rightarrow 0) \) the standard \( T = 0 \) Feynman rules can be used to evaluate these diagrams trivially. It turns out that the result obtained from a more sophisticated evaluation (e.g., using non-equilibrium Martin-Schwinger-Keldysh theory) has the same algebraic structure as that obtained from a simple analysis (formally similar results can also be obtained using various kinetic-equation methods). However, the result in a given order in perturbation theory is usually expressed in terms of lower-order quantities. At that point, one may replace the lower order quantities (e.g., propagators, spectral functions, denominators, LFCs, etc.) by fully renormalized ‘self-consistent’ quantities by further resummations or insertions of vertex corrections, self-energies etc. However, this involves pitfalls in the context of non-equilibrium systems, not only with diagrammatic methods, but even more so with kinetic-equation methods (as discussed below). Even at the level of single-particle band-structure calculations at \( T = 0 \), one is reminded of GW calculations. If they are made ‘more self-consistent’ by adding vertex corrections, self-energy insertions etc., they give worse results because such seemingly ‘more self-consistent’ improvements may not actually give a conserving approximation.

The energy relaxation rate \( dE_{i}/dt \) via cm is given by Dharma-wardana and Perrot (DWP) in Eq. [50], Ref. 6. However, the shortcomings in our notation and in our proof-reading seem to have confused a number of readers. The electron-ion interaction in the numerator is correctly given as \( U_{ei} \) and discussed in detail in various parts of the paper; it is not identical to the Coulomb interaction \( V_{ei} \) but reduces to a Coulomb potential \( V_{ei} \) only for large \( r \) (or small \( k \)). Nevertheless many writers have sim-
The equation given by Daligault et al. [14] in their restatement of our work, e.g. in Eq. (25) of Daligault and Dimonte (DD), they then concluded that the theory fails in the classical regime. The spectral functions used in Eqs. (47)-(50) of DWP have also perhaps been a source of confusion although they are clearly defined and the typographical errors etc., sort themselves out if one re-derives Eq. (50) from Eq. (47) of DWP. We give below Eq.(50) of DWP for energy relaxation via coupled modes, with the arguments $k, \omega$ suppressed for brevity.

$$dE_{\epsilon}/dT = \int \frac{dk^3}{(2\pi)^3} \frac{\omega d\omega}{2\pi} |U_{\epsilon i}(k)|^2 \mathcal{R}$$  \hspace{1cm} (21)

$$\mathcal{R} = -\frac{(1/2)}{|1 - U_{\epsilon i}(k)\chi_{\epsilon i}|^2}$$  \hspace{1cm} (22)

$$A_{j}(k, \omega) = -2\chi_{jj}, F_{jj'} = 1 - G_{jj'}$$  \hspace{1cm} (23)

$$\chi_{jj} = \chi_{jj}^0/D_{jj}$$  \hspace{1cm} (24)

$$D_{jj} = [1 - V_{jj}F_{jj}\chi_{jj}^0].$$  \hspace{1cm} (25)

The Coupled denominator emerges explicitly if one brings down the denominators for $\chi_{jj}$ and incorporate them into the factor \{|1 - U_{\epsilon i}^2(k)\chi_{\epsilon i}|^2\}.

$$D = D_{ei}D_{ii} - D_{ei},$$  \hspace{1cm} (26)

$$D_{ei}(k) = |U_{ei}|^2(k)^0\chi_{ii}^0$$  \hspace{1cm} (27)

$$|U_{ei}(k)|^2 \simeq (1 - G_{ie})(1 - G_{ei})V_{ei}(k)^2$$  \hspace{1cm} (28)

The last equation is only approximate, since we do not determine $U_{ei}$ from the LFCs. The $A_{e}, A_{i}$ used in the above equations are the spectral functions based on independent subsystems, as defined in Eq. 4 in terms of $\chi_{jj}$ which has a simple denominator. If the spectral functions are defined in terms of the two-fluid model using a coupled-mode denominator $D$ then the spectral function is denoted by $A_{cm}$ in Eq. (47) of DWP, together with a $\Delta N_{cm}$ for the excess Boson population that drives the energy relaxation. However Eq. (47) is transformed to eq. (50) of DWP, which is Eq. (22) given above. This contains only the independent-subsystem spectral functions $A_{j}, j = e, i$.

We give below the coupled mode form given by Daligault and Dimonte [14]. The quantities used in the formulation by DD are marked with an asterisk, *, to distinguish them from our definitions.

$$dE_{\epsilon}/dT = \int \frac{dk^3}{(2\pi)^3} \frac{\omega d\omega}{2\pi} |V_{ei}(k)|^2 [1 - G_{ei}^*] \mathcal{R}^*$$  \hspace{1cm} (29)

$$\mathcal{R}^* = -\frac{(1/2)}{|1 - U_{ei}^2(k)\chi_{ei}^*|^2}$$  \hspace{1cm} (30)

$$|U_{ei}^*(k)|^2 \simeq (1 - G_{ii}^*)(1 - G_{ei}^*)V_{ei}(k)^2$$  \hspace{1cm} (31)

$$A_{j}^* = -2\chi_{jj}^*$$  \hspace{1cm} (32)

$$\chi_{jj}^* = \chi_{jj}^0/[1 - V_{jj}(1 - G_{jj})]$$  \hspace{1cm} (33)

The equation given by Daligault et al. has a numerator $|V_{ei}(k)|^2(1 - G_{ei}^*)$ which is in second order only in the Coulomb part of the potential, while the denominator contains $|V_{ei}(k)|^2\{1 - G_{ei}^*\}(1 - G_{ei}^*)$.

It is actually necessary to use $\omega$ dependent LFCs in these equations. However, most of the work so far has replaced $G_{jj'}(k, \omega)$ by $G_{jj'}(k, 0)$. We examine these equations in more detail below to clarify the differences between DWP and DD formulations.

**Interactions potentials, local-field corrections and the 2T-equation of state.**

The DD-equations use Coulomb potentials $V_{jj'}$ corrected by their LFCs $(1 - G_{jj'})$ (taken in the static approximation). It appears that they are calculated from the Ornstein-Zernike equation for a two-temperature plasma at $T_e, T_i$ ‘self-consistently’. Similarly, it may be that even $\chi_{ii}^*$ is similarly ‘self-consistent’. This self-consistency is deliberately not included in the DWP formulation of 2T-quasiequilibrium systems. As explained in Ref. [2], and discussed at length in the Appendix there, in regard to the quasi-equation of state. We consider a system of electrons and ions both initially at equilibrium at $T_i$, when the electrons are very rapidly raised to a temperature $T_e$ by a short-pulse pump laser. The objective is to describe the system within time scales shorter than $\tau_{ei}$ such that the ions have had no time to relax to an equilibrium state. The ion-ion LFCs etc., remain ‘frozen’ at their initial values $G_{ii}(T_i = T_e)$, $g_{ii}(r, T_i = T_e)$, $S_{ii}(k, T_i = T_e)$ etc. Hence they are not what is self-consistent with the new-electron distribution at $T_e$.

Thus, in our view, the use of a ‘self-consistent’ $G_{ii}^*$ etc., is not consistent with the assumptions of the quasi-equilibrium 2T state normally generated in laser experiments. On the other hand, the electrons readjust to the new conditions in femto-second time scales; the $G_{ee}$ become $G_{ec}(T_e)$ in the external field of the ions still specified by the initial $g_{ii}(k, T_i = T_e)$ etc. Thus our LFCs $G_{ee}$ are also different from the $G_{ee}^*$ used by DD. The $G_{ee}$ used in the DWP calculation was constructed in linear response to the unmodified $g_{ii}(T_i, T_e = T_i)$ initial state of the ion distribution which was generated from the electron-ion pseudopotential $U_{ei}(k)$ calculated at $T_e = T_i$, i.e., the initial state when the energy was deposited by an ultra-fast laser pulse. The initial state $U_{ei}(k), g_{ii}(r)$ etc. were calculated using the NPA+MHNC procedure (sec. ).

The validity of the NPA+MHNC procedure used by us has been checked over the years, and also in recent calculations of the 2T-EOS for Al, Na and Li (at normal density and under some compressions). There the Helmholtz 2T-Free energy $F(T_e, T_i)$ and derived quantities like the internal energy $E(T_e, T_i)$, pressure $P(T_e, T_i)$ were evaluated using the NPA+MHNC as well as DFT+MD, and shown to agree very well in the range where DFT+MD could be implement [20] (the compar-
ison is limited to low $T/E_F$ since DFT+MD using codes like VASP or ABINIT can only be implemented up to about $T/E_F < 0.5$ when the number of electronic states that have to be included becomes prohibitive). Furthermore, the validity of such codes in such regimes had not been addressed up to then. Our NPA+MHNC calculations mutually validate the procedures used, and the NPA+MHNC could be seamlessly used for arbitrarily higher $T$. In the above procedure, the 2T static electron quantities like $g_{ei}(r), S_{ei}(k), \chi_{ee}(k), g_{ei}(k)$ are readily available from NPA as well as classical-map HNC calculations [22].

In contrast, $g_{ii}(r)$ and other quantities used in DD, and possibly in Benedict et al. [1] may be quantities derived from a self-consistent two-component 2T-simulation where two thermostats are assumed to maintain the systems in equilibrium at $T_i$ and $T_c$. The physical quantities that enter into the two-thermostat problem are different from those of the one thermostat problem. Clearly, the DW equations and the DD equations closely agree when applied to such systems with two thermostats, or when applied to systems with the ions clamped at the initial state, when appropriately computed after recognizing what system is being studied.

It should be noted that the direct-correlation functions $c(k)$ of Onstein-Zernike (OZ) theory are related to the LFCs used with the neutral-pseudo-atom potentials, as elucidated by Perrot, Furutani and Dharma-wardana [27]. Using Eq.(24) of Ref. [27] or other equations, it is seen that:

$$F_{jj'} = 1 - G_{jj'}(k) = 1 - \tilde{c}_{jj'}(T/V_{jj'})$$  \hspace{1cm} (34)

where $\tilde{c}_{jj'}$ is the short-ranged direct correlation function of OZ theory.

We have used a different notation $U_{ei}$ distinguishing it from the Coulomb potential, and discussed its calculation from a full quantum Kohn-Sham equation (and fitted to an extended Heine-Abaraknov pseudopotential for convenience), as given in Eq. (60) of DWP. But our $U_{ei}(k)$ is set to a bare Coulomb potential by DD perhaps to be in line with other Coulomb interactions. Then DD claim (Ref. [14]) in item (b) just before their conclusion that “Unlike our model, the DWP model diverges logarithmically at large k ... the integrand scales like 1/k at large k...”. The DW model at the FGR level, and at the cm level are free of such large-k (or small-k) divergencies, and includes both quantum and classical short-range (large-k) corrections in $U_{ei}(k)$ appropriately, satisfying the Friedel sum rule, and even dealing correctly with bound-state formation in the quantum case [22].

A more detailed look at $U_{ei}(k)$, calculated via the Kohn-Sham equations of the NPA model [28, 29] will be presented below. Although $U_{ei}(k)$ is an ‘all-order’ interaction, it has been derived to be compatible with linear response theory where interactions are treated to second-order in the screened interactions, and hence we believe that the inclusion of $U_{ei}$ in the numerator is consistent as long as higher-order terms are not included. Our experience with electrical conductivity calculations using $U_{ei}(k)$ in the Ziman formula confirm this conclusion.

The electron-ion pseudopotential derived from the Neutral-Pseudo-atom model.

The electron-ion interaction is given as a weak pseudopotential having the form

$$U_{ei}(q) = -ZV_q M_q$$

where $V_q$ is the Coulomb potential $4\pi q^2$, and $M_q$ is the ‘matrix element’ or form factor that regularizes the interaction to be compatible with second-order perturbation theory. The appropriate pseudopotentials are derived from density-functional theory (DFT) calculations using the NPA-average atom model as given by Perrot and Dharma-wardana (PDW) [28, 29]. The PDW model is different from a number of other available AA models, e.g., Purgatorio, MUZE [33] etc., which confine the electrons to a Wigner-Seitz sphere, and lead to several definitions of the mean ionization $Z$ which disagree with each other especially at high densities and low $T$. Blenski et al. find that the estimate of $Z$ in their model also leads to difficulties at low $T$ and normal densities, as they illustrate via the case of aluminum [41]. In our codes the free electrons are not confined to the Wigner-Seitz sphere, and the model is valid at low- or high $T$, and at all densities except when clustering effect become important. However, at the regimes of $T$ and ion density $\rho$ considered by Ref. [1], all AA models for the calculation of the free-electron charge-density at a nucleus, viz., $\Delta n_f(r) - \bar{n}$ and the associated free-electron density $Z$ per ion should be quite reliable.

The integral of $\Delta n_f(r)$ calculated from the Kohn-Sham equation extending over the the whole of space (i.e. up to $R_{ei} = 10 a_{ei}$, in our codes) yields $Z$ (the ionic charge) without ambiguity. The exact procedure for the determination of the mean ionic charge $Z$ to satisfy the Friedel sum rule etc. is discussed in more detail in Ref. [41]. The $e$ and $i$ interaction potentials are given by

$$U_{ei}(q) = \Delta n_f(q)/\chi_{ee}(q,0)$$  \hspace{1cm} (35)

$$U_{ei}(q) = Z^2 V_q + [U_{ei}(q)2\chi_{ee}(q,0)].$$  \hspace{1cm} (36)

Hence the static electron response function $\chi(q)$ and the Kohn-Sham density pile up around the ion completely define a weak local (s-wave) pseudopotential and the ion-ion pair-potential, with no ad hoc parameters. This linear-response pseudopotential $U_{ei}(q)$ can be legitimately used in the ER-calculations using linear response functions etc., as needed in the FGR and coupled-mode calculations. There we use $U_{ei}(q)$ to denote the electron-ion pseudopotential. Thus short-range corrections of the form $(1 - G_{ei}^*)$ introduced in the LB-type kinetic-equations at an unknown level of consistency (or
The ‘meaning’ of the two-temperatures in two coupled subsystems.

The Hamiltonian of the system is made up of $H = H_e + H_f + H_{ei}$. Temperature is a quantity which is not represented by an operator in a simple Hilbert space, but has a meaning only in quantum statistical mechanics where the system is attached to a heat bath. The temperatures $T_e, T_i$ are the Lagrange multipliers associated with the conservation of $H_e, H_i$ relevant to the time scales of the study $t < \tau_{ei}$. If only the ions are thermostatted, then $H_e$ is conserved for timescales $t < \tau_{ei}$. Other statistical quantities like $Z, \mu_e, \mu_i$, are also Lagrange multipliers for the conservation of global charge neutrality and the conservation of particle numbers. However, in writing down the partition function, or in implementing the HNC equations for such a 2T-two-component system, the question of what temperature to use for the $H_{ei}$ term can arise. This question is meaningless in ultra-fast matter where $H_{ei}$ drives the time evolution in a dissipative manner. The 2T-implementations of the NPA+MHNC took account of this by noting that $H_{ei}$ and related quantities can be calculated in linear response theory if the interaction potential occurring in $H_{ei}$ could be replaced by a weak pseudopotential $U_{ei}(k)$ but including non-linear short-range and long-range corrections and also quantum effects via the Kohn-Sham calculation. Given the $U_{ei}(k)$, the electron profile $n(k, T_e)$ and the ion profile $\rho(k, T_i)$ caused by it could be calculated with the linear response functions and hence $<H_{ei}>$ can be evaluated without any prescription for a $T_{ei}$ but using a development based on the Ornstein-Zernike equation. [52]

Subsequently, if needed, the resulting $E_{ei}, g_{ei} = n(r)/n_e$ etc., could be examined to obtain a model for $T_{ei}$ if needed. That will of course be only a fit parameter without the meaning of a Lagrange multiplier for energy conservation, unlike for $T_e, T_i$. Benedict et al. [1] have in fact considered how the energy $E_{ei}$ should be partitioned between the two subsystems in their recent MD study. Given that their $\Gamma_{ii}$ is typically 12, and $\Gamma_{ee}$ would also range from 12 for $T_e = T_i$ to a factor of 100 smaller, $\Gamma_{ei} = \sqrt{\Gamma_{ii} \Gamma_{ee}}$ would also range form 0.01 to 12. The $\Gamma_{ie} = 12$, or smaller $\Gamma$ interactions can easily be replaced by a weak NPA-pseudopotential $U_{ei}$ and linear response theory may be used to partition $<E_{ei}>$ so that the total energy can be written as $E = E_i + E_e$. It is not clear if this will agree with the method used by Benedict et al. where $E_{ei}$ has been ‘partitioned equally’ between the two subsystems.

In fact, in MD simulations involving $T$-dependent potentials (or otherwise) and with $T/E_f \sim 1$, the temperature cannot be simply estimated form kinetic considerations alone, although such approximations are made in simple kinetic models like those of Lenard and Balescu. In the NPA+HNC approach or in any similar reduced approach yielding weak pseudopotentials, the pair-potential can be written down correctly in second-order theory. Then the HNC or MHNC equations give the $g_{ii}(r)$. Hence the total free energy $F(T_e, T_i)$ as well as the component-subsystem free energies are explicitly available, even without a coupling constant integration over the pair-distribution functions, since one can use Eq. (17) of Ref. [29]. This is sufficient for the range of $\Gamma$ used in Ref. [1]. The free energies and specific heats estimated from the MD simulations can be compared with such a reduced approach and estimates of the temperature that match the MD can be determined by inverting the data. That is, as long as a reduced approach (e.g., NPA + MHNC) can be found, one can give a definite meaning to the $T_e, T_i$ even in a strongly coupled system.

Returning to the question of ‘dividing’ the interaction energy term $F_{12}(T_1, T_2)$ of a coupled system made up of two subsystems 1 and 2, we can write the Hamiltonian and its free energy as:

$$H = H_1(T_1) + H_2(T_2) + H_{12}$$

$$H_{12} = \sum_{k,q} U_{12}(q) n(k) \rho(k + q)$$

$$F = F_1 + F_2 + F_{12}$$

The problem is to partition $F_{12}$ in a meaningful way. We assume that $U_{12}(q)$ has been constructed to be a weak pseudopotential using a model like the NPA where the non-linear corrections and effects of the bound-electron core are absorbed into the pseudopotential which is no longer that of a point ion. In such a case, $F_{12} \ll F$ is a reasonable assumption, and we write:

$$f_i = \frac{\exp(-F_i/T_i) F_{12}}{\{\exp(-F_1/T_1) + \exp(-F_2/T_2)\}}$$

The individual subsystem free energies $F_i(T_i)$ are known, and this partitions the interaction free energy $F_{12}$ proportionately. The quantities $f_i(T_i)$ from then on are assumed to be functions of $T_i$ alone, and the corrected individual subsystem energies $\tilde{F}_i = F_i + f_i$. Then the corresponding partitioned contributions add to the internal energy $E_i$ to give $\tilde{E}_i = -d\{\beta_i (F_i + f_i)\}/d\beta_i$. This also enables a simple estimate of the specific heat and the pressure contributions entirely in terms of corrections from the partitioned quantities. The method works as long as $F_{12}$ is small compared to $F_1, F_2$. Explicit calculations of $F_1, F_2, F_{12}$ for 2T WDM systems using the NPA may be found in Ref. [26].

Benedict et al. give in their Fig. 6 (Ref. [1]) an HNC calculation for an ion-ion $g(r)$ at $\Gamma_{ii} \sim 12$. One would expect the HNC to agree well with the MD, even without any bridge corrections which are quite small here.
Since a system involving $T_e \neq T_i$, with $T_e/E_F \approx 1$ is being used, perhaps this is a system where a properly constructed classical map for the quantum electrons is needed. The somewhat outdated QSPs used by Hansen and McDonald have not been demonstrated to recover Quantum Monte Carlo (QMC) PDFs or energies for partially degenerate $T_e/E_F \leq 1$ although they perform well at much higher temperatures. The use of coupled HNC equations suggests that Benedict et al. assume a two-thermostat model for their $T_e, T_i$ UFM system.

The classical-map hyper-netted-chain (CHNC) equations [22] accurately map quantum electrons to a classical Coulomb fluid from full degeneracy ($T = 0$) to the fully classical limit, and accurately recover spin-dependent Quantum Monte Carlo (QMC) $g_{ee}$ and other quantities at $T = 0$. It also recovers the path-integral Monte Carlo simulations at finite $T$ [30, 31] that became available a decade later. The attempts to calculate $g_{ee}(r)$ in the degenerate regime using quantum-kinetic equations had invariably led to $g(r)$ which had unphysical negative regions as soon as the coupling constant reached even a value of $r_s = 2$ [32, 33]. The CHNC was the first model [34] that could accurately generate $g_{ee}(r), S_{ee}(k)$ etc., at $T = 0$ closely agreeing with QMC, and also yield $g_{ee}(r)$ and $k, T$-dependent LFCs $G_{ee}(k; T)$ at arbitrary spin-polarizations and at finite-$T$. The accuracy of the CHNC $g_{ee}(r, T)$ and other results at finite-$T$ was confirmed more than a decade later by the PIMC calculations of Brown et al [35].

The CHNC can be used for fully ionized hydrogen [36] as well as for more complex electron-ion systems [37]. While the CHNC equations work well for fully ionized systems, their use with bare Coulomb potentials $Z/r$ where $Z$ is the mean ionic charge is found to be unsatisfactory for ions with a significant bound core (e.g., aluminum, $Z = 3$) [38]. However, the CHNC is easily applicable in the regime free of bound states examined by studies on energy relaxation. CHNC is as easily implemented as the HNC itself and accurately includes quantum effects.

The case of repulsive ion-electron interactions.

Daligault et al. have used their equations to interpret molecular-dynamics ER rates for two subsystems of like charge, i.e., ‘repulsive hydrogen’. This is a valuable idea for obtaining reliable simulation results without the need for unphysical cutoffs needed to control attractive Coulomb interactions. They have studied ‘like-charged’ classical ‘repulsive hydrogen’ plasmas for $\bar{n} = n_e = 1.6 \times 10^{24}$ particles/cm$^3$, i.e, $r_s = r_{ws} = 1.0, \rho = 2.63$ g/cm$^3$, for $\Gamma = 1/(r_T T)$ in the range 0.001 to 1. In a classical Coulomb plasma calculation only the values of $\Gamma, T_e T_i$ are needed in an ER rate estimate.

Noting that $V_{ee} = V_{ii} = Z^2 v, Z = 1, v = V_k$, the cm denominator $D$ becomes

$$D = 1 - v \Sigma_j f_{jj} \chi_{jj} - v \Delta F \chi_{ee}^0 \chi_{ii}^0$$ (41)

$$\Delta F = F_{ee} F_{ii} - F_{ei} F_{ie}$$ (42)

Clearly, for repulsive hydrogen, setting $\Delta F = 0$ is a valid approximation and we have the simplified form for the denominator:

$$D_{sim} = 1 - v \Sigma_j f_{jj} \chi_{jj}$$ (43)

The numerator contains the second-order interaction $U_{ei}(k)$, as well as $A_i A_j \Delta N$, where all the factors are calculated in the independent-subsystem approximation, as in Eq. (50) of DWP. Any attempt to include terms beyond the second-order treatment using renormalized quantities (e.g., by replacing spectral functions by ones with higher-order corrections) is likely to fail. If such higher-order terms are retained, corresponding contributions from the three-vertex diagrams are also needed, as is well known from theory of the electron liquid [42, 43]. Hence we do not attempt to go beyond the 2nd-order form of Eq. (21). Our final form for the ER-rate in ‘repulsive hydrogen’ is given by

$$dE_e/dt = -2 \int \frac{dk^3}{(2\pi)^3} \omega d\omega \left| U_{ei}(k) \right|^2 \frac{3 \chi_{ee}^0 \chi_{ii}^0 \Delta N_{ei}}{|D_{sim}|^2}$$ (44)

Thus we see that the RPA approximations of neglecting LFCs is a good approximation to the ‘repulsive-hydrogen’ model. If similar simplifications are carried out on the DD-form of the cm-ER rate we obtain an identical equation, except for the differences in specifying $U_{ei}, U_{ei}^*, G_{jj}, G_{jj}^* \chi_{jj}^*$ etc., due to our different interpretations of the ultra-fast matter system that has to be studied. The reduced form is convenient for numerical computations, where $\chi_{ee}$ should be retained as an expansion in $\omega$ near $\omega = 0$, while $\chi_{ee}$ should be approximated by its large-$\omega$ expansion. However, the pitfalls of such expansions are discussed in the next section.

Attempts to simplify the coupled-mode calculation.

Several attempts to simplify the coupled-mode calculation, or introduce reduced alternatives, have appeared in the literature. Daligault and Mozynsky [44] and also Chapman et al. [45] have proposed a variant of the cm-formula where the ion-ion interaction $V_{ii}(k)$ is screened by the e-e RPA static dielectric function, leading to terms of the form

$$W = \frac{V_{ii} \chi_{ii}^0}{1 - \{V_{ii}/\epsilon_{ee}(k, 0)\} \chi_{ii}^0}$$ (45)

Here $\epsilon_{ee}(k, 0)$ is the static electron dielectric function. It is of course quite impossible to have such screening of the fundamental interaction $V_{ii}$ as this requires a Dyson
equation within a Dyson equation. Any insertions of particle-hole loops into an interaction line leads to no new contributions, and hence it is evident that this is erroneous although kinetic-equation methods do not have such safe guards as those built into Feynman techniques.

During our work on the reduction of the ER-rate formula using the f-sum rule as given in Hazak et al. \[11\] the present author tried to construct a similar reduced formula for the cm-ER rate. This was in fact part of our effort regarding classical constructs for dealing with quantum electrons interacting with ions. The first stage of the project was to construct a classical map of the quantum electrons, which can then be used together with the ions to generate static quantities like $S_{ee}(k), S_{ci}(k), S_{ii}(k)$. The CHNC successfully achieves this but does not give dynamic quantities. But ER-rate calculations need dynamic quantities in addition to static PDFs.

**Conditions for a conserving approximation**

In Ref. \[11\] a first-order expansion in $\omega$ was used for the relevant response functions. In dealing with cm-ER one can try such expansions, retaining the small-$\omega$ regime in $\chi_{cc}$, and the large $\omega$ regime $\chi_{ii}$, and using approximations that preserve the pole structure of the denominators. However, such expansions in $\omega$ require the satisfaction of a number of strict conditions.

1. Since real and imaginary parts are retained after approximation, it is necessary to ensure that the Kramers-Kröning relations are satisfied in some sense.

2. Since we are retaining a finite number of higher-order terms in an $\omega$ expansion, the frequency-moment sum rules, e.g., to third order, have to be satisfied by suitably readjusting the expansion coefficients. A simple example of the need for such adjustment is found already in the plasmon-pole approximation to the RPA-response function $\chi_{jj}$ which is constructed to preserve the pole structure ($\omega \pm \omega_k$) of the inverse dielectric function. But it is well known that the form $\Im[\epsilon(k,\omega)]^{-1} \simeq \omega_k [\delta(\omega - \omega_k) - \delta(\omega + \omega_k)]$ does not satisfy the f-sum rule while the modified form $\Im[\epsilon(k,\omega)]^{-1} \simeq \omega_p [\delta(\omega - \omega_k) - \delta(\omega + \omega_k)]$ does.

The third-moment sum has the form, with $e_q = q^2/2$:

\[
< \omega^3 > = \omega_p^2 \{ e_q^2 + 4e_q T/N + \omega_p^2 J(q) \}
\]

\[46\]

\[
J(q) = (1/N) \sum_{q \neq 0} \left( \frac{k^2 q^2}{k^2 - q^2} \right) \{ S(\vec{k} - \vec{q}) - S(\vec{k}) \}
\]

\[47\]

The third moment involves the mean kinetic energy per particle $< T/N >$ and hence its satisfaction is needed in a problem involving subsystem temperatures. Since we need the convenience of treating the LFCs in their static approximation, the expansion coefficients in powers of $\omega$, chosen to satisfy the sum rules, will help to overcome the short-comings of using static LFCs.

3. The compressibility sum rule has no clear meaning for non-equilibrium system, but, at least for 2T quasi-equilibrium systems, one can demand that the subsystem compressibilities, calculated from the subsystem 2T NPA equation of state agree with the compressibility obtained from the $k \to 0$ limit of the subsystem $S(k)$.

4. The $\chi_{ii}$ obtained from this procedure yields a $S(k)_{ii,m}$ obtained from the model. This should agree with the actual $S_{ii}(k)$ obtained from MD, or form the pair-potential and the MHNC or HNC equation.

\[
S_{ii,m}(k) = \int \{ d\omega/2\pi \} \{ -23 \chi_{ii}(k,\omega) \}. 
\]

\[48\]

If the model response function is unsatisfactory, then even the positivity of the $S(k)_{ii,m}$ and the $g(r)$ obtained from it is not guaranteed. In fact, for the $\Gamma_{ii}$ used in Benedict et al., the RPA response function (even without any $\omega$-expansion approximations) would fail to give a positive definite $g(r)$.

The above scheme was constructed with several of the above conditions imposed via Lagrange multiplies, and an attempt was made by the present author to solve for an optimal set of expansion coefficients in terms of $\omega$ giving a conserving approximation. This effort towards the construction of a model cm-response function was not too successful and so was not pursued; instead we concentrated on studying the successful effort with the CHNC calculations for the static quantities. In fact, the construction of such dynamic approximations for the response functions have to be undertaken within the context of generating effective potentials, their static functions like $S(k), g(r)$, and their phonons, as the phonon spectrum is closely linked with the ion-ion $S(k,\omega)$, with the longitudinal branches surviving in the WDM fluid. Our very simple codes achieve this as demonstrated recently \[24\] for room temperature phonons and also for phonons under WDM conditions. On the other hand, we do not as yet have a simple dynamical calculation of $S_{ii}(k,\omega)$ that can be used reliably for ER-rate calculations, (except for the costly possibility of MD simulations using the NPA potentials). Chapman et al. \[43\] have published a somewhat successful reduced cm-approach where they have attempted an $\omega$ expansion and curtailment of the denominators and other relevant quantities of the response functions entering into the ER-rate calculation. However, they have not
explicitly stated if they treat a system with two ther-
mostats or not, as this crucially changes the local fields
to be used. Furthermore, the extent of validation of the
above sum rules and conditions needed for a conserving
approximation have not been stated, perhaps because of
their greater concern for computational efficiency. In-
stead of checking sum rules, they have opted to check
their results by directly computing the full cm-expression
by \( \omega, k \) integrations and claim good agreement in some
regimes of density and \( T_\rho, T_e \). In their Fig.1 they have
also reported regimes where the cm contribution is very
large. Surprisingly, this is also the regime where any cm-
modes would be least damped, and hence not likely to be
relevant to energy relaxation. Hence, our suggestion is
to check if the approximations are valid in this regime (e.g.,
Fig. 1, \( n_e > 10^{22} \text{ cm}^{-3} \) and very high \( T_e \)) by comput-
ing the accuracy of the previously mentioned sum rules,
Kramers-Krönig and other relations. We suspect that
those analytical constraints are probably not well satis-
figures in their model, and it is likely that the PDFs (\( g_{j,j'} \))
calculated from the model response functions of Chap-
manet al. contain regions where they become negative and
hence unphysical.

Benedict et al. [1] have also made a frontal attack on
the problem by doing MD simulations in the regime in
question, and do not find the large effects found by Chap-
man et al., although the ER rates obtained from the sim-
ulations are in fact lower than those from the \( f \)-sum form
of the Fermi Golden rule.

**Strongly coupled systems**

The method of replacing the electron-ion interaction by
a weak pseudopotential \( U_{\text{cs}}(k) \) via the Kohn-Sham tech-
niques used in NPA seems to work well even at very high
compressions as far as static properties are concerned,
and here we refer to some recent studies [26, 46, 47], and
do not give an exhaustive list of previous calculations
going back to many decades, as they have been sum-
arized elsewhere [18]. Only very few dynamic calcula-
tions have been attempted using NPA potentials [49].
The phonons calculated from the hottest systems that
could be handled by DFT+MD agreed quite well with
those calculated from the NPA potentials [26]. This is a
very stringent test of the small-\( \omega \), small-\( k \) regime of the
\( S_{ii}(k, \omega) \) that can be obtained from the methods we use.

In fact, the regime studied by Benedict et al. imply
\( r_{WS} \simeq 0.2525 \text{ a.u.} \), even though \( \Gamma_{ii} \) is moderate. One can
envisage a carbon plasma, or carbon impurities in the
H-plasma, where \( Z \sim 6 \), and hence the \( \Gamma \) goes to 432.
In such systems, the local structure of the ion is essen-
tially quasi-crystalline, and each ion is ‘trapped’ within
a local cage of other ions. The ions acquire energy by
hopping from their cage to another nearby cage where
there may be a lattice-like vacancy. Thus the determin-
ant energy for this process is the *Frenkel frequency* \( \omega_{Fw} \)
and the corresponding energy \( \hbar \omega_{Fw} \). As the ions become
hot, the hops become more frequent and the particles
become more moderately coupled, with ions streaming
about rather than being locally trapped. This can be
examined in more detail by a calculation of the Frenkel
energy as a function of \( \Gamma_{ii} \), and expressing ER-rates via
such hopping processes.

The regime of moderate coupling may perhaps be ex-
amined using an approach similar to that of Feynman
and Cohen [50] where the \( S(k, \omega) \) of liquid helium is modeled
using the static \( S(k) \) and a weakly coupled excitation spectrum. In our case, given the NPA second-
order \( U_{\text{cs}}(k) \) and its ion-ion pair potential \( U_{ii}(k) \), the
\( S(k) \) can be obtained accurately using the MHNC equa-
tion. Also, the ion-ionic structure factor under weak
coupling but having the cm-denominator \( D \) would have
ion-excitation poles given by:

\[
\omega_{ii}(k) = \omega_{\text{pi}}/\epsilon_{ee}(k), \quad \omega_{\text{pi}} = \sqrt{(4\pi\rho M_i)} \quad (49)
\]

\[
\epsilon(k) = 1 - V_{ee}(k)(1 - G_{ee}(k))\chi_{ee}(k) \quad (50)
\]

This has the behaviour of an acoustic wave for \( k < k_c \)
and then tends to a relatively dispersionless value of \( \omega_{\text{pi}} \)
for large \( k \). That part of the dispersion is analogous to
the ‘optical-like’ folded branch of the acoustic dispersion
of a monoatomic cubic lattice. Following the spirit of the
Feynman and Cohen formula, an approximate form for the
ion-acoustic excitation spectrum under strong cou-
lping, and the dynamic ion-ion structure factor are given
by:

\[
\omega_i(k, \omega) = \omega_i(k)/S(k), \Gamma_{ik} = \gamma_i(k, \omega)/S(k) \quad (51)
\]

\[
\chi_{ii}(k, \omega) = Z(k, \omega)/[(\omega - \omega_i(k))^2 + \Gamma_i(k, \omega)] \quad (52)
\]

\[
S_{ii}(k, \omega) = -23\chi_{ii}(k, \omega)/[1 - \exp(-\omega/T_i)] \quad (53)
\]

The numerator contains an unknown function \( Z(k, \omega) \)
whose weak-coupling form is known. Adjustable param-
eters are needed in \( Z(k, \omega) \) and in \( \omega_i(k) \) to fit the selected
form to the sum rules as discussed earlier, to obtain reli-
able results. I do not know if some workers in the WDM
community have already tried such an approach or not.

However, the general scheme followed by us proceeds
as follows:

(a) We input the target free-electron density \( n_e \), nuclear
charge \( Z_N, T_c \) and \( T_i \) into the NPA-average atom code
to output the mean ionization \( Z \), ion density \( \rho \), pseudo-
potential \( U_{\text{cs}}(k) \), and the pair potential \( U_{ii}(k) \). Phase
shifts of continuum states, Kohn-Sham bound states and
energies are also available at this stage.

(b) The NPA potentials are used to generate PDFs and
structure factors.

(c) They are used to compute basic EOS quantities.
like the free energies, specific heats, compressibilities, and pressures, both for equilibrium, and for 2T quasi-equilibrium systems
(d) Dynamical quantities like the phonon spectra, electrical conductivity $\sigma$ and the X-ray Thomson scattering profiles are calculated, and where possible compared with DFT+MD available from (A).
(e) If $T_s \neq T_i$, the FGR $f$-sum energy-relaxation rate is calculated assuming a one-thermostat model where $T_i$ is fixed as the low-$T$ subsystem.
(f) The calculation of the dynamic ion-ion structure factor $S_{ii}(k, \omega)$ using a generally applicable reduced model has so far not been successful.
(g) But good phonon spectra, i.e., $S_{ii}(k, \omega)$ in the harmonic approximation for specific $g(r)$ are available.

The steps (a)-(e), (g) are sufficiently simple that they can be done in negligible time using a small laptop. Steps A and (f) are currently expensive and time-consuming, while (f) is not in effect available.

The possibility of addressing condensed matter physics and statistical mechanics using only pair-distribution functions and density functionals (i.e., without wavefunction calculations) is discussed in a more general framework in chapters 8-9 of the book listed in Ref. [51].

CONCLUSION

We have reviewed the available results on energy relaxation in 2T-WDM systems, starting from our original formulation of the ER-rate problem using the Fermi Golden rule and the couple mode forms from two decades ago, and their variants proposed since then. Numerically the most useful result has been the application of the $f$-sum to the Fermi Golden rule for the ER rate. The full expressions for the cm-form, e.g., those of Daligault and Dimonte using plasma-kinetic equations, or of Vorberger and Gerike using the Lenard-Balescu equations, are in general agreement with each other for second-order results using screening interactions, and with those of Dharma-wardana and Perrot [4], when correctly interpreted. Sophisticated, demanding molecular dynamics simulations have been carried out recently, showing that many brave simplifications of the coupled-mode energy relaxation formula are probably not reliable for even moderate ion-ion coupling. An alternative method besides the MD simulations for testing proposed simplifications of the cm-formula is to determine if the reduced versions satisfy well-known sum rules adequately.

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