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Ion dynamics and energy relaxation rate in nonequilibrium electron-ion systems

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We rigorously derive an analytical expression for the energy equilibration rate in nonequilibrium electron-ion systems that is valid for a large class of systems including solid and liquid metals, warm dense matter, and hot, weakly coupled plasmas. To this end we first derive a generalized Langevin equation that describes the motion of the classical ions in the quantum mechanical environment of the electrons. A general expression for the energy relaxation rate is then obtained assuming that each subsystem is in thermal equilibrium with itself. Direct approximations naturally reproduce the popular results of Landau and Spitzer for hot plasmas and the "Fermi golden rule" result for dense matter. We propose a method to evaluate numerically the energy relaxation rate with finite-temperature density functional theory calculations in difficult regimes such as the warm dense matter regime where neither quantum nor strong coupling effects can be ignored.

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I. INTRODUCTION

In most laboratory experiments, plasmas are created and probed by depositing energy into matter, driving it far from equilibrium. Depending on the details of the energy deposition, the deposited energy is mostly dumped into one of the particle species, electrons or ions, thereby leading to an imbalance between the electronic and ionic systems. For instance, in short-pulse laser-plasma interaction experiments, the laser energy preferentially heats the electrons, whereas in shock experiments, the shock wave preferentially heats the ionic subsystem. In the study of the evolution to equilibrium of nonequilibrium plasmas, a subject that has received considerable attention is temperature relaxation. Knowledge of temperature relaxation rates is of critical importance not only to understand general nonequilibrium physics but also for explicit practical purposes. Such information is crucial, for example, to simulate the evolution of the fusion capsule in inertial confinement fusion experiments [1] or to interpret the measurements of diagnostics [2,3].

Because of the disparity between the masses of electrons and ions in a plasma, the energy exchange between the two subsystems occurs on a time scale that is much slower than the time scale of energy equilibration within each subsystem. It therefore makes sense to attribute a temperature to each subsystem and to consider the subsequent relaxation toward equilibrium of the resulting two-temperature system (for definiteness we consider one species of ions only) that occurs as a result of the interaction between the two subsystems. The rate at which the electronic and ionic subsystems come into thermal equilibrium depends on the physical conditions (temperatures, densities) and, in particular, on the strength of the coupling among the particles and the degree of quantum degeneracy of the electrons. A variety of analytical expressions for the electron-ion energy equilibration rate were derived, which apply to specific physical regimes. The first description of energy relaxation in electron-ion systems originates with the works of Landau and Spitzer [4], and it is appropriate for dilute, hot, and therefore weakly coupled plasmas for which the thermal energy of the particles greatly exceeds the potential energies. Their approach considers the energy loss due to classical binary electron-ion Coulomb collisions and, as a consequence, necessitates introducing two *ad hoc* cutoff parameters k_{min} and k_{max} to mimic the quantum interference and finite-ion-size effects for short-distance collisions as well as the Coulomb screening of the charges. These cutoffs appear in the relaxation rate in the so-called Coulomb logarithm $\ln\Lambda=\ln(k_{max}/k_{min})$. Further developments based on classical and quantum kinetic equations (e.g., Boltzmann, Lenard-Balescu) were proposed in order to improve and predict the value of the Coulomb logarithm [5]. An interesting work in that respect was recently presented by Brown *et al.*, who used the method of dimensional regularization (originally developed in quantum field theory) to obtain an expression for the temperature equilibration rate which is exact to leading and next-to-leading orders in the plasma coupling parameter [6]. More recently, Dharma-wardana and Perrot [7] and Hazak *et al.* [8] proposed energy transfer models in regimes for which electron degeneracy and strong Coulomb coupling effects cannot be neglected. Using linear response theory, they derived a formula that is valid if the electron-ion coupling is weak. This formula is nothing but the extension to plasmas of the "Fermi golden rule" formula derived by Kogan [9] for the electron-phonon relaxation rate in metals and semiconductors. In [8], the authors showed that the Fermi golden rule result reduces to the Landau-Spitzer form in the nondegenerate electron limit. Dharma-wardana and Perrot also proposed a formula, the coupled-mode formula, that incorporates strong electron-ion coupling effects [7]. This formula predicts a strong dependence of the relaxation on the ion temperature and, surprisingly, does not seem to

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converge toward the well-established Landau-Spitzer result at high temperature.

The goal of the present work is to rigorously derive a general expression for the energy equilibration rate in a nonequilibrium electron-ion system (1) that is valid for a large class of physical systems, (2) that reproduces the popular results previously mentioned in the appropriate limiting regimes, and (3) that is amenable to numerical simulations for physical regimes like the warm dense matter regime that are difficult to model analytically. Our final result is valid whenever the ion subsystem can be treated as a classical system of particles, which encompass most situations encountered in plasma physics. In particular, no assumption is made about the strength of the electron-ion coupling or the degree of degeneracy of the electronic gas. To achieve this goal, we first derive in Sec. II an equation that describes the motion of classical ions of a nonequilibrium electron-ion system in the quantum mechanical environment of the electrons. To this end, we use the so-called influence functional technique of Feynman and Vernon [10,11] to eliminate the electronic degrees of freedom and to obtain an effective equation of motion for the ions only. The latter is a generalized Langevin equation whose stochastic nature describes the fluctuations in the forces that the electrons exert on the ions and that are responsible for the heat transfer between the two subsystems. Then, in Sec. III, we use the ionic equation of motion to derive a general expression for the energy relaxation rate assuming that each subsystem is in thermal equilibrium with itself. In Sec. IV, we show that simple approximations to the relaxation rate naturally reproduce, for instance, the popular results of Landau and Spitzer for hot plasmas and the Fermi golden rule result for weakly coupled electron-ion systems. Finally, in Sec. V, we propose a scheme to calculate numerically the energy relaxation rate with quantum molecular dynamics calculations in difficult regimes (e.g., the warm dense matter regime) where quantum and strong coupling effects certainly play an important role. The present presentation focuses on the general formalism. A future presentation will be devoted to the application of our formal results to specific physical regimes [12].

II. IONIC EQUATION OF MOTION

We consider an electron-ion system consisting of N_i ions of mass M and charge Ze and of N_e electrons of mass m and charge $-e$. The total Hamiltonian H_{tot} of the system is the sum of a purely ionic term H_i, a purely electronic term H_e, and an electron-ion interaction V. Thus

$$H_{tot} = H_i(q) + H_e(r) + V(r,q)$$

with

$$H_i = \sum_{J=1}^{N_i} \frac{\mathbf{P}_J^2}{2M} + V_i(q),$$

$$H_e = \sum_{j=1}^{N_e} \frac{\mathbf{p}_j^2}{2m} + \frac{1}{2}\sum_{j,k=1}^{N_e} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|},$$

$$V(r,q) = \sum_{J=1}^{N_i}\sum_{j=1}^{N_e} v_{ei}(\mathbf{r}_j - \mathbf{R}_J),$$

where the symbols $q=\{\mathbf{R}_1,\ldots,\mathbf{R}_{N_i}\}$ and $r=\{\mathbf{r}_1,\ldots,\mathbf{r}_{N_e}\}$ denote the set of ionic and electronic positions, respectively. It is convenient to introduce the ion density operator $n_{ion}(\mathbf{R})=\Sigma_{J=1}^{N_i}\delta(\mathbf{R}-\mathbf{R}_J)$ and the electron density operator $n_e(\mathbf{r})=\Sigma_{j=1}^{N_e}\delta(\mathbf{r}-\mathbf{r}_j)$, and to rewrite the electron-ion energy as

$$V = \int d\mathbf{r}\, v(\mathbf{r}) n_e(\mathbf{r}) \quad \text{with } v(\mathbf{r}) \equiv \int d\mathbf{R}\, n_{ion}(\mathbf{R}) v_{ei}(\mathbf{r}-\mathbf{R}).$$

It is important to mention that the following derivation allows us to consider pure Coulomb electron-nucleus interactions for fully ionized plasmas as well as partially ionized systems with electron-ion interactions represented by a pseudopotential v_{ei} when a nucleus and its tightly bound electrons behaves as a rigid entity.

Before going into the details of the somewhat lengthy derivation, we find it worthwhile at this point to enumerate its main steps. For most physical situations the ions can be treated classically while the electrons require a quantum mechanical treatment. Our first goal is to extract the classical motion of the ions in the quantum environment of the electrons. To this end, we eliminate the electronic degrees of freedom and focus on the density matrix of the ions, Eq. (1). The equation of motion of the ions under the influence of the quantal fluctuations in the electronic subsystem is obtained from the path-integral formulation of Feynman and Vernon, Eqs. (2) and (3), by a cumulant expansion to second order in the off-diagonal elements of the ionic density matrix. After some efforts we obtain the expression (11) for the propagator of the ionic system. The latter describes the ion dynamics as a stochastic process governed by the stochastic equation of motion (14). The ion-ion interactions appear in the classical ion-ion force while the influence of the electrons gives rise to two terms, namely, a systematic deterministic force that describes the average friction of the electrons on the ions together with a stochastic force that describes the coupling of the ionic motion to the quantal fluctuations in the electronic subsystem. For short-time dynamics, the systematic force can be expressed as the sum of the instantaneous Coulomb force (which reduces to the Born-Oppenheimer force when the system is at equilibrium) together with a friction term proportional to the ion velocities. The latter is related to the fluctuating force via a fluctuation-dissipation relation. The resulting equation for the ionic motion is the generalized Langevin equation (17). It is this equation that we use in Sec. III to derive the expression (28) for the energy relaxation rate.

The complete information on the dynamics of the ions is contained in the reduced density matrix

$$\rho_i(t) \equiv \mathrm{Tr}_e\, \rho_{tot}(t), \tag{1}$$

which is obtained from the total density matrix $\rho_{tot}(t)=e^{(-i/\hbar)H_{tot}(t-t_0)}\rho_{tot}(t_0)e^{(i/\hbar)H_{tot}(t-t_0)}$ by tracing out the electronic variables. Following the path-integral approach of Feynman and Vernon [10,11], the coordinate representation of ρ_i at time t can be related to its initial value at time t_0 as

$$\langle q|\rho_i(t)|q'\rangle=\int dq_0\int dq_0'\langle q_0|\rho_i(t_0)|q_0'\rangle\mathcal{L}(q,q',t;q_0,q_0',t_0), \tag{2}$$

where the propagator $\mathcal{L}$ may be expressed as the double path integral

$$\mathcal{L}(q,q',t;q_0,q_0',t_0)=\int_{q_0}^{q}\mathcal{D}q\int_{q_0'}^{q'}\mathcal{D}^*q' \times\exp\left(-\frac{i}{\hbar}\{S_i[q]-S_i[q']\}\right)I(q,q'). \tag{3}$$

Here $\mathcal{D}q=\lim_{N\to\infty}\int dq_1\cdots dq_N(M/2\pi i\epsilon)^{N/2}$ is the path-integral measure and $\epsilon=(t-t_0)/N$. The quantity $S_i[q]$ is the classical action induced by the ionic Hamiltonian $\hat{H}_i$ along the path q_t [13],

$$S_i[q]=\int_{t_0}^{t}\left(\frac{M\dot{q}_{t'}^2}{2}-V_i(q_{t'})\right)dt'.$$

Finally the functional $I(q,q')$ is called the influence functional and describes the effect of the electronic subsystem on the time evolution of the ionic subsystem [$I(q,q')=1$ for zero electron-ion coupling]. The influence functional can be written as an average of two time-evolution operators, namely,

$$I(q,q')=\langle U_{t,t_0}^{\dagger}[q']U_{t,t_0}[q]\rangle, \tag{4}$$

where $U_{t,t_0}[q]=T\exp[-(i/\hbar)\int_{t_0}^{t}H(t')dt']$ is the time-evolution operator between times t_0 and t for the electronic time-dependent Hamiltonian $H(t)\equiv H_e(r)+V(r,q_t)$ in which the ions act like a time-dependent external perturbation as they move along the path q_t. Here T is the time-ordering operator and $\langle\cdots\rangle$ means the average over the electronic bath, namely, $\mathrm{Tr}[\rho_e(t_0)\cdots]$ where $\rho_e\equiv\mathrm{Tr}_i\rho_{tot}$ is the electron density matrix at time t_0.

Equation (3) is an exact representation of the quantum propagator for the ionic subsystem interacting with the electronic subsystem [14]. In order to proceed further, it is convenient to introduce the "center-of-mass" and "relative" coordinates of ions $x=(q+q')/2$ and $y=q-q'$, and to rewrite the matrix elements (2) as [15]

$$\langle q|\rho_i(t)|q'\rangle=\left\langle x+\frac{y}{2}|\rho_i(t)|x-\frac{y}{2}\right\rangle =\int dx_0\int dy_0\,\rho(x_0,y_0,t_0)\mathcal{L}(x,y,t;x_0,y_0,t_0),$$

with

$$\mathcal{L}(x,y,t;x_0,y_0,t_0)=\int_{x_0}^{x}\mathcal{D}x\int_{y_0'}^{y}\mathcal{D}y \times\exp\left[\frac{i}{\hbar}\int_{t_0}^{t}dt'M\dot{x}_{t'}\dot{y}_{t'}-V_i\left(x_{t'}+\frac{y_{t'}}{2}\right)+V_i\left(x_{t'}-\frac{y_{t'}}{2}\right)\right]\mathcal{I}(x,y) \tag{5}$$

and

$$\mathcal{I}(x,y)\equiv I\left(x+\frac{y}{2},x-\frac{y}{2}\right)=\left\langle U_{t,t_0}^{\dagger}\left[x-\frac{y}{2}\right]U_{t,t_0}\left[x+\frac{y}{2}\right]\right\rangle. \tag{6}$$

The path x_t measures propagation along the diagonal of the ion density matrix, while the path y_t is a measure of how far the system gets off diagonal while propagating. In the full classical limit, the density matrix becomes diagonal [16]. In order to extract the motion followed by the ions in the presence of the quantal fluctuations in the electronic subsystem, the central idea is then to expand $\rho(x,y,t)$ around its diagonal values by assuming that the off-diagonal components y are small. This is done by using a cumulant expansion of the integrand in Eq. (5).

We first consider the influence functional Eq. (6), which involves the time-evolution operators for the Hamiltonians,

$$H_{\pm}(t)=H_e(r)+V\left(r,x_t\pm\frac{y_t}{2}\right)=\left[H_e(r)+V(r,x_t)\right]+\delta V_{\pm}(t).$$

Here the term $\delta V_{\pm}(t)\equiv V(r,x_t\pm y_t/2)-V(r,x_t)$ measures the deviations of the electron-ion potential from its value on the diagonal path x_t due to the off-diagonal excursions. For small off-diagonal elements y_t, the corrections $\delta V_{\pm}$ are small and linear in y_t,

$$\delta V_{\pm}(t)\approx\pm\frac{y_t}{2}\cdot V'(r,x_t)\quad\text{with } V'(r,x_t)\equiv\left.\frac{\partial V}{\partial q}\right|_{q=x_t},$$

and, therefore, $\delta V_{\pm}(t)$ can be treated as a perturbation to the Hamiltonian $H_e(r)+V(r,x_t)$. Applying second-order perturbation theory to Eq. (6), we expand $\mathcal{I}(x,y)$ into powers of the off-diagonal components y up to order y^2,

$$\mathcal{I}(x,y)=1+\frac{i}{\hbar}\int_{t_0}^{t}\sum_k y_k(t')\langle F_k(t')\rangle dt' -\frac{1}{\hbar^2}\int_{t_0}^{t}dt'\int_{t_0}^{t'}ds\sum_k\sum_j y_k(t')y_j(s)\langle\{F_k(t'),F_j(s)\}\rangle +O(y^3) \tag{7}$$

where $\{\cdot,\cdot\}$ is the anticommutator. Here we have defined the operators

$$F_k(t) = -U^{\dagger}_{t,t_0}[x]\left.\frac{\partial V}{\partial q_k}\right|_{q=x_t} U_{t,t_0}[x], \quad k=1,\ldots,3N_e, \quad (8)$$

which we write in the compact form

$$F(t) = -U^{\dagger}_{t,t_0}[x]V'(r,x_t)U_{t,t_0}[x]$$

. Some contributions to the infinite series (7) for $\mathcal{I}(x,y)$ can be summed up in a closed form by reexponentiation, which automatically sums up an infinite number of terms. The resulting approximate influence functional is

$$\mathcal{I}(x,y) = \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} y_{t'}\cdot\langle F(t')\rangle dt' - \frac{1}{\hbar^2}\int_{t_0}^{t} dt'\int_{t_0}^{t'} ds\, y_{t'}\cdot C^{[x]}(t',s)\cdot y_s\right). \quad (9)$$

Here we have introduced the symmetric correlation function between the components (8),

$$C^{[x]}_{kj}(t',s) \equiv \frac{1}{2}\langle\{F_k(t')-\langle F_k(t')\rangle, F_j(s)-\langle F_j(s)\rangle\}\rangle,$$

where the superscript $[x]$ denotes the dependence upon the trajectory x_t. Substituting Eq. (9) into Eq. (5) and expanding the potential $V_i(x\pm y/2)$ to second order in the off-diagonal path y, we arrive at the following expression for the propagator:

$$\mathcal{L}(x,y,t;x_0,y_0,t_0) = e^{i\phi}\int_{x_0}^{x}\mathcal{D}x\int_{y_0}^{y}\mathcal{D}y\,\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt'\, y_{t'}\cdot\left(M\ddot{x}_{t'}+\frac{\partial V_i}{\partial q}(x_{t'})-\langle F(t')\rangle\right)\right]\exp\left(-\frac{1}{\hbar^2}\int_{t_0}^{t} dt'\int_{t_0}^{t'} ds\, y_{t'}\cdot C^{[x]}(t',s)\cdot y_s\right) \quad (10)$$

$$= e^{i\phi}\int_{x_0}^{x}\mathcal{D}x\int\mathcal{D}\xi^{[x]}\mathcal{P}[\xi^{[x]}]\,\delta\left(M\ddot{x}_{t'}+\frac{\partial V_i}{\partial q}(x_{t'})-\langle F(t')\rangle-\xi^{[x]}(t')\right), \quad (11)$$

where $\phi = M(\dot{x}_t y_t - \dot{x}_0 y_0)/\hbar$ is an irrelevant phase factor. In the following paragraphs, we interpret the previous expressions for the propagator and derive the equation governing the ionic dynamics.

Let us start with Eq. (10). The integrand is the product of two exponentials. In the first one $y(t)$ enters only linearly while the second exponential is Gaussian in $y(t)$. The first exponential would be the only term present had we truncated the power expansion (7) at the first-order term in y. In that case $\mathcal{L}$ would simply look like the propagator of a system of particles under the influence of deterministic external force $\langle F(t)\rangle$; indeed the y integral can then be performed and leads to

$$\mathcal{L}(x,y,t;x_0,y_0,t_0) \propto \int_{x_0}^{x}\mathcal{D}x\,\delta\left(M\ddot{x}_{t'}+\frac{\partial V_i}{\partial q}(x_{t'})-\langle F(t')\rangle\right).$$

Thus, in this approximation, the ions are constrained to follow classical trajectories according to Newton's equation of motion,

$$M\ddot{x}_{t'} = -\frac{\partial V_i}{\partial q}(x_{t'}) + \langle F(t')\rangle.$$

The force is the sum of the classical force $-(\partial V_i/\partial q)(xt')$ due to the ion-ion interaction together with the deterministic force $\langle F(t)\rangle$ which, as we shall see below, describes the systematic friction force due to the electronic environment.

Higher-order approximations allow one to describe the effect of the fluctuations in the electron gas. These are crucial since they are responsible for the energy exchange between the two subsystems. Here, these fluctuations are described by the second exponential, quadratic in $y(t)$, which confines the excursions of the off-diagonal components to small values [17]. This term acts as a stochastic, Gaussian noise on the trajectory $x(t)$. The Gaussian noise may be interpreted as the effect of an associated fluctuating force $\xi^{[x]}(t)$ acting on the ions and describes the unknown nondeterministic fluctuations in the electronic subsystem [11]. To see this, using the properties of Gaussian integrals, we note that the Gaussian term can be written as an average over a Gaussian stochastic process as

$$\exp\left(-\frac{1}{\hbar^2}\int_{t_0}^{t} dt'\int_{t_0}^{t'} ds\, y(t')\cdot C^{[x]}(t',s)\cdot y(s)\right) = \left\langle\exp\left(\frac{i}{\hbar}\int_{t_0}^{t} dt'\, y(t')\cdot\xi^{[x]}(t')\right)\right\rangle_{\xi} = \int\mathcal{D}\xi^{[x]}\mathcal{P}[\xi^{[x]}]\exp\left(\frac{i}{\hbar}\int_{t_0}^{t} dt'\, y(t')\cdot\xi^{[x]}(t')\right), \quad (12)$$

where

$$\mathcal{P}[\xi^{[x]}] = \exp\left(- \frac{1}{2} \int_{t_0}^{t} dt' \int_{t_0}^{t} ds \xi^{[x]}(t') \cdot [C^{[x]}(t',s)]^{-1} \cdot \xi^{[x]}(s) \right)$$

is a Gaussian probability distribution (its normalization is absorbed in the measure $\mathcal{D}\xi$) characterized by a zero average $\langle \xi_k^{[x]}(t) \rangle_\xi = 0$, and the covariance matrix

$$\langle \xi_k^{[x]}(t) \xi_j^{[x]}(t') \rangle_\xi = C_{kj}^{[x]}(t,t'), \quad k,j = 1, \ldots, 3N_i. \tag{13}$$

When the transformation (12) is substituted in (10), the off-diagonal element y now occurs only linearly in the propagator and the path integral $\mathcal{D}y$ can easily be evaluated to yield the second expression, Eq. (11). This new expression for the propagator can be interpreted as follows. The motion of the ions is constrained to follow the stochastic integro-differential equation,

$$M\ddot{x}_k(t) + \left. \frac{\partial V_i}{\partial q_k} \right|_{q=x(t)} - \langle F_k(t) \rangle = \xi_k^{[x]}(t). \tag{14}$$

The term $\langle F(t) \rangle$ is a deterministic, retarded force that describes the average effect of the electrons on the ions. The random term $\xi^{[x]}(t)$ describes the effect of the coupling to the fluctuations in the electronic subsystem and undergoes a Gaussian stochastic process characterized by a zero average and the variance (13).

The systematic friction force $\langle F(t) \rangle$, Eq. (8), can be made explicit if one looks at the short-time dynamics. To this end, we use the fact that on a short time scale $x_s \approx x_t - (t-s)\dot{x}_t$, and the evolution operator $U_{t,t_0}[x]$ can be approximated as

$$U_{t,t_0}[x] = \mathcal{U}_{t,t_0}[x] \times \left(1 + \frac{i}{\hbar} \dot{x}_t \cdot \int_{t_0}^{t} (t-s) \mathcal{U}_{s,t_0}^{\dagger}[x] V'(r,x_t) \mathcal{U}_{s,t_0}[x] ds \right),$$

where $\mathcal{U}_{t,t_0}[x] = e^{-(i/\hbar)[\hat{H}_e(r) + \hat{V}(r,x_t)](t-t_0)}$. When this approximation is introduced in Eq. (8), the systematic force reads

$$\langle F_k(t) \rangle = \langle \mathcal{F}_k(t) \rangle + \sum_j \dot{x}_j(t) \int_{-\infty}^{t-t_0} ds\, s \mathcal{R}_{k,j}(s),$$

where

$$\mathcal{F}(s) \equiv - \mathcal{U}_{s,t_0}^{\dagger}[x] V'(r,x_t) \mathcal{U}_{s,t_0}[x],$$

and $\mathcal{R}_{k,j}$ is defined below. The total systematic force consists of two terms. The force $\mathcal{F}(t)$ is the instantaneous force between the ion density and the electron density,

$$\langle \mathcal{F}_k(t) \rangle = - \frac{\partial}{\partial q_k} \left[\int d\mathbf{r}\, v(\mathbf{r}) \langle n_e(\mathbf{r},t) \rangle \right]_{q=x_t}, \tag{15}$$

and is merely the Born-Oppenheimer force when the system is at equilibrium. The second term represents the systematic friction that the ions undergo as they move in the surrounding electronic bath. The friction depends on the fluctuations $\delta\mathcal{F}_k(t) = \mathcal{F}_k(t) - \langle \mathcal{F}_k(t) \rangle$ of the averaged force $\mathcal{F}(t)$ via

$$\mathcal{R}_{k,j}(t-s) = - \frac{i}{\hbar} \langle [\delta\mathcal{F}_k(t), \delta\mathcal{F}_j(s)] \rangle \theta(t-s), \tag{16}$$

where θ is the Heaviside step function. The equation of motion (14) takes the form of a generalized Langevin equation

$$M\ddot{x}_k(t) + \left. \frac{\partial V_i}{\partial q_k} \right|_{q=x(t)} + \frac{\partial}{\partial q_k} \left[\int d\mathbf{r}\, v(\mathbf{r}) \langle n_e(\mathbf{r},t) \rangle \right]_{q=x_t} - \sum_j \dot{x}_j(t) \int_{-\infty}^{t-t_0} ds\, s \mathcal{R}_{kj}(s) = \xi_k^{[x]}(t), \tag{17}$$

where the Gaussian noise $\xi^{[x]}$ satisfies

$$\langle \xi_k^{[x]}(t) \xi_j^{[x]}(s) \rangle_\xi \equiv \mathcal{C}_{k,j}^{[x]}(t-s) = \frac{1}{2} \langle \{ \delta\mathcal{F}_k(t), \delta\mathcal{F}_j(s) \} \rangle. \tag{18}$$

Up to this point, no assumption has been made about the state of the two subsystems. When the electronic averaging $\langle \cdots \rangle$ is performed over a canonical ensemble at temperature T_e, each matrix element $\mathcal{R}_{k,j}$ can be interpreted as a retarded response function as defined in linear response theory [18]. In agreement with this theory, the response function $\mathcal{R}_{k,j}$ and the symmetric correlation function $\mathcal{C}_{k,j}$ are related by a fluctuation-dissipation relation. In other words, when a temperature can be assigned to the electronic subsystem, the friction term and the noise term are related by a fluctuation-dissipation relation although the global system is not in equilibrium.

In order to rewrite the previous results in terms of more familiar physical quantities, we shall evaluate the averages $\langle \cdots \rangle$ assuming that the electron subsystem is in equilibrium at temperature T_e. Using the notation defined at the beginning, the response functions (16) and correlation functions (18) can be written as

$$\mathcal{R}_{k,j}^{[x]}(t) = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, v_k'(\mathbf{r}_1) v_j'(\mathbf{r}_2) \chi_{ee}^{[x]}(\mathbf{r}_1, \mathbf{r}_2, t),$$

$$\mathcal{C}_{k,j}^{[x]}(t) = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, v_k'(\mathbf{r}_1) v_j'(\mathbf{r}_2) S_{ee}^{[x]}(\mathbf{r}_1, \mathbf{r}_2, t) \tag{19}$$

with $v_k'(\mathbf{r}) = \partial v(\mathbf{r}) / \partial q_k$. We have defined

$$\chi_{ee}^{[x]}(\mathbf{r}_1, \mathbf{r}_2, \tau) = - \frac{i}{\hbar} \langle [\delta n_e(\mathbf{r}_1, \tau), \delta n_e(\mathbf{r}_2)] \rangle \theta(\tau), \tag{20}$$

$$S_{ee}^{[x]}(\mathbf{r}_1, \mathbf{r}_2, \tau) = \frac{1}{2} \langle \{ \delta n_e(\mathbf{r}_1, \tau), \delta n_e(\mathbf{r}_2) \} \rangle, \tag{21}$$

which are the electron-electron density response function and correlation function for an electron system in the external potential of the fixed ionic configuration x, respectively. According to linear response theory, these two quantities are related by the fluctuation-dissipation relation

$$S_{ee}^{[x]}(\mathbf{r}_1,\mathbf{r}_2,\omega) = -\hbar\,\coth\left(\frac{\hbar\omega}{2k_BT_e}\right)\text{Im}\,\chi_{ee}^{[x]}(\mathbf{r}_1,\mathbf{r}_2,\omega),$$

where we defined the temporal Fourier transform $f(\omega) = \int_{-\infty}^{\infty} f(t)e^{i\omega t}$. Using Eq. (19), we find that a similar relation holds between $\mathcal{C}_{k,j}$, and $\mathcal{R}_{k,j}$,

$$\mathcal{C}_{k,j}^{[x]}(\omega) = -\hbar\,\coth\left(\frac{\hbar\omega}{2k_BT_e}\right)\text{Im}\,\mathcal{R}_{k,j}^{[x]}(\omega). \tag{22}$$

In most situations the electronic correlation time τ_e is much smaller than the ionic correlation time τ_i, $\tau_e/\tau_i \ll 1$, because the electron collision time is rather short. In that case, we can safely approximate the colored noise (18) with a white noise, i.e.,

$$\mathcal{C}_{k,j}^{[x]}(\tau) \approx \delta(\tau)\int_{-\infty}^{\infty} dt\,\mathcal{C}_{k,j}^{[x]}(t), \tag{23}$$

and Eq. (17) by

$$M\ddot{x}_k(t) + \left.\frac{\partial V_i}{\partial q_k}\right|_{q=x(t)} + \frac{\partial}{\partial q_k}\left[\int d\mathbf{r}\,v(\mathbf{r})\langle n_e(\mathbf{r},t)\rangle\right]_{q=x_t} + M\sum_j \gamma_{kj}\dot{x}_j(t) = \xi_k^{[x]}(t), \tag{24}$$

where

$$\begin{aligned}\gamma_{kj} &= -\frac{1}{M}\int_{-\infty}^{\infty} tR_{k,j}(t)dt = \text{Im}\,\frac{\partial}{\partial\omega}R_{k,j}(\omega=0)\\ &= -\frac{1}{M}\int dr_1\int dr_2\,v_k'(\mathbf{r}_1)v_j'(\mathbf{r}_2)\\ &\quad\times\text{Im}\,\frac{\partial}{\partial\omega}\chi_{ee}^{[x]}(\mathbf{r}_1,\mathbf{r}_2,\omega=0).\end{aligned} \tag{25}$$

Combining Eqs. (18), (19), (22), (23), and (25), we find that the Gaussian stochastic force $\xi^{[x]}$ has a white spectrum [19]

$$\langle\xi_k[x,t]\xi_j[x,s]\rangle_\xi = 2Mk_BT_e\gamma_{kj}\delta(t-s). \tag{26}$$

The equation generalizes to nonequilibrium situations the white noise for classical Brownian motion.

Equations (24)–(26) constitute the first important result of this paper upon which the following results for the energy relaxation rate are all based. Since Eq. (24) is stochastic, one cannot speak at any given time t of the instantaneous positions and velocities of the ions but rather of their probability distribution. We also note that this equation applies to both equilibirum and nonequilibrium situations. The effect of the electrons, which is still treated quantum mechanically, has been partitioned into a systematic part and a fluctuating part (or noise). The systematic force is composed of two terms. The first one is equal to the instantaneous mean field force due to the instantaneous Coulomb interaction of the ions with the averaged electron density. Unlike systems interacting through short-range forces, this mean-field term cannot be discarded in Coulomb systems. The fluctuations in the mean field give rise to the second part of the systematic force and to the noise term. The former acts as a frictional force proportional to the particle velocities [20]. The noise term is zero on average and is related to the systematic friction through the fluctuation-dissipation relation (26). It is beyond the scope of this paper to discuss all the implications of Eq. (24) and, in the following, we will restrict ourselves to the energy relaxation problem.

III. TEMPERATURE RELAXATION RATE

In this section, we use the equation of motion (24) to compute the rate at which the electronic and ionic subsystems come into thermal equilibrium. We suppose that the electron-ion energy exchange occurs on a time scale much larger than the energy exchange within the two subsystems. In other words, we assume that on a dissipational time scale γ_{kj}/M the ionic velocities are thermally distributed at a temperature T_i, i.e.,

$$M\langle\dot{x}_k\dot{x}_j\rangle_i = \delta_{kj}k_BT_i,$$

where $\langle\cdots\rangle_i$ denotes the equilibrium average at temperature T_i over the ionic ensemble. By multiplying Eq. (24) by x_t and averaging over the ensemble of ions, we obtain the equation of evolution for the total instantaneous energy E_{ion} of the ionic system,

$$\frac{dE_{ion}}{dt} = \frac{d}{dt}\left\langle\sum_{I=1}^{N_i}\frac{M\dot{\mathbf{R}}_I^2}{2} + U(\{\mathbf{R}_I\})\right\rangle_i = -\left(\sum_k^{3N_i}\gamma_{kk}\right)k_BT_i + \langle\xi_t\cdot\dot{x}_t\rangle_i, \tag{27}$$

where $U = V_i + V$ is the total instantaneous potential energy of the ionic subsystem. The last term in the right-hand side of Eq. (27) can be evaluated by noting that on the fast time scale of the noise $\xi(t)$, Eq. (24) transforms into $M\ddot{x}_t \approx \xi_t$. Then, substituting $\dot{x}_t = (1/M)\int^t dt'\,\xi_{t'}$ into the last term of Eq. (24) and averaging over the noise with the use of the fluctuation-dissipation relation (26), we obtain an equation for the time evolution of the energy of the ionic subsystem in the traditional form,

$$\frac{1}{k_B}\frac{dE_{ion}}{dt} = g(T_e - T_i).$$

The coefficient $g = \sum_k \gamma_{kk}$ is the electron-ion energy relaxation rate. Using Eq. (25), we obtain the compact expressions

$$
\begin{aligned}
g &= -\frac{1}{M}\sum_{k}^{3N_i}\left\langle \int d\mathbf{r}_1 \int d\mathbf{r}_2\, v'_k(\mathbf{r}_1) v'_k(\mathbf{r}_2)\,\mathrm{Im}\,\frac{\partial}{\partial\omega}\chi_{ee}^{[x]}(\mathbf{r}_1,\mathbf{r}_2,\omega=0)\right\rangle_i \\
&= -\frac{1}{M}\,\mathrm{Im}\int d\mathbf{R}\int d\mathbf{r}_1\int d\mathbf{r}_2 \frac{\partial}{\partial\mathbf{r}_1}v_{ei}(\mathbf{r}_1-\mathbf{R})\cdot\frac{\partial}{\partial\mathbf{r}_1}v_{ei}(\mathbf{r}_2-\mathbf{R})\left\langle n_{ion}^{[x]}(\mathbf{R})\frac{\partial\chi_{ee}^{[x]}}{\partial\omega}(\mathbf{r}_1,\mathbf{r}_2,\omega=0)\right\rangle_i \\
&= -\frac{1}{M}\,\mathrm{Im}\,\frac{1}{V}\sum_{\mathbf{k},\mathbf{k}'}\mathbf{k}\cdot\mathbf{k}'\,v_{ie}(-\mathbf{k})v_{ie}(\mathbf{k}')\left\langle n_{ion}^{[x]}(-\mathbf{k}+\mathbf{k}')\frac{\partial\chi_{ee}^{[x]}}{\partial\omega}(\mathbf{k},\mathbf{k}',\omega=0)\right\rangle_i . \qquad (28)
\end{aligned}
$$

In the last expression, we have introduced the spatial Fourier representation of the potential and of the response function, namely,

$$
\begin{aligned}
\chi_{ee}^{[x]}(\mathbf{k},\mathbf{k}',t) &= \frac{1}{V}\int d\mathbf{r}_1\, e^{-i\mathbf{k}\cdot\mathbf{r}_1}\int d\mathbf{r}_2\, e^{i\mathbf{k}'\cdot\mathbf{r}_2}\chi_{ee}^{[x]}(\mathbf{r}_1,\mathbf{r}_2,t) \\
&= -\frac{1}{V}\frac{i}{\hbar}\langle[n_e(\mathbf{k},t),n_e(-\mathbf{k}')]\rangle .
\end{aligned}
$$

Equation (28) is the second central result of this paper and we will discuss it in depth in Sec. V. In the next section, we show that direct approximations to (28) lead to the familiar Landau-Spitzer and Fermi golden rule results.

IV. REDUCTION TO FAMILIAR RESULTS

Despite its apparent simplicity, the expression (28) is in general difficult to evaluate analytically for two main reasons. First, the response function $\chi_{ee}^{[x]}(\mathbf{r}_1,\mathbf{r}_2,\omega=0)$ of an interacting electron system in the external potential of the ionic configuration $[x]$ is a complicated object that is poorly known. Second, the average $\langle\cdots\rangle_i$ over the ionic configurations may be difficult to perform.

The calculation can be greatly simplified if one assumes that the average over the ionic configurations washes out the effect of the underlying ionic structure, which leads to the approximation

$$
\left\langle n_{ion}^{[x]}(\mathbf{R})\frac{\partial\chi_{ee}^{[x]}}{\partial\omega}(\mathbf{r}_1,\mathbf{r}_2,\omega=0)\right\rangle_i \approx n_{ion}\frac{\partial\chi_{ee}^{jel}}{\partial\omega}(\mathbf{r}_1,\mathbf{r}_2,\omega=0), \qquad (29)
$$

where $n_{ion}=\langle n_{ion}^{[x]}(\mathbf{R})\rangle_i=N_i/V$ is the ionic particle density and $\chi_{ee}^{jel}(\mathbf{r},\mathbf{r}',\omega)$ is the electron density-density response function of the homogeneous interacting electron gas in the jellium model. In this model, the actual discrete structure of the ionic background on which the electrons roam is replaced by a homogeneous continuum density of positive charge. The approximation (29) amounts to the supposition that the two subsystems are weakly coupled in the sense that the properties of the electrons are not affected by their interactions with the inhomogeneities of the underlying ionic potential. This is nothing but the approximation used by Kogan [9], by Dharma-wardana and Perrot [7], and by Hazak *et al.* [8] to derive the energy relaxation rate using linear response theory mentioned in the Introduction. The approximation (29) should therefore reproduce the Fermi golden rule result when introduced in Eq. (28). Since in the jellium model $\chi_{ee}^{jel}(\mathbf{k},\mathbf{k}',\omega)=\chi_{ee}^{jel}(\mathbf{k},\omega)\delta_{\mathbf{k},\mathbf{k}'}$, it is straightforward to show that Eq. (28) indeed reduces to the Fermi golden rule result [8],

$$
\begin{aligned}
g &= -\frac{n_{ion}}{M}\int\frac{d\mathbf{k}}{(2\pi)^3}\mathbf{k}^2|v_{ie}(\mathbf{k})|^2\,\mathrm{Im}\,\frac{\partial\chi_{ee}^{jel}}{\partial\omega}(\mathbf{k},0) \\
&= -\frac{n_{ion}}{M}\int\frac{d\mathbf{k}}{(2\pi)^3}\mathbf{k}^2|v_{ie}(\mathbf{k})|^2 \\
&\quad\times\frac{\mathrm{Im}(\partial\chi^0/\partial\omega)(\mathbf{k},0)}{\{1-(4\pi e^2/k^2)[1-G(k,0)]\mathrm{Re}\,\chi^0(\mathbf{k},0)\}^2}, \qquad (30)
\end{aligned}
$$

where, in the second expression, we have expressed χ_{ee}^{jel} in terms of the free-particle response function $\chi^0(\mathbf{k},\omega)$ and the local field correction $G(\mathbf{k},\omega)$. Equation (30) corresponds to the Fermi golden rule result obtained when assuming that ions are much more massive than electrons or, equivalently, that the relaxation rate is not sensitive to the fluctuations in the ionic subsystem (see [8] for the details). Assuming $v_{ie}(r)=-Ze^2/r$ and taking the nondegenerate electron limit of χ_{ee}^{jel}, Eq. (30) reduces to the Landau-Spitzer form

$$
g = 4n_i\frac{(2\pi mM)^{1/2}}{(Mk_BT_e)^{3/2}}Z^2e^4n_e\ln\Lambda,
$$

in terms of the Coulomb logarithm,

$$
\ln\Lambda \equiv \int\frac{dk}{k}\frac{k^4}{\{k^2+k_{De}^2[1-G(k,0)]\}^2}\exp\left(-\frac{\lambda_e^2}{8}k^2\right).
$$

Here $k_{De}=\sqrt{4\pi n_e e^2/k_BT_e}$ is the electronic Debye wave vector and $\lambda_e=\hbar/\sqrt{mk_BT_e}$ is the electronic thermal de Broglie wavelength.

The original diverging Landau-Spitzer formula can be more straightforwardly obtained if, in Eq. (29), one uses the response function of a classical free-electron gas $\chi_{cl}^0(k,\omega)$, thereby neglecting the electron-electron interactions [21],

$$\left\langle n_{ion}^{[x]}(-\mathbf{k}+\mathbf{k}')\frac{\partial\chi_{ee}^{[x]}}{\partial\omega}(\mathbf{k},\mathbf{k}',\omega=0)\right\rangle_i$$

$$\approx n_{ion}\frac{\partial\chi_{cl}^{0}}{\partial\omega}(k,\omega=0)$$

$$=-n_{ion}n_e\sqrt{\frac{\pi}{2}}\frac{m_e^{1/2}}{(k_BT_e)^{3/2}}\frac{1}{k},$$

with $n_e=N_e/V$ the electronic number density. When introduced in Eq. (28), we easily recover the well-known Landau-Spitzer result

$$k_B\frac{dT_i}{dT}=\frac{2}{3n_{ion}}\frac{dE_{ion}}{dt}=\frac{T_e-T_i}{\tau_{LS}},$$

where

$$\frac{1}{\tau_{LS}}=\frac{2}{3n_{ion}}g=\frac{8}{3}\frac{(2\pi mM)^{1/2}}{(Mk_BT_e)^{3/2}}Z^2e^4n_e\ln\Lambda$$

is the Landau-Spitzer energy relaxation rate with $\ln\Lambda_{LS}=\int dk(1/k)$ the Coulomb logarithm mentioned in the Introduction [4].

Similarly, it is straightforward to show that Eq. (28) reproduces the relaxation rate predicted by the Lenard-Balescu equation when $\chi_{ee}^{[x]}$ is approximated by the electron-electron response function of a two-component plasma in the random-phase approximation.

V. DISCUSSION AND PROSPECTS

We have derived a compact expression, Eq. (28), for the energy relaxation rate of a two-temperature electron-ion system. The quantum character of the electron system and the electron-electron interactions enter in the quantity $\chi_{ee}^{[x]}$, the effect of electron-ion interactions is included through the dependence of $\chi_{ee}^{[x]}$ on the ionic configurations x, and, finally, the dependence on the ion-ion interactions is described by the average $\langle\cdots\rangle_i$. The conditions of validity of this formula are that the electron-ion energy exchange is slow compared with the energy relaxation within each subsystem (two-temperature assumption) and that the ion dynamics occurs on a time scale larger than the electron dynamics (heavy ion approximation). As a consequence, the rate of energy relaxation between electrons and ions is not sensitive to the details of the ionic spectrum of fluctuations and depends only on the low-frequency properties $\omega\simeq 0$ of the density fluctuations of the electron gas in the external potential of the fixed ions, averaged over the ionic configurations sampled at temperature T_i. There is no restriction on the strength of the electron-ion coupling or on the degeneracy of the electronic system. Our formula therefore applies to a large class of systems including room temperature solid metals, liquid metals, warm dense matter, and hot plasmas.

It is in general very difficult to derive an exact analytical expression for the response functions $\chi_{ee}^{[x]}$. When the electron-ion coupling is very weak, a good approximation for $\chi_{ee}^{[x]}$ is probably the jellium response function discussed in Sec. IV. Physical regimes where electron-ion interactions are not weak (e.g., in the warm dense matter regime) are difficult to deal with analytically although, in principle, Eq. (28) applies. We shall address the question of inclusion of the effect of the ions in the low-frequency behavior $\chi_{ee}^{[x]}$ in a future presentation [12].

An important merit of our result (28) is, however, that it expresses the energy relaxation rate in terms of quantities that can in principle be evaluated with *ab initio* simulation methods. Equation (28) can be looked at as a "nonequilibrium Kubo relation" similar to the well-known Kubo relations that define the transport coefficients of systems at equilibrium in terms of correlation functions. *Ab initio* methods, such as quantum molecular dynamics (QMD), have been successfully used in the description of equilibrium properties of condensed matter and warm dense matter [22]. In QMD, for instance, the active electrons receive a full quantum mechanical treatment within the finite-temperature density functional theory while ions are propagated classically according to Newton's equations, in which the electron-ion force is calculated in the Born-Oppenheimer, adiabatic approximation. Unfortunately, most existing *ab initio* approaches are adequate to investigate equilibrium properties of materials ($T_e=T_i$), such as the equation of state properties or the electrical conductivity, and cannot be applied to nonequilibrium situations. However, since our expression (28) depends on averages over equilibrium ensembles, we believe that it is amenable to such *ab initio* calculations with slight, well-controlled modifications of the existing simulation codes. To conclude this paper, we propose an approach based on finite-temperature density functional calculations such as QMD that, in principle, could be implemented to estimate the energy relaxation rates in a two-temperature plasma with electron temperature T_e and ion temperature T_i. It is beyond our scope to discuss here the technical details and we just outline the following possible approach. (1) Given a fixed ionic configuration x, calculate the electron density-density response function $\chi_{ee}^{[x]}$ at temperature T_e. To this end, solve the finite-temperature Kohn-Sham (KS) equations at temperature T_e for the KS orbitals $\phi_j(\mathbf{r})$ and KS energies ϵ_j, and compute the KS density response function$\chi_{KS}^{[x]}$,

$$\chi_{KS}^{[x]}(\mathbf{r},\mathbf{r}',\omega)=\sum_{jk}(n_j-n_k)\frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{\omega-(\epsilon_j-\epsilon_k)+i0^+},$$

where $n_j=1/[\exp(\epsilon_j/k_BT_e)-1]$ is the Fermi occupation number. The required response function $\chi_{ee}^{[x]}$ is obtained by solving the Dyson equation

$$\chi_{ee}^{[x]}(\mathbf{r},t;\mathbf{r}',t')=\chi_{KS}^{[x]}(\mathbf{r},t;\mathbf{r}',t')+\int d\mathbf{x}\int d\tau\int d\mathbf{x}'\int d\tau'\,\chi_{KS}^{[x]}(\mathbf{r},t;\mathbf{x},\tau)\left(\frac{\delta(\tau-\tau')}{|\mathbf{x}-\mathbf{x}'|}+f_{xc}[n_0](\mathbf{x},\tau;\mathbf{x}',\tau')\right)\chi_{ee}^{[x]}(\mathbf{r},t;\mathbf{r}',t')$$

with $f_{xc}[n_0](\mathbf{r},t;\mathbf{r}',t')=[\delta v_{xc}[n](\mathbf{r},t)/\delta n(\mathbf{r}',t')]|_{n_0}$ and v_{xc} the exchange-correlation potential.

(2) The same calculation must then be repeated for all the configurations representative of the ionic system at temperature T_i immersed in the electronic bath at temperature T_e. Such a sampling could be obtained via molecular dynamics techniques using for the electron-ion force the "nonequilibrium" Born-Oppenheimer force Eq. (15), and a numerical thermostat (e.g., Nose-Hoover) to impose the temperature T_i.

(3) Finally, the rate of energy relaxation is obtained using (28) by averaging the diverse $\chi_{ee}^{[x]}$ from the previous two steps.

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[13] In the text a function f that depends on the time t is alternatively denoted $f(t)$ or f_t with no risk of confusion.

[14] For simplicity, Eq. (3) actually assumes that the initial total density matrix can be factorized as a product of the ionic and electronic density operators. More general initial conditions taking into account correlations between the subsystems may be considered as well [10; U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 1993)]. The final results derived in this paper are not affected by the factorizing assumption.

[15] Note that the Fourier transform of $\rho(x,y,t)$ with respect to the off-diagonal elements y,

$$f(x,p,t)=\int\frac{dy}{(2\pi\hbar)^{3N_i}}\rho(x,y,t)e^{-ipy/\hbar},$$

is the Wigner distribution function, which generalizes the classical phase space distribution function to quantum systems.

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[17] Were we to include the higher-order term in (7), such as y^3, etc., the noise would become non-Gaussian, which would have made the following derivations much more complicated. However, we are dealing with a situation in which the electronic correlation time τ_e is quite short compared to the ionic time scale τ_i. For instance, the electronic relaxation time is of the order of a few femtoseconds for $T_e > 10^4$ K, while $\tau_i \sim h/k_B\Theta_{Debye} \sim 100$ fs. Therefore the noise averages over the trajectory, and via the central limit argument becomes effectively Gaussian. Thus, only quadratic terms in y are important.

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[19] Indeed,

$$\begin{aligned}\langle\xi_k[x,t]\xi_j[x,s]\rangle_\xi &= \delta(t-s)\,\mathcal{C}_{k,j}^{[x]}(\omega=0)\\ &= \delta(t-s)\lim_{\omega\to 0} -\hbar\,\coth\left(\frac{\hbar\omega}{2k_BT_e}\right)\mathrm{Im}\,\mathcal{R}_{k,j}^{[x]}(\omega)\\ &= -2k_BT_e\,\mathrm{Im}\,\frac{\partial}{\partial\omega}\mathcal{R}_{k,j}^{[x]}(\omega=0)\,\delta(t-s)\\ &= 2Mk_BT_e\gamma_{kj}\delta(t-s).\end{aligned}$$

[20] Let us consider the equation of motion (24) for the component $k=(I,x)$ (I is the ion label and x is one of the three Cartesian directions). In Eq. (24) the total friction acting on $x_k=R_{Ix}$ involves all the velocity components $\dot{R}_{Jy}$ of all the particles $J=1,\ldots,N_i$. In fact, the magnitude of the friction terms γ_{IxJy} strongly varies with J and y, and most of the friction comes from the term $\gamma_{IxIx}\dot{R}_{Ix}$, as in the Langevin equation for a Brownian particle. To illustrate this, we approximate $\chi_{ee}^{[x]}$ by the response function of a nondegenerate electron gas in the random-phase approximation and straightforwardly obtain,

$$\begin{aligned}\gamma_{Ix,Jy} &\propto \int d\mathbf{k}\frac{k_xk_y}{k^5}\frac{e^{-\lambda_e^2k^2/8}}{k}e^{i\mathbf{k}\cdot(\mathbf{R}_I-\mathbf{R}_J)}\\ &\propto \delta_{x,y}\int_0^\infty dk\frac{k^3}{(k^2+k_{De}^2)^2}\frac{\sin(kR_{IJ})}{kR_{IJ}}e^{-(\lambda_e^2/8)k^2},\end{aligned}$$

where $R_{IJ}=\|\mathbf{R}_I-\mathbf{R}_J\|$ is the distance between particles I and J, k_{De} is the electron Debye wave vector, and λ_e is the thermal de Broglie wavelength (see Sec. IV). The previous estimate shows that, on average, $\gamma_{Ix,Jy}=0$ when $x\neq y$ and that $\gamma_{Ix,Jx}$ decays rapidly with the interparticle distance R_{IJ}.

[21] The classical free-particle response function for a system of density n and temperature T is $\chi_{cl}^0(k,\omega) = -(n/k_BT)Z(\omega/k\sqrt{2k_BT/m})$ where $Z(x)=(1/\sqrt{\pi})\int_{-\infty}^{\infty}dy\,e^{-y^2}/y - x - i\delta$. See, for instance, S. Ichimaru, *Basic Principles of Plasma Physics* (Benjamin, London, 1973).

[22] See, for example, S. Mazevet, M. P. Desjarlais, L. A. Collins, J. D. Kress, and N. H. Magee, Phys. Rev. E **71**, 016409 (2005) and references therein.