PHYSICAL REVIEW A VOLUME 33, NUMBER 3 MARCH 1986

Statistical mechanics of a two-temperature, classical plasma

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(Received 12 August 1985)

Weakly coupled, nonequilibrium plasmas have often been described by assigning separate temperatures to the electron and ion velocity distributions. In this paper we present a model for the complete phase-space probability function which describes a two-temperature ensemble for arbitrary coupling. We discuss the "thermodynamics" predicted by the model, and in the limit of weak electron-ion coupling, we obtain explicit expressions for both the static and dynamic structure factors, which remain valid even for strong ion-ion coupling. When the ions become weakly coupled, our results for the static structure factors reduce to those of Salpeter. However, even in this limit there remains a small difference from Salpeter's dynamic structure factor due to the nonergodicity of the ensemble.

I. INTRODUCTION

Many plasmas of practical interest cannot be described by equilibrium statistical mechanics, and some appropriate nonequilibrium model has to be constructed. A very successful method for weakly coupled, spatially uniform plasmas has been to assign separate temperatures to the electron and ion velocity distributions. Such a model can be justified because of the relatively long time that it takes to exchange energy between electrons and ions in comparison to the equilibration times of the individual species.[1]

In this paper, we are interested in extending the usual descriptions of weakly coupled two-temperature plasmas[2,3] to include plasmas in which the ions are cold and highly charged, and the electrons are hot. In such a plasma the ions will be strongly coupled, even though the electrons are weakly coupled. As will be discussed later, the electron-ion equilibration time in such a plasma can still be expected to be much longer than the individual equilibration times. Hence, we will attempt to describe plasmas with strongly coupled ions in terms of a two-temperature model for the complete phase-space probability function.[4–6] This probability function will then be used to calculate various ensemble averages of interest to lowest order in the electron-ion coupling parameter. No assumptions concerning the strength of the ion-ion coupling, aside from the obvious constraint imposed by charge neutrality, will be made.

The physical basis of our model is the assumption that the ions in the plasma move slowly enough that the electrons can view them as the source of a constant external potential in which they come to equilibrium at temperature $T_e = 1/k_B\beta_e$. The given ion configurations are then weighted by a Maxwell distribution at temperature $T_i = 1/k_B\beta_i$, but with the ion-ion interactions in a given configuration reduced by the electron-free energy A_e in that configuration. Specifically, we write our model phase-space probability function as[5]

$$\rho = Q^{-1} Q_e^{-1} e^{-\beta_i(H_i + A_e)} e^{-\beta_e(H_e + V_{ei})} , \tag{1.1}$$

where A_e is defined by

$$A_e \equiv -\beta_e^{-1} \ln Q_e , \tag{1.2}$$

and the partition functions Q_e and Q are given by

$$Q_e \equiv \int d\Gamma_e e^{-\beta_e(H_e + V_{ei})} , \tag{1.3a}$$

$$\begin{aligned} Q &\equiv \int d\Gamma_i d\Gamma_e e^{-\beta_i(H_i + A_e)} Q_e^{-1} e^{-\beta_e(H_e + V_{ei})} \\ &= \int d\Gamma_i e^{-\beta_i(H_i + A_e)} . \end{aligned} \tag{1.3b}$$

In the above, $d\Gamma_e$ and $d\Gamma_i$ represent integration over the space and momentum coordinates of the N_e electrons and N_i ions.

The Hamiltonian for the plasma is given by

$$H = (K_i + V_{ii}) + (K_e + V_{ee}) + V_{ei} = H_i + H_e + V_{ei} , \tag{1.4}$$

where

$$K_i = \sum_{j=1}^{N_i} \frac{p_j^2}{2m_i} , \quad K_e = \sum_{j=1}^{N_e} \frac{p_j^2}{2m_e} ,$$

$$\begin{aligned} V_{ii} &= \frac{1}{\Omega} \sum_{\substack{j,k \\ (1 \le j < k \le N_i)}} \sum_q{}' \tilde{v}_{ii}(q) e^{i\mathbf{q}\cdot(\mathbf{r}_j - \mathbf{r}_k)} \\ &= \sum_{\substack{j,k \\ (1 \le j < k \le N_i)}} v_{ii}(\mathbf{r}_j - \mathbf{r}_k) , \end{aligned}$$

$$\begin{aligned} V_{ee} &= \frac{1}{\Omega} \sum_{\substack{j,k \\ (1 \le j < k \le N_i)}} \sum_q{}' \tilde{v}_{ee}(q) e^{i\mathbf{q}\cdot(\mathbf{r}_j - \mathbf{r}_k)} \\ &= \sum_{\substack{j,k \\ (1 \le j < k \le N_i)}} v_{ee}(\mathbf{r}_j - \mathbf{r}_k) , \end{aligned}$$

$$\begin{aligned} V_{ei} &= \frac{1}{\Omega} \sum_{j=1}^{N_e} \sum_{k=1}^{N_i} \sum_q{}' \tilde{v}_{ei}(q) e^{i\mathbf{q}\cdot(\mathbf{r}_j - \mathbf{r}_k)} \\ &= \sum_{j=1}^{N_e} \sum_{k=1}^{N_i} v_{ei}(\mathbf{r}_j - \mathbf{r}_k) . \end{aligned}$$

The prime on the sums indicates that the $q=0$ term is not included, Ω is the volume of the system, and for ions of net charge Ze,

$$\tilde{v}_{ee}(q)=-\frac{1}{Z}\tilde{v}_{ei}(q)=\frac{1}{Z^2}\tilde{v}_{ii}(q)=\frac{4\pi e^2}{q^2}\ . \tag{1.5}$$

It should be noted that when the temperatures are equal, Eq. (1.1) reduces to the proper equilibrium probability function for a classical plasma. Furthermore, Eq. (1.1) could be used, at least in principle, to describe plasmas of arbitrary coupling strength. However, in what follows, we will limit our discussion to cases in which the electron-ion coupling parameter is small. We define the electron-ion and electron-electron coupling parameters through

$$\gamma_{ei}=Z\gamma_{ee}=Z\beta_e e^2/\lambda_e=\frac{Z\Omega}{4\pi N_e\lambda_e^{-3}}\ , \tag{1.6}$$

where

$$1/\lambda_e\equiv k_e=(4\pi\beta_e^2 N_e e/\Omega)^{1/2}=\left[\frac{Z\beta_e}{\beta_i}\right]^{1/2}k_i\ .$$

Requiring these parameters to be small should not be a serious limitation, because of the wide variety of plasmas which are of this type. In addition, it allows us to use an approach which is very similar to the linear-response description of liquid metals[7] and ionic liquids.[8,9] The primary difference is that here the electrons are considered to be classical instead of degenerate. In the spirit of these previous theories, we evaluate $\ln Q_e$ to second order in the electron-ion interaction in Sec. II, and in Sec. III we evaluate the static structure factors to the same order. The "thermodynamics" predicted by the model is studied in Sec. IV, and in Sec. V we evaluate the dynamic structure factors. The results of the paper are discussed in the final section.

II. THE ELECTRON PARTITION FUNCTION

In this section we will evaluate the electron-free energy in an arbitrary ionic configuration to second order in the electron-ion interaction. Such an evaluation will be appropriate when the electron-ion coupling parameter Eq. (1.6) is small. In order to evaluate Eq. (1.3a), we first note that V_{ei} may be written in the form

$$V_{ei}=\sum_{j=1}^{N_e}w_e(\mathbf{r}_j)\ , \tag{2.1}$$

where

$$w_e(\mathbf{r}_j)\equiv\sum_{k=1}^{N_i}v_{ei}(\mathbf{r}_j-\mathbf{r}_k) \tag{2.2}$$

depends upon the position of only a single electron (but all of the ion positions). By defining

$$\phi_e(\mathbf{r}_i)\equiv e^{-\beta_e w_e(\mathbf{r}_j)}-1\ , \tag{2.3}$$

we can write Q_e as

$$Q_e=\int d\Gamma_e e^{-\beta_e H_e}\prod_{j=1}^{N_e}[1+\phi_e(\mathbf{r}_j)]\ . \tag{2.4}$$

We may now exploit the fact that $\phi_e(\mathbf{r}_j)$ is a single-electron function to obtain, through a standard cluster-expansion approach,[10]

$$\ln(Q_e/Q_e^{(0)})=\sum_{l=1}^{\infty}\frac{n_e^l}{l!}b_l\ , \tag{2.5}$$

where $Q_e^{(0)}$ is the partition function for the electron gas in a uniform neutralizing background $n_e=N_e/\Omega$, and

$$b_l\equiv\int d^3r_1\cdots d^3r_l h_e^{(l)}(r_1,\ldots,r_l)\phi_e(\mathbf{r}_1)\cdots\phi_e(\mathbf{r}_l)\ . \tag{2.6}$$

The $h_e^{(l)}(r_1,\ldots,r_l)$'s are the total correlation functions for the electron gas,

$$\begin{aligned}&h_e^{(1)}(r_1)=1\ ,\\&h_e^{(2)}(\mathbf{r}_1-\mathbf{r}_2)=g_e^{(2)}(\mathbf{r}_1-\mathbf{r}_2)-1\ ,\end{aligned} \tag{2.7}$$

etc. In the above, $g_e^{(2)}(r)$ is the radial distribution function for the electron gas.[11]

To obtain our approximate free energy, we expand Eq. (2.5) to second order in $\beta_e w_e$. From Eqs. (2.3) and (2.6), it is clear that all terms in the series beyond the first two need not be considered to this order. The first-order term from b_1 vanishes, and the second-order terms from b_1 and b_2 combine to give

$$\begin{aligned}\ln(Q_e/Q_e^{(0)})&=\frac{\beta_e^2 n_e}{2\Omega}\sum_{j=1}^{N_i}\sum_{k=1}^{N_i}\sum_q{}'\tilde{v}_{ei}^2(q)[1+n_e\tilde{h}_e(q)]e^{i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}\\&=\frac{\beta_e}{2\Omega}\sum_{j,k}\sum_q{}'\tilde{v}_{ii}(q)[\beta_e n_e\tilde{v}_{ee}(q)S_e(q)]e^{i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}\\&=\frac{\beta_e}{2\Omega}\sum_{j,k}\sum_q{}'\tilde{v}_{ii}(q)[1-\epsilon_e^{-1}(q,0)]e^{i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}\ ,\end{aligned} \tag{2.8}$$

where $\epsilon_e(q,0)$ and $S_e(q)$ are the static dielectric function and structure factor, respectively, for the electron gas.[11] Thus, the electron free energy is, to second order in the electron-ion interaction,

$$\begin{aligned}A_e=&V_{ii}^{(s)}-V_{ii}-\beta_e^{-1}\ln Q_e^{(0)}\\&-\frac{N_i}{2}[v_{ii}(\mathbf{r}=0)-v_{ii}^{(s)}(\mathbf{r}=0)]\ ,\end{aligned} \tag{2.9}$$

where the screened interaction is defined by

$$\begin{aligned}V_{ii}^{(s)}&\equiv\frac{1}{\Omega}\sum_{\substack{j,k\\(1\le j<k\le N_i)}}\sum_q{}'\tilde{v}_{ii}(q)\epsilon_e^{-1}(q,0)e^{i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}\\&=\sum_{\substack{j,k\\(1\le j<k\le N_i)}}v_{ii}^{(s)}(\mathbf{r}_j-\mathbf{r}_k)\ .\end{aligned} \tag{2.10}$$

Finally, from Eq. (2.9), (1.1), and (1.2), the phase-space probability function becomes

$$\rho=\frac{1}{Q_i^{(s)}}e^{-\beta_i(K_i+V_{ii}^{(s)})}\left[\frac{1}{Q_e}e^{-\beta_e(H_e+V_{ei})}\right], \tag{2.11}$$

$$Q_i^{(s)}\equiv\int d\Gamma_i e^{-\beta_i(K_i+V_{ii}^{(s)})}, \tag{2.12}$$

and we see that it is just the product of the probability functions for electrons in the external field of the ions and a system of screened ions.

III. DENSITY CORRELATIONS

The density-density correlation functions for the plasma are very important quantities. Not only are their Fourier transforms directly measurable through various scattering experiments,[12] but knowledge of them is sufficient to evaluate the ensemble averages of many quantities of interest. In this section we will use the phase-space probability function defined in Eq. (1.1) to evaluate the density-density correlation functions to lowest order in the electron-ion coupling parameter.

The density correlation functions to be calculated are defined by

$$G_{ab}(\mathbf{r},\mathbf{r}')\equiv\langle n_a(\mathbf{r})n_b(\mathbf{r}')\rangle, \tag{3.1}$$

where the angular brackets indicate averaging with respect to the ensemble described in the previous sections, and the densities $n_a(\mathbf{r})$ are defined by

$$n_a(\mathbf{r})\equiv\sum_{j=1}^{N_a}\delta(\mathbf{r}-\mathbf{r}_j). \tag{3.2}$$

The structure factors for the plasma are related to these correlation functions through a Fourier transform

$$\sqrt{n_a n_b}S_{ab}(q)\equiv\int d^3r\, e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}[G_{ab}(\mathbf{r},\mathbf{r}')-n_a n_b], \tag{3.3}$$

where the average densities are

$$\langle n_a(\mathbf{r})\rangle=N_a/\Omega=n_a. \tag{3.4}$$

Formally, the simplest of these correlation functions to calculate is G_{ii}. From its definition and Eq. (2.11), it is found to be

$$\begin{aligned}G_{ii}(\mathbf{r},\mathbf{r}')&\equiv\langle n_i(\mathbf{r})n_i(\mathbf{r}')\rangle\\&=\frac{1}{Q_i^{(s)}}\int d\Gamma_i e^{-\beta(K_i+V_{ii}^{(s)})}n_i(\mathbf{r})n_i(\mathbf{r}')\\&=\langle n_i(\mathbf{r})n_i(\mathbf{r}')\rangle_{\text{ions}}\equiv G_i(\mathbf{r}-\mathbf{r}').\end{aligned} \tag{3.5}$$

The structure factor S_{ii} is then given by

$$S_{ii}(q)=\frac{1}{n_i}\int d^3r\, e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}[G_i(\mathbf{r}-\mathbf{r}')-n_i^2]\equiv S_i(q). \tag{3.6}$$

Thus, we see that G_{ii} and S_{ii} are, to lowest order in γ_{ei}, simply given by the corresponding functions for a one-component system of ions interacting through an electron-screened potential [screened one-component plasma (OCP)].[7] In the limit of weak coupling, S_i is given by the well-known result

$$S_i(q)=\frac{q^2+k_e^2}{q^2+k_D^2},\quad k_D^2\equiv k_e^2+k_i^2 \tag{3.7}$$

while for strong coupling it must be calculated by some other method, such as solving the hypernetted chain (HNC) equation.[13]

The next most difficult correlation function to calculate, G_{ei}, can also be reduced to an average over ions only, by noting that

$$\begin{aligned}G_{ie}(\mathbf{r},\mathbf{r}')&\equiv\langle n_i(\mathbf{r})n_e(\mathbf{r}')\rangle\\&=-\frac{1}{\beta_e}\left\langle n_i(\mathbf{r})\frac{\delta\ln Q_e}{\delta w_e(\mathbf{r}')}\right\rangle_{\text{ions}}.\end{aligned} \tag{3.8}$$

Using Eq. (2.5) to evaluate the functional derivative gives

$$G_{ie}(\mathbf{r},\mathbf{r}')=\sum_{l=1}^{\infty}\frac{n_e^l}{(l-1)!}\langle n_i(\mathbf{r})[\phi_e(\mathbf{r}')+1]\int d^3r_2\cdots d^3r_l h_e^{(l)}(r',r_2,\ldots,r_l)\phi_e(\mathbf{r}_2)\cdots\phi_e(\mathbf{r}_l)\rangle_{\text{ions}}. \tag{3.9}$$

When this is expanded to second order in $\beta_e w_e$, there are contributions from all terms in the series for which $l\leq 3$. Evaluating the electron total correlation functions in these terms to lowest order in γ_{ee} (Ref. 14) yields, after a fair amount of manipulation,

$$\begin{aligned}G_{ie}(\mathbf{r},\mathbf{r}')-n_i n_e=&-\frac{\beta_e n_e n_i}{\Omega}\sum_q\tilde{v}_{ei}(q)S_e(q)S_i(q)e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\\&+\frac{\beta_e^2 n_e n_i}{2\Omega^2}\sum_{q,q'}\tilde{v}_{ei}(q)S_e(q)\tilde{v}_{ei}(q')S_e(q')S_e(q+q')C_{iii}^{(3)}(\mathbf{q},\mathbf{q}')e^{i(\mathbf{q}+\mathbf{q}')\cdot(\mathbf{r}-\mathbf{r}')},\end{aligned} \tag{3.10}$$

where the triplet correlation function in the above is defined by

$$C_{iii}^{(3)}(\mathbf{q},\mathbf{q}')\equiv\int\int d^3r'd^3r''e^{i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r})}e^{i\mathbf{q}'\cdot(\mathbf{r}''-\mathbf{r})}\times\langle\delta n_i(\mathbf{r})\delta n_i(\mathbf{r}')\delta n_i(\mathbf{r}'')\rangle_{\text{ions}}\ , \tag{3.11}$$

where $\delta n_a(\mathbf{r})=n_a(\mathbf{r})-n_a$.

From this result we find S_{ei} to be

$$S_{ei}(q)=\sqrt{Z}\,(k_e^2/q^2)S_e(q)S_i(q)+\frac{Z^{3/2}}{2n_e}S_e(q)\times\int\frac{d^3q'}{(2\pi)^3}\frac{k_e^2}{q'^2}\frac{k_e^2}{|q-q'|^2}\times S_e(q')S_e(\mathbf{q}-\mathbf{q}')C_{iii}^{(3)}(\mathbf{q}',\mathbf{q}'-\mathbf{q})\ . \tag{3.12}$$

The first term in this equation is Salpeter's result,[2] generalized to include strong ion-ion coupling effects. Essentially, this term represents the correlations between an ion and the electrons in the induced "cloud" surrounding another ion. The second term represents distortions of the cloud by the presence of a third correlated ion. By scaling q and q' to k_e, this term can be seen to be of higher order in the electron-ion coupling γ_{ei}.

Similarly, we find for G_{ee},

$$G_{ee}(\mathbf{r},\mathbf{r}')\equiv\langle n_e(\mathbf{r})n_e(\mathbf{r}')\rangle=\frac{1}{\beta_e^2}\left\langle\frac{\delta^2\ln Q_e}{\delta w_e(r)\delta w_e(r')}+\frac{\delta\ln Q_e}{\delta w_e(r)}\frac{\delta\ln Q_e}{\delta w_e(r')}\right\rangle_{\text{ions}}\ . \tag{3.13}$$

If we once again evaluate the functional derivatives to second order in $\beta_e w_e$, and the $h_e^{(l)}$'s to lowest order in γ_{ee}, we obtain

$$S_{ee}(q)=S_e(q)+ZS_i(q)[(k_e^2/q^2)S_e(q)]^2+\frac{Z}{n_e}\int\frac{d^3q'}{(2\pi)^3}S_i(q')\left[\frac{k_e^2}{q'^2}S_e(q')\right]^2\times[S_e(\mathbf{q}'-\mathbf{q})-1]S_e^2(q)\ . \tag{3.14}$$

The first two terms reduce, in the limit of weak ion-ion coupling, to Salpeter's result,[2] and represent, respectively, the density correlations in an electron gas and the correlations between electrons in the clouds surrounding two correlated ions. The third term represents effects due to "cloud polarization," and is also higher order in γ_{ei}.

In summary, the structure factors representing the density correlations in a two-temperature plasma are given to lowest order in γ_{ei} by

$$\begin{aligned}S_{ii}(q)&=S_i(q)\\&\equiv\frac{1}{n_i}\int d^3r\,e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\langle n_i(\mathbf{r})n_i(\mathbf{r}')\rangle_{\text{ions}}\ ,\\S_{ei}(q)&=\sqrt{Z}\,(k_e^2/q^2)S_e(q)S_i(q)\ ,\\S_{ee}(q)&=S_e(q)+ZS_i(q)\left[\frac{k_e^2}{q^2}S_e(q)\right]^2\ .\end{aligned} \tag{3.15}$$

These results are very similar to Salpeter's,[2] and generalize his results to include strong ion-ion coupling.

IV. "THERMODYNAMICS"

In standard textbook derivations,[15] the connection between thermodynamics and equilibrium statistical mechanics is established by making statistical-mechanical definitions of the thermodynamic functions, and then proving that the relationships among them are the same as predicted by their thermodynamic definitions. In this section, we will define the internal energy, the entropy, and the pressure in terms of appropriate two-temperature ensemble averages and then show that these definitions are consistent with a plausible two-temperature generalization of ordinary thermodynamics.

The most obvious definition is that of the internal energy U in terms of the ensemble average of the Hamiltonian. From Eqs. (1.3) and (1.4) it is easy to establish that

$$U\equiv\langle H\rangle=-\left[\frac{\partial\ln Q}{\partial\beta_i}\right]_{\beta_e}-\frac{\beta_e}{\beta_i}\left[\frac{\partial\ln Q}{\partial\beta_e}\right]_{\beta_i}\ . \tag{4.1}$$

In addition, since H is expressible entirely in terms of one-particle and two-particle functions, its average may be written in terms of the structure factors defined in the previous section. Specifically, we find

$$U=\frac{3N_e}{2\beta_e}+\frac{3N_i}{2\beta_i}+(Z+1)\frac{e^2N_e}{\pi}\int_0^\infty dq[S_{zz}(q)-1]\ , \tag{4.2}$$

where S_{zz} is the charge-charge structure factor defined by

$$S_{zz}(q)=\frac{1}{Z+1}[S_{ee}(q)+ZS_{ii}(q)-2\sqrt{Z}S_{ei}(q)]\ . \tag{4.3}$$

The entropy of the plasma can be defined in terms the average of $\ln\rho$,

$$\bar{S}\equiv-k_B\int d\Gamma_i d\Gamma_e\rho\ln\rho\ , \tag{4.4}$$

where the overbar is to prevent confusion with symbol for the structure factors. It will prove useful in what follows to break $\bar{S}$ into electron and ion contributions. This may be accomplished by defining

$$\rho_i\equiv\int d\Gamma_e\rho=\frac{1}{Q}e^{-\beta_i(H_i+A_e)}\rightarrow\frac{1}{Q_i^{(s)}}e^{-\beta_i(K_i+V_{ii}^{(s)})} \tag{4.5}$$

and

$$\rho_e=\rho/\rho_i=\frac{1}{Q_e}e^{-\beta_e(H_e+V_{ei})}\ . \tag{4.6}$$

The entropy may now be written as

$$\bar{S}=\bar{S}_e+\bar{S}_i \ , \tag{4.7}$$

where

$$\begin{aligned}\bar{S}_i &\equiv -k_B\int d\Gamma_i\rho_i\ln\rho_i=k_B(\ln Q+\beta_i\langle H_i+A_e\rangle)\\ &\to k_B(\ln Q_i^{(s)}+\beta_i\langle K_i+V_{ii}^{(s)}\rangle)\end{aligned} \tag{4.8}$$

and

$$\begin{aligned}\bar{S}_e &\equiv -k_B\int d\Gamma_i\rho_i\int d\Gamma_e\rho_e\ln\rho_e\\ &=k_B(\langle\ln Q_e\rangle+\beta_e\langle H_e+V_{ei}\rangle) \ .\end{aligned} \tag{4.9}$$

The ion contribution, for $\gamma_{ei} \ll 1$, is just the entropy of the screened OCP, and the electron contribution is the entropy of the electrons in an external field, averaged over ionic configurations. The connections between both contributions and the partition function are easily established, and we obtain[5]

$$\bar{S}_i=-k_B\beta_i^2\left[\frac{\partial\beta_i^{-1}\ln Q}{\partial\beta_i}\right]_{\beta_e}=\left[\frac{\partial\beta_i^{-1}\ln Q}{\partial T_i}\right]_{T_e} \tag{4.10}$$

and

$$\bar{S}_e=-k_B\beta_e^2\left[\frac{\partial\beta_i^{-1}\ln Q}{\partial\beta_e}\right]_{\beta_i}=\left[\frac{\partial\beta_i^{-1}\ln Q}{\partial T_e}\right]_{T_i} \ . \tag{4.11}$$

Similarly, the pressure of the plasma can be related to the average of the stress tensor. Taking into account the translational and rotational symmetry of the plasma, we find[16]

$$\begin{aligned}\langle\tau_{\mu\nu}\rangle &=\frac{n_e}{m_e}\int d^3p\,p_\mu p_\nu\phi_e(p)+\frac{n_i}{m_i}\int d^3p\,p_\mu p_\nu\phi_i(p)\\ &\quad-\frac{n_e^2}{2}\int d^3r\frac{r_\mu r_\nu}{|\mathbf{r}|}\frac{\partial v_{ee}(r)}{\partial r}\\ &\qquad\times[g_{ee}^{(2)}(r)+g_{ii}^{(2)}(r)-2g_{ei}^{(2)}(r)]\\ &=p\delta_{\mu\nu} \ ,\end{aligned} \tag{4.12}$$

where $\phi_a(p)$ is the normalized Maxwell-Boltzmann distribution for species a, and the pressure is

$$p=\frac{n_e}{\beta_e}+\frac{n_i}{\beta_i}+(Z+1)\frac{e^2n_e}{3\pi}\int_0^\infty dq[S_{zz}(q)-1] \ . \tag{4.13}$$

This result is identical to that obtained by scaling the lengths in Eq. (1.3b) to $\Omega^{1/3}$ and differentiating $\ln Q$ with respect to Ω. Hence, we have established that

$$p=\frac{\partial\beta_i^{-1}\ln Q}{\partial\Omega} \ . \tag{4.14}$$

All of these results suggest that we define the total free energy by[5]

$$A\equiv-\beta_i^{-1}\ln Q \ . \tag{4.15}$$

By combining Eqs. (4.1), (4.10), and (4.11), we see that, with this definition, the free energy and the internal energy are related through a two-temperature Legendre transformation

$$A=U-T_eS_e-T_iS_i \ . \tag{4.16}$$

Thus, to this point, we have related the internal energy, entropy, pressure, and free energy of a two-temperature plasma to the partition function, Eq. (1.3b), and, therefore, to each other. It remains to determine how these quantities change when a small quantity of heat dQ is absorbed by the system and, thereby, establish their thermodynamic relations.

To this end we generalize the first two laws of ordinary thermodynamics to include this two-temperature system. The first law of thermodynamics is just a statement of energy conservation, so it remains essentially unchanged,

$$dU=dQ-p\,d\Omega \ . \tag{4.17}$$

The second law of thermodynamics relates the heat absorbed in a reversible process to the entropy change of the system. To generalize this law, we view dQ as the sum of an electron and an ion contribution, each of which is related to the change in the corresponding contribution to the entropy in the usual way. In other words, we generalize the second law by writing[5]

$$dQ=dQ_e+dQ_i=T_edS_e+T_idS_i \ . \tag{4.18}$$

This expression is certainly rigorous for two isolated systems for which reversible processes can be independently defined, and such a separation of dQ makes sense physically, since it is possible to pump heat into either the electrons or ions along. For example, electromagnetic radiation is absorbed by the electrons, while shock waves heat the ions.

Hence, Eq. (4.18) is a plausible two-temperature generalization of the second law for infinitesimal processes that are reversible in the sense that they leave the functional form of Eq. (1.1) unaltered. In addition, we note that by combining the first and second laws, as stated above, and using Eq. (4.16), we can reproduce the relationships among A, p, S_i, and S_e previously derived. A final self-consistency check on the thermodynamics and statistical mechanics can be obtained by demanding that dS_e (and dS_i) be exact differentials to arrive at[5,6]

$$\left[\frac{\partial U}{\partial\Omega}\right]_{T_e,T_i}=T_e\left[\frac{\partial p}{\partial T_e}\right]_{\Omega,T_i}+T_i\left[\frac{\partial p}{\partial T_i}\right]_{\Omega,T_e}-p \ . \tag{4.19}$$

It is straightforward to verify that Eqs. (4.1) and (4.14) satisfy this relationship.

Having previously established the relationship between the internal energy and the ensemble average of the Hamiltonian, it is interesting to look at the fluctuations of the energy in the "canonical" ensemble defined by Eq. (1.1). Differentiating U with respect to β_i and combining the result with its derivative with respect to β_e yields

$$\begin{aligned}&\left[\frac{\partial U}{\partial\beta_i}\right]_{\Omega,\beta_e}+\left[\frac{\beta_e}{\beta_i}\right]\left[\frac{\partial U}{\partial\beta_e}\right]_{\Omega,\beta_i}\\ &\quad=\int d\Gamma_id\Gamma_e\rho H\left[A-T_i\frac{\partial A}{\partial T_i}-T_e\frac{\partial A}{\partial T_e}-H\right]\end{aligned} \tag{4.20}$$

or

$$T_iC_i+T_eC_e=\langle (U-H)^2\rangle /k_BT_i\ . \tag{4.21}$$

In the above we have identified the heat capacities C_a by

$$C_a\equiv\left[\frac{\partial U}{\partial T_a}\right]_{\Omega,T_{\overline{a}\neq a}}\ . \tag{4.22}$$

From the combined first and second laws, we also find that

$$C_a=\sum_{b=e,i}C_{ba}\ , \tag{4.23}$$

where

$$C_{ab}\equiv T_a\left[\frac{\partial \overline{S}_a}{\partial T_b}\right]_{\Omega,T_{\overline{b}\neq b}} \tag{4.24}$$

represents the amount of heat absorbed by species a when the temperature of species b is changed.[5,6]

It is particularly interesting to calculate the "cross" heat capacity C_{ei}. From its definition, we get

$$\begin{aligned}C_{ie}&=-k_B\beta_e^2\left[\frac{\partial\langle v_{ii}^{(s)}\rangle}{\partial\beta_e}-\left\langle\frac{\partial v_{ii}^{(s)}}{\partial\beta_e}\right\rangle\right]\\&=-k_B\beta_e^2\int\frac{d^3q}{(2\pi)^3}\tilde{v}_{ii}^{(s)}(q)\frac{\partial S_i(q)}{\partial\beta_e}\ ,\end{aligned} \tag{4.25}$$

and using the weak-coupling estimate of S_i, we find

$$C_{ie}\rightarrow -k_BN_i\frac{k_D-k_e}{k_D+k_i}\frac{k_e}{k_D}\frac{\beta_eZ^2e^2}{\lambda_e}\left[1+\frac{\beta_e}{n_e}\frac{\partial n_e}{\partial\beta_e}\right]\ . \tag{4.26}$$

If the density of free electrons does not change with T_e, then this should always be a small number. However, if the system is still ionizing in the temperature range of interest, then[17]

$$-\beta_e\frac{1}{n_e}\frac{\partial n_e}{\partial\beta_e}\sim 5-10$$

and this term may be significant.

To study fluctuations in the number densities of the plasma requires that we create the grand ensemble corresponding to Eq. (1.1). To do this, we concentrate on a subvolume of the system which is small compared to Ω, but is still macroscopic. By neglecting surface effects, and generalizing a standard argument,[15] the probability of finding N_{e1} electrons and N_{i1} ions in the subvolume Ω_1 in a given configuration is found to be

$$\begin{aligned}\rho_G=&\frac{Q(N_e-N_{e1},N_i-N_{i1},\Omega-\Omega_i,T_e,T_i)}{Q(N_e,N_i,\Omega,T_e,T_i)}\\&\times e^{-\beta_i(H_i^{(1)}+A_e^{(1)})}\frac{1}{Q_e^{(1)}}e^{-\beta_e(H_e^{(1)}+V_{ei}^{(1)})}\ ,\end{aligned} \tag{4.27}$$

where the superscript 1 on the right-hand side indicates that all the spatial coordinates must be in the subvolume. From Eq. (4.15), we obtain

$$\begin{aligned}\ln&\left[\frac{Q(N_e-N_{e1},N_i-N_{i1},\Omega-\Omega_i,T_e,T_i)}{Q(N_e,N_i,\Omega,T_e,T_i)}\right]\\&=-\beta_ip\Omega+\beta_i(N_{e1}\mu_e+N_{i1}\mu_i)\ ,\end{aligned} \tag{4.28}$$

where we have used Eq. (4.14), and the definition

$$\mu_a=\left[\frac{\partial A}{\partial N_a}\right]_{\Omega,T_e,T_i,N_{\overline{a}\neq a}}\ . \tag{4.29}$$

Thus, we obtain for the grand partition function,

$$Q_G=\sum_{N_e(\geq 0)}\sum_{N_i(\geq 0)}e^{N_i\beta_i\mu_i}e^{N_e\beta_i\mu_e}Q(N_e,N_i)=e^{-\beta_ip\Omega}\ . \tag{4.30}$$

Note that both sums are independent, and charge neutrality is guaranteed by requiring

$$\langle N_e\rangle=Z\langle N_i\rangle\ ,$$

where

$$\langle N_a\rangle=\beta_i^{-1}\left[\frac{\partial\ln Q_G}{\partial\mu_a}\right]_{\Omega,T_e,T_i,\mu_{\overline{a}\neq a}}\ . \tag{4.31}$$

Fluctuations about the average densities are measured by

$$\langle N_aN_b\rangle-\langle N_a\rangle\langle N_b\rangle=\beta_i^{-1}\frac{\partial\langle N_i\rangle}{\partial\mu_b}=\sqrt{n_an_b}S_{ab}(q=0)\ , \tag{4.32}$$

which establishes another connection between the thermodynamics and statistical mechanics of the plasma. Note that only β_i appears explicitly in the above. The thermodynamic derivative in Eq. (4.32) may be related to the compressibility through a standard derivation,[12] and we obtain the following expression for the compressibility sum rule:[7]

$$\kappa^{-1}\equiv -\Omega\left[\frac{\partial p}{\partial\Omega}\right]_{T_e,T_i}=\frac{\sqrt{n_an_b}}{\beta_iS_{ab}(q=0)}=\frac{n_ik_BT_i}{S_i(q=0)}\ . \tag{4.33}$$

Self-consistency between this result and Eq. (4.13) is achieved by only a very few of the available methods for calculating structure factors.[18,19]

V. DYNAMIC STRUCTURE FACTORS

The dynamic structure factors for weakly coupled two-temperature plasmas were first investigated by Salpeter[3] who calculated the density-density time correlation functions, defined in terms of a long-time average, from the solution to the Vlasov equation. In this section we will define the density-density time-correlation functions in terms of an ensemble average, and then derive a short-time kinetic equation from which we will evaluate them. As with the static structure factors, we will obtain results which include strong ion-ion coupling effects. However, we will also find small differences from Salpeter, which persist even for weak coupling, that are due to the nonergodicity of the ensemble.

The density-density time-correlation functions are defined by

$$G_{ab}(\mathbf{r}\mathbf{r}';t)\equiv\langle n_a(\mathbf{r},t)n_b(\mathbf{r}',0)\rangle\ , \tag{5.1}$$

and they can be expressed in terms of the correlation of the phase-space density

$$\begin{aligned} f_a(\mathbf{r}\mathbf{p};t)&\equiv\sum_{j=1}^{N_a}\delta(\mathbf{r}-\mathbf{r}_j(t))\delta(\mathbf{p}-\mathbf{p}_j(t)) \\ &=\delta f_a(rp,t)+\langle f_a(rp,t)\rangle \end{aligned} \tag{5.2}$$

through

$$G_{ab}(\mathbf{r}\mathbf{r}';t)-\langle n_a(t)\rangle\langle n_b\rangle=\int d^3p_1d^3p'_1U_{a;b}(1;1'\,|\,t)\ , \tag{5.3}$$

where the two-point function is defined by

$$U_{a;b}(1,1'\,|\,t)\equiv\langle\delta f_a(r_1p_1;t)\delta f_b(r'_1p'_1;0)\rangle\ . \tag{5.4}$$

Using standard methods[20] it can be shown that the Laplace transform of Eq. (5.4),

$$\widetilde{U}_{a;b}(1;1'\,|\,z)\equiv-i\int_0^\infty dt\,e^{izt}U_{a;b}(1;1'\,|\,t)\ , \tag{5.5}$$

obeys a formally exact kinetic equation of the form

$$\begin{aligned} &(z+i\mathbf{p}_1\cdot\nabla_1/m_a)\widetilde{U}_{a;b}(1;1'\,|\,z) \\ &\quad-i\sum_{\bar{a}}\int d\bar{1}\,\Phi_{a;\bar{a}}(1;\bar{1}\,|\,z)\widetilde{U}_{\bar{a};b}(\bar{1}:1'\,|\,z) \\ &\qquad=U_{a;b}(1;1'\,|\,t=0)\ , \end{aligned} \tag{5.6}$$

where $\Phi_{a;b}$ is referred to as the memory function, and the initial value of $U_{a;b}$ is given by

$$\begin{aligned} &U_{a;b}(1;1'\,|\,t=0) \\ &\quad=n_a\phi_a(p_1)[\delta_{ab}\delta(1-1')+n_b\phi(p'_1)h^{(2)}_{ab}(\mathbf{r}_1-\mathbf{r}'_1)] \\ &\quad=\lim_{z\to\infty}z\widetilde{U}_{a;b}(1;1'\,|\,z)\ . \end{aligned} \tag{5.7}$$

The key approximation of this second is to replace $\Phi_{a;b}$ by its high-frequency (short-time) limit $B_{a;b}$ given by[20]

$$B_{a;b}(1;1')=\sum_{\bar{a},\bar{b}}\int d2\,d\bar{2}\,\nabla_1v_{a\bar{a}}(12)\cdot\frac{\partial}{\partial\mathbf{p}_1}U_{a\bar{a};\bar{b}}(12;\bar{2}\,|\,t=0)U^{-1}_{\bar{b};b}(\bar{2};1'\,|\,t=0)\ , \tag{5.8}$$

where

$$\begin{aligned} U_{a\bar{a};b}(12;1'\,|\,t=0)&=n_an_{\bar{a}}\phi_a(p_1)\phi_{\bar{a}}(p_2)\{g^{(2)}_{a\bar{a}}(\mathbf{r}_1-\mathbf{r}_2)[\delta_{ab}\delta(1-1')+\delta_{\bar{a}b}\delta(2-1')]+n_b\phi_b(p'_1)[g^{(3)}_{a\bar{a}b}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}'_1)-g^{(2)}_{a\bar{a}}(\mathbf{r}_1-\mathbf{r}_2)]\} \\ &=\lim_{z\to\infty}z\widetilde{U}_{a\bar{a};b}(12;1'\,|\,z) \end{aligned} \tag{5.9}$$

and

$$U^{-1}_{a;b}(1;1'\,|\,t=0)=n_a^{-1}[\delta_{ab}\phi_a^{-1}(p)-c_{ab}(\mathbf{r}_1-\mathbf{r}'_1)]\ . \tag{5.10}$$

In the above, $h^{(2)}_{ab}=g^{(2)}_{ab}-1$, $g^{(2)}_{ab}$ is the radial distribution function for species a and b, and $g^{(3)}_{abc}$ is the triplet correlation function for species a, b, and c. The direct correlation functions c_{ab} are defined, just as in the equilibrium case, from the Ornstein-Zernike equations

$$\begin{aligned} c_{ab}(\mathbf{r}_1-\mathbf{r}_2)&=h^{(2)}_{ab}(\mathbf{r}_1-\mathbf{r}_2) \\ &\quad-\sum_{\bar{a}}n_{\bar{a}}\int d^3r_3h^{(2)}_{a\bar{a}}(\mathbf{r}_1-\mathbf{r}_3)c_{\bar{a}b}(\mathbf{r}_3-\mathbf{r}_2)\ . \end{aligned} \tag{5.11}$$

Substituting Eq. (5.8) into (5.6) gives us an explicit kinetic equation to solve subject to the above initial conditions,

$$\begin{aligned} &(z+i\mathbf{p}_1\cdot\nabla_1/m_a)\widetilde{U}_{a;b}(1:1'\,|\,z) \\ &\quad-i\sum_{\bar{a}}\int d\bar{1}\,B_{a;\bar{a}}(1;\bar{1})\widetilde{U}_{\bar{a};b}(\bar{1};1'\,|\,z) \\ &\qquad=U_{a;b}(1,1'\,|\,t=0)\ . \end{aligned} \tag{5.12}$$

This equation is valid for any plasma density or temperatures, provided the frequencies of interest are much larger than the frequency of collisions. This limitation is not a serious one though, since the "equilibrium" described by Eq. (1.1) will be destroyed in several collision times.

In the case of equilibrium statistical mechanics, it is possible to express $B_{ab}(1,1')$ entirely in terms of two-body functions.[20–23] This may be accomplished only approximately for the two-temperature problem, but it is shown in the Appendix that the corrections, all of which involve three-body functions, are small whenever $\gamma_{ei}\ll1$.

The notation used in the Appendix can be made more compact by introducing the functions

$$\widetilde{S}_{ab}(kz;p)\equiv\int d^3r\,e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\int d^3p'\widetilde{U}_{a;b}(1;1'\,|\,z)\ . \tag{5.13}$$

By integrating Eqs. (A11) and (A12) over d^3p' and Fourier transforming them on the relative spatial variable, we obtain

$$\begin{aligned} &(z-\mathbf{p}\cdot\mathbf{k}/m_a)\widetilde{S}_{ab}(kz;p) \\ &\quad-\beta_an_a\frac{\mathbf{p}\cdot\mathbf{k}}{m_a}\phi_a(p)\sum_{\bar{a}}\widetilde{w}_{a\bar{a}}(k)\int d^3\bar{p}\,\widetilde{S}_{\bar{a}b}(kz;\bar{p}) \\ &\qquad=\sqrt{n_an_b}\phi_a(p)S_{ab}(k)\ , \end{aligned} \tag{5.14}$$

where the effective potentials $w_{ab}(k)$ are

$$\omega_{ee}(k)=\tilde{v}_{ee}(k)\ , \tag{5.15}$$

$$\omega_{ei}(k)=\tilde{v}_{ei}(k)\ , \tag{5.16}$$

$$\omega_{ii}(k)=\tilde{v}_{ii}(k)-[\beta_i^{-1}\tilde{C}_i(k)+v_{ii}^{(s)}(k)]\ . \tag{5.17}$$

We note that when the ions are also weakly coupled, $\tilde{C}_i(k)\rightarrow-\beta_i v_{ii}^{(s)}(k)$, and Eq. (5.14) represents the usual linearized Vlasov equations for a two-temperature plasma.[11]

The electron scattering function can now be found from the relation

$$\begin{aligned} S_{ab}(k,\omega)&=-2\,\mathrm{Im}\int d^3p\,\tilde{S}_{ab}(k,\omega+i\eta;p)\\ &\equiv-2\,\mathrm{Im}\tilde{S}_{ab}(k,\omega+i\eta)\ . \end{aligned} \tag{5.18}$$

Solving Eq. (5.14) for $\tilde{S}_{ee}(k,z)$ gives

$$\tilde{S}_{ee}(k,z)=\frac{1}{z\epsilon(k,z)}\left[\epsilon_i(k,z)[n_e+\beta_e^{-1}\tilde{\chi}_e(k,z)]S_{ee}(k)+\left[\frac{n_e}{n_i}\right]^{1/2}\chi_e(k,z)[n_i+\beta_i^{-1}\tilde{\chi}_i(k,z)]w_{ei}S_{ei}(k)\right]\ , \tag{5.19}$$

where

$$\begin{aligned} &\epsilon_a(k,z)=1-\tilde{\omega}_{aa}(k)\tilde{\chi}_a(k,z)\ ,\\ &\epsilon(k,z)=\epsilon_e(k,z)\epsilon_i(k,z)-\tilde{\omega}_{ei}^2(k)\tilde{\chi}_i(k,z)\tilde{\chi}_e(k,z)\ , \end{aligned} \tag{5.20}$$

and

$$\tilde{\chi}_a(k,z)\equiv\beta_a n_a\int d^3p\frac{(\mathbf{p}\cdot\mathbf{k}/m_a)\phi_a(p)}{z-\mathbf{p}\cdot\mathbf{k}/m_a}\ . \tag{5.21}$$

Taking the imaginary part of the above gives

$$\begin{aligned} S_{ee}(k,\omega)=-2&\left[\frac{\mathrm{Im}\tilde{\chi}_e(k,\omega)}{\beta_e\omega}\frac{|\epsilon_i(k,\omega)|^2}{|\epsilon(k,\omega)|^2}+\frac{\tilde{\omega}_{ei}^2|\tilde{\chi}_e(k,\omega)|^2}{|\epsilon(k,\omega)|^2}\frac{\mathrm{Im}\tilde{\chi}_i(k,\omega)}{\beta_i\omega}\right]\\ &+2\left[\frac{\beta_e}{\beta_i}-1\right]S_e(k)\tilde{\omega}_{ei}^2(k)|\epsilon(k,\omega)|^{-2}\left[\frac{\mathrm{Im}\tilde{\chi}_e(k,\omega)}{\beta_e\omega}\beta_e n_e[\mathrm{Re}\tilde{\chi}_i(k,\omega)-\tilde{\omega}_{ii}(k)|\tilde{\chi}_i(k,\omega)|^2]\right.\\ &\qquad\left.+\frac{\mathrm{Im}\tilde{\chi}_i(k,\omega)}{\beta_i\omega}\left[\beta_i n_e\mathrm{Re}\tilde{\chi}_e(k,\omega)+\frac{\beta_i}{\beta_e}|\chi_e(k,\omega)|^2\right]\right]\ . \end{aligned} \tag{5.22}$$

The first line of Eq. (5.22) reduces in the limit of weak ion coupling precisely to Salpeter's result.[3] The remainder of Eq. (5.22), proportional to the temperature difference, survives even in this limit, but we note that due to the large ratio of the electron to ion plasma frequencies it is never numerically significant (on the order of two percent in ion peak of hydrogen). The source of this small discrepancy is the fact that the ions are not really stationary, and their motion over long times alters the ensemble in Eq. (1.1).

Finally, the size of the ratio of the ion and electron plasma frequencies can be exploited to write an approximate expression for the electron scattering function,

$$S_{ee}(k,\omega)\rightarrow S_e(k,\omega)+\left[\frac{\beta_e n_e\tilde{w}_{ei}(k)}{\epsilon_e(k,0)}\right]^2 S_i(k,\omega)\ , \tag{5.23}$$

where

$$S_e(k,\omega)=\frac{-2}{\beta_e\omega}\frac{\mathrm{Im}\tilde{\chi}_e(k,\omega)}{|\epsilon_e(k,\omega)|^2}\ , \tag{5.24}$$

$$S_i(k,\omega)=\frac{-2}{\beta_i\omega}\frac{\mathrm{Im}\tilde{\chi}_e(k,\omega)}{|1+\beta_i^{-1}\tilde{C}_i(k)\tilde{\chi}_i(k,\omega)|^2}\ . \tag{5.25}$$

In other words $S_{ee}(k,\omega)$ can be approximately expressed in terms of the dynamic structure factors for the electron gas and the screened OCP.

VI. DISCUSSION

The model phase-space probability function proposed in Sec. I of this paper describes a nonequilibrium ensemble of classical ions and electrons, which have established separate equilibrium states at temperatures T_e and T_i. For this model to be plausible, the electrons and ions must establish these equilibria very quickly in comparison with the time required for them to come to equilibrium with each other. Using stopping-power arguments, it can be shown that the ratio of the electron-ion equilibration time τ_{ei} to the ion-ion equilibration time τ_{ii} is well estimated by[5,24]

$$\tau_{ei}/\tau_{ii}=Z\left[\frac{m_iT_e}{m_eT_i}\right]^{1/2}\frac{\ln\Lambda_{ii}}{\ln\Lambda_{ei}}\,, \tag{6.1}$$

where $\ln\Lambda_{ii}$ and $\ln\Lambda_{ei}$ are the "Coulomb logarithms" describing the ion-ion and electron-ion collisions in the plasma. For weakly coupled plasmas, their ratio is of order unity, so it is clear that $\tau_{ei} \gg \tau_{ii}$, as desired. If the ions become strongly coupled, however, it is possible that $\ln\Lambda_{ii}$ will be much smaller than $\ln\Lambda_{ei}$, and the desired condition is not guaranteed. Recent computer simulations[25] appear to show that τ_{ei} (and, therefore, $\ln\Lambda_{ei}$) is well approximated by its weak-coupling form even in strongly coupled systems. If this turns out to be true also for τ_{ii}, then it would seem that $\tau_{ei} \gg \tau_{ii}$ is guaranteed virtually everywhere.

However, from molecular-dynamics studies of self-diffusion in a classical one-component plasma,[26] it seems that the effective value of $\ln\Lambda_{ii}$ may behave as

$$\ln\Lambda_{ii}\sim 0.347\overline{\Gamma}_i^{-1.16}\,, \tag{6.2}$$

where

$$\overline{\Gamma}_i=(Z^2e^2/k_BT_i)(4\pi n_i/3)^{1/3}\,.$$

Using this estimate for $\ln\Lambda_{ii}$ and the standard weak-coupling expression for $\ln\Lambda_{ei}$,[27] we find that for $\overline{\Gamma}_i \geq \frac{1}{3}$,

$$\tau_{ei}/\tau_{ii} \geq \left[\frac{m_i}{Zm_e}\right]^{1/2} \tag{6.3}$$

whenever

$$\overline{\Gamma}_i^{1.16} \lesssim 0.115Z(ZT_e/T_i)^{1/2}/\ln(ZT_e/T_i)^{1/2}\,. \tag{6.4}$$

Therefore, we see that there exists a large, interesting region in which our results are applicable.

The principal thrust of this manuscript has been to extend the existing weak-coupling expressions[2,3] for the density correlation functions in a plasma to include the possibility of cold, highly charged ions. This was accomplished by using our two-temperature ensemble to evaluate the static and dynamic structure factors to lowest order in γ_{ei}. While the static structure factors obtained here reduce exactly to Salpeter's in the limit of weak coupling, the dynamic structure factors do not. The differences, proportional to T_e-T_i, are attributable to the fact that Salpeter's structure factors were defined in terms of long-time averages, while those calculated here were defined in terms of ensemble averages. The ergodic theorem requires these two averages to give identical results only in equilibrium. There remains a serious theoretical question as to which type of average is really measured in an experiment, but it appears from Eq. (5.22) that any discrepancies between the averaging procedures will never be very large.

In Sec. IV, we demonstrated that the statistical mechanics implied by Eq. (1.1) is consistent with a plausible two-temperature thermodynamics. In particular, we have shown that knowledge of the static structure factors is sufficient to calculate many ensemble averages with clear thermodynamic significance. In addition, we demonstrated that one of the most stringent self-consistency checks on the structure and thermodynamics of a system, the compressibility sum rule, can be generalized to a two-temperature plasma.

ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

APPENDIX

The purpose of this appendix is to demonstrate that $B_{a,b}(1,1')$ defined in Eq. (5.8) can be approximately expressed entirely in terms of two-body functions. We begin by noting that

$$\nabla_1 g_{ea}^{(2)}(\mathbf{r}_1-\mathbf{r}_2)=-\beta_e g_{ea}^{(2)}(\mathbf{r}_1-\mathbf{r}_2)\nabla_1 v_{ea}(\mathbf{r}_1-\mathbf{r}_2)-\beta_e\sum_{\bar a}n_{\bar a}\int d^3r_3 g_{ea\bar a}^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\nabla_1 v_{e\bar a}(\mathbf{r}_1-\mathbf{r}_3)\,, \tag{A1}$$

$$\begin{aligned}\nabla_1 g_{ii}(\mathbf{r}_1-\mathbf{r}_2)=&-\beta g_{ii}^{(2)}(\mathbf{r}_1-\mathbf{r}_2)\nabla_1 v_{ii}(\mathbf{r}_1-\mathbf{r}_2)-\beta_i\sum_{\bar a}n_{\bar a}\int d^3r_3 g_{i i\bar a}^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\nabla_1 v_{i\bar a}(\mathbf{r}_1-\mathbf{r}_3)\\&-(\beta_e-\beta_i)\Big[g_{ii}(\mathbf{r}_1-\mathbf{r}_2)\nabla_1 u_{ii}(\mathbf{r}_1-\mathbf{r}_2)+n_i\int d^3r_3 g_{iii}^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\nabla_1 u_{ii}(\mathbf{r}_1-\mathbf{r}_3)\\&+n_e\int d^3r_3 g_{iie}^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\nabla_1 v_{ie}(\mathbf{r}_1-\mathbf{r}_3)\Big]\,,\end{aligned} \tag{A2}$$

and

$$\begin{aligned}\nabla_1 g_{ie}(\mathbf{r}_1-\mathbf{r}_2)=&-\beta_i g_{ie}^{(2)}(\mathbf{r}_1-\mathbf{r}_2)\nabla_1 v_{ie}(\mathbf{r}_1-\mathbf{r}_2)-\beta_i\sum_{\bar a}n_{\bar a}\int d^3r_3 g_{ie\bar a}^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\nabla_1 v_{i\bar a}(\mathbf{r}_1-\mathbf{r}_3)\\&-(\beta_e-\beta_i)\Big[g_{ie}^{(2)}(\mathbf{r}_1-\mathbf{r}_2)\nabla_1 v_{ie}(\mathbf{r}_1-\mathbf{r}_2)+n_i\int d^3r_3 g_{iei}^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\nabla_1 u_{ii}(\mathbf{r}_1-\mathbf{r}_3)\\&+n_e\int d^3r_3 g_{iee}^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\nabla_1 v_{ie}(\mathbf{r}_1-\mathbf{r}_3)\Big]\,,\end{aligned} \tag{A3}$$

where $u_{ii}=v_{ii}-v_{ii}^{(s)}$. Using the first of these, and Eqs. (5.7) and (5.9), we obtain

$$B_{e;b}(1;1')=n_e\phi_e(p)\frac{\mathbf{p}_1\cdot\nabla_1}{m_e}c_{eb}(\mathbf{r}_1-\mathbf{r}_1') \tag{A4}$$

which is precisely the usual equilibrium answer.[23]

From Eqs. (A2) and (A3) and Eqs. (5.7) and (5.9), we get

$$B_{i;b}(1,1')=n_i\phi_i(p)\left[\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}c_{i,b}(\mathbf{r}_1-\mathbf{r}_1')+(\beta_e-\beta_i)\Delta_{i,b}(1;1')\right], \tag{A5}$$

where

$$\Delta_{i,i}(1;1')=\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}u_{ii}(\mathbf{r}_1-\mathbf{r}_1')+n_i\int d^3r_2\Delta\widetilde{h}_{iii}(\mathbf{r}_1\mathbf{r}_1'\mathbf{r}_2)\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}u_{ii}(\mathbf{r}_1-\mathbf{r}_2)+n_e\int d^3r_2\Delta\widetilde{h}_{iie}(\mathbf{r}_1\mathbf{r}_1'\mathbf{r}_2)\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}v_{ie}(\mathbf{r}_1-\mathbf{r}_2) \tag{A6}$$

and

$$\Delta_{i,e}(1;1')=\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}v_{ei}(\mathbf{r}_1-\mathbf{r}_1')+n_i\int d^3r_2\Delta\widetilde{h}_{iei}(\mathbf{r}_1\mathbf{r}_1'\mathbf{r}_2)\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}u_{ii}(\mathbf{r}_1-\mathbf{r}_2)+n_e\int d^3r_2\Delta\widetilde{h}_{iee}(\mathbf{r}_1\mathbf{r}_1'\mathbf{r}_2)\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}v_{ie}(\mathbf{r}_1-\mathbf{r}_2)\,. \tag{A7}$$

In the above, we have defined

$$\Delta\widetilde{h}_{abc}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)=\Delta h^{(3)}_{abc}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)-\sum_{\bar{a}}n_{\bar{a}}\int d^3r_4\Delta h^{(3)}_{ab\bar{a}}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_4)c_{\bar{a}c}(\mathbf{r}_4-r_3) \tag{A8}$$

with

$$\Delta h^{(3)}_{abc}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)=h^{(3)}_{abc}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)-h^{(c)}_{abc}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)\,. \tag{A9}$$

The quantity $h^{(c)}_{abc}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)$ is the "convolution approximation" to the triplet correlation function

$$\begin{aligned}h^{(c)}_{abc}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)={}&h^{(2)}_{ab}(\mathbf{r}_1-\mathbf{r}_2)h^{(2)}_{bc}(\mathbf{r}_2-\mathbf{r}_3)+h^{(2)}_{ab}(\mathbf{r}_1-\mathbf{r}_2)h^{(2)}_{ac}(\mathbf{r}_1-\mathbf{r}_3)\\&+h^{(2)}_{ac}(\mathbf{r}_1-\mathbf{r}_3)h^{(2)}_{bc}(\mathbf{r}_2-\mathbf{r}_3)+\sum_{\bar{a}}n_{\bar{a}}\int d^3r_4h^{(2)}_{a\bar{a}}(\mathbf{r}_1-\mathbf{r}_4)h^{(2)}_{b\bar{a}}(\mathbf{r}_2-\mathbf{r}_4)h^{(2)}_{c\bar{a}}(\mathbf{r}_3-\mathbf{r}_4)\,.\end{aligned} \tag{A10}$$

The third terms in Eqs. (A6) and (A7) are higher order in γ_{ei} than the first terms and are therefore negligible. Because of the cluster property of $\Delta\widetilde{h}_{abc}$ and the fact that u_{ii} is the difference between the screened and unscreened potentials, the second terms may be shown to be of order T_i/ZT_e. If the ions are strongly coupled and the electrons are weakly coupled, then this must also be a small parameter.

Therefore, we obtain the following kinetic equations, valid for weakly coupled electrons, but arbitrarily coupled ions,

$$\begin{aligned}(z+i\mathbf{p}_1\cdot\nabla_1/m_i)\widetilde{U}_{i;b}(1;1'\,|\,z)&-in_i\phi_i(p)\int d\bar{1}\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}[c_{ii}(\mathbf{r}_1-\bar{\mathbf{r}}_1)+(\beta_e-\beta_i)u_{ii}(\mathbf{r}_1-\bar{\mathbf{r}}_1)]\widetilde{U}_{i;b}(\bar{1},1'\,|\,z)\\&-in_i\phi_i(p)\int d\bar{1}\frac{\mathbf{p}_1\cdot\nabla_1}{m_i}[c_{ie}(\mathbf{r}_1-\bar{\mathbf{r}}_1)+(\beta_e-\beta_i)v_{ie}(\mathbf{r}_1-\bar{\mathbf{r}}_1)]\widetilde{U}_{e;b'}(\bar{1};1'\,|\,z)=U_{i;b}(1;1'\,|\,t=0)\end{aligned} \tag{A11}$$

and

$$\begin{aligned}&(z+i\mathbf{p}_1\cdot\nabla_1/m_e)\widetilde{U}_{e;b'}(1;1'\,|\,z)\\&\quad-in_e\phi_e(p)\sum_{\bar{a}}\int d\bar{1}\frac{\mathbf{p}_1\cdot\nabla_1}{m_e}c_{e\bar{a}}(\mathbf{r}_1-\bar{\mathbf{r}}_1)\widetilde{U}_{\bar{a}b}(\bar{1};1'\,|\,z)\\&\qquad=U_{e;b}(1;1'\,|\,t=0)\,.\end{aligned} \tag{A12}$$

In order for these equations to be consistent with the results of Sec. III, the direct correlation functions must be given by

$$c_{ee}(r)=-\beta_e v_{ee}(r)\,, \tag{A13}$$

$$c_{ei}(r)=-\beta_e v_{ei}(r)\,, \tag{A14}$$

$$c_{ii}(r)=c_i(r)-\beta_e[v_{ii}(r)-v^{(s)}_{ii}(r)]\,, \tag{A15}$$

where $c_i(r)$ is the direct correlation function for the screened OCP,

$$c_i(r)\equiv\frac{1}{n_i}\int\frac{d^3k}{(2\pi)^3}[1-1/S_i(k)]e^{i\mathbf{k}\cdot\mathbf{r}}\,. \tag{A16}$$

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