Memoirs of the Faculty of Engineering, Okayama University, Vol. 22, March 1988

Thermodynamic Sum Rules for Mixtures of Charged Particles

Hiroo Totsuji *

(Received March 16, 1988)

Abstract

Several methods to derive thermodynamic sum rules for a system including charged particle are proposed and applied to charged mixtures as well as one-component systems. The validity of the statements is examined carefully with respect to the ordering in the powers of the wave number. As for the mixture of electrons and ions, it is shown how the aspect of the one-component plasma or the ionic mixture appears when electrons become strongly degenerate.

1. Introduction

The behavior of response functions in the limit of low frequency and long wavelength are related to thermodynamic functions of the system. These relations have been used to construct approximation schemes for response functions or to check their thermodynamic consistency.

In the case of charged particles, these sum rules take different forms from those for systems of neutral particles reflecting the long range nature of the Coulomb interaction. In this paper, we analyse the long wavelength limit of density response functions in mixtures of charged particles by taking the long range nature in several different ways and clarify how sum rules in various idealized models, such as one-component plasma, are related to the properties of the original systems which the models try to describe.

2. Sum Rules

2.1 Long Wavelength Behavior of Density Response Functions

We consider a mixture of charged particles in thermal equilibrium at the temperature T in a volume V. We denote the quantities related to electrons by

---

* Department of Electrical and Electronic Engineering

the subscript 0 and use the subscripts α=1, 2,... to denote ions of species α: Roman letters will be used as running parameters including electrons, e.g., i=0, 1, 2,.... In order to include the cases of one-component plasma and ionic mixtures, the existence of uniform background is assumed when the charged particles under consideration are not charge neutral. We denote the charge, the total number, and the number density of charges of species i=0, 1, 2,... by e_i, N_i, and n_i, respectively.

We now introduce into the system an infinitesimal fictitious test charge density $\delta\rho_{ex,i}$ which interacts only with the charges of the species i. We assume that the wavelength of perturbation is sufficiently large and all quantities related to the perturbation have the spatial and temporal dependence $\exp(i\mathbf{k}\cdot\mathbf{r}-i\omega t)$ with ω=0.

The condition for the chemical potential of the species j, $\delta\mu_j=0$, is written as

$$\Sigma_k \mu_{jk} \delta n_k + v(k) e_j \delta_{ij} \delta\rho_{ex,i} + v(k) e_j \Sigma_k e_k \delta n_k = O(k^2), \tag{2.1}$$

where

$$v(k)=4\pi/k^2 \tag{2.2}$$

is the Fourier transform of the Coulomb interaction and

$$\mu_{jk} = \partial\mu_j / \partial n_k = \mu_{kj}. \tag{2.3}$$

The first term on the left hand side of (2.1) is the change of the chemical potential due to induced densities, δn_k, the second term is the interaction with the test charge, and the third term is the potential energy due to induced mean field. The induced charge density is given by the density response function $\chi_{ij}(k,\omega=0)$ as

$$\delta n_k = v(k) \chi_{ki} e_i \delta\rho_{ex,i}, \tag{2.4}$$

where

$$\chi_{ij}(\mathbf{k},\omega) = (i/\hbar V)\int_0^\infty dt \ \langle[\rho_i(\mathbf{k},t), \rho_j(-\mathbf{k},t=0)]\rangle \exp(i\omega t), \tag{2.5}$$

and $\rho_j(\mathbf{k},t)$ is the density fluctuation of species j

$$\rho_j(\mathbf{k},t) = \sum_{i=1}^{N_j} \exp[-i\mathbf{k}\cdot\mathbf{r}_i(t)]. \tag{2.6}$$

We thus have

$$\Sigma_k[\mu_{jk} + e_je_kv(k)]\chi_{ki} + \delta_{ij} = O(k^2),$$

or, in terms of the inverse of the density response function $\chi^{-1}{}_{ij}$,

$$\mu_{ij} + e_ie_jv(k) + \chi^{-1}{}_{ij} = O(k^2). \tag{2.7}$$

It is to be noted that we have not assumed that the system is classical nor degenerate.

The above relations can also be obtained by introducing an imaginary background charge density $\delta\rho_b$ to maintain the charge neutrality as

$$\delta\rho_b = -\Sigma_k e_k \delta n_k. \tag{2.8}$$

In this case, both the test charge density $\delta\rho_{ex,i}$ and the introduced background $\delta\rho_b$ equivalently work as the external charge density for our system. The induced density δn_k is thus given by

$$\delta n_k = v(k)\ [\chi_{ki}e_i\delta\rho_{ex,i} + (\Sigma_m\chi_{km}e_m)\delta\rho_b]. \tag{2.9}$$

Since the charge neutrality is maintained, the condition for the chemical potential of the species j is now written as

$$\Sigma_k\mu_{jk}\delta n_k + v(k)e_j\delta_{ij}\delta\rho_{ex,i} \doteq O(k^2), \tag{2.10}$$

the term due to mean filed being absent. From Eqs. (2.8), (2.9), and (2.10), we have the same results (2.7).

The static form factor for species i and j is defined by

$$S_{ij}(k) = \langle\rho_i(k)\rho_j(-k)\rangle/(N_iN_j)^{1/2}, \tag{2.11}$$

where < > denotes the statistical average. For classical systems, the static density response function is related to the static form factor by the fluctuation-dissipation theorem as

$$\chi_{ij}(k,0) = -[(n_in_j)^{1/2}/k_BT]S_{ij}(k), \tag{2.12}$$

where k_B is the Boltzmann constant.

2.2 Compressibility Sum Rule

The relation between the compressibility of a system and the long wavelength behavior of the response function or the static form factor is called compressibility sum rules.[1] The compressibility sum rule is included in the relations derived in 2.1.

Since the Helmholtz free energy F is written as $F(T, V, N_0, N_1, ...) = Vf(T, n_0, n_1, ...)$, the pressure of charged mixture (defined by the volume derivative of the Helmholtz free energy F) is given by $P = -(\partial F/\partial V)_{T,N_0,N_1,..} = -f + \Sigma_j n_j \mu_j$, and the isothermal compressibility κ_T is calculated as

$$1/\kappa_T = -V(\partial P/\partial V)_{T,N_0,N_1,...} = n(\partial P/\partial n)_{T,x_0,x_1,...} = \Sigma_{ij} n_i n_j \mu_{ij}. \tag{2.13}$$

Here n is the total (unperturbed) number density and x_j is the concentration of species j:

$$n = \Sigma_j n_j, \tag{2.14}$$

$$x_j = n_j/n. \tag{2.15}$$

From (2.7) and (2.13) we have

$$\Sigma_{ij} n_i n_j \chi^{-1}{}_{ij} + n^2 \langle e\rangle^2 v(k) + 1/\kappa_T = O(k^2). \tag{2.16}$$

Here < > denotes the average as

$$\langle Q\rangle = \Sigma_j n_j Q_j/n. \tag{2.17}$$

The above equation relates the long wavelength limit of the inverse density response function and the compressibility of the charged mixture.

The compressibility sum rule for charge mixtures (2.16) can also be obtained by applying the test charge densities $\delta\rho_{ex,i}$, i=0, 1, 2, ..., adjusted so as to induce the number densities δn_j in proportion to the unperturbed number densities n_j, simulating the volume change of the system:

$$\delta n_j = A n_j \quad (j = 0, 1, 2, ...), \tag{2.18}$$

where A is an arbitrary infinitesimal constant. From

$$\delta n_j = v(k) \Sigma_k \chi_{jk} e_k \delta\rho_{ex,k}, \tag{2.19}$$

the test charge densities are determined as

$$e_k \delta \rho_{ex,k} = Av(k)^{-1} \Sigma_m \chi^{-1}_{km} n_m. \qquad (2.20)$$

The force on charges (per unit volume)

$$-ikv(k)[\Sigma e_i n_i \delta \rho_{ex,i} + \Sigma_i e_i n_i \Sigma_j e_j \delta n_j]$$

is balanced by the pressure gradient

$$-ik(\partial P/\partial n)_{T,x_i} \Sigma_j \delta n_j$$

as

$$-ikv(k)[\Sigma e_i n_i \delta \rho_{ex,i} + \Sigma_i e_i n_i \Sigma_j e_j \delta n_j] -ik(\partial P/\partial n)_{T,x_i} \Sigma_j \delta n_j = 0. \qquad (2.21)$$

From (2.20) and (2.21), the relation (2.16) is again derived.

3. Examples

3.1 One-Component Plasma

The one component plasma (OCP) is a system of charged particles of one species in a uniform neutralizing background of opposite charges. We denote the charge and the number density by e and n, respectively. In this case with only one species, the relations (2.7) and (2.16) are identical:

$$n^2 \chi^{-1} + n^2 e^2 v(k) + 1/\kappa_T = O(k^2). \qquad (3.1)$$

Here we note that $1/\kappa_T$ is the compressibility of charges in uniform background and may become negative without causing any instability of the system.[2]

Especially when these charges are classical, we have the long wavelength behavior of the static structure factor to the order of k^2 as

$$S(k) = -(k_B T/n)\chi = 1/[k_D/k^2 + \kappa^0_T/\kappa_T], \qquad (3.2)$$

where k_D is the Debye wave number defined by

$$k_D^2 = 4\pi n e^2/k_B T, \qquad (3.3)$$

and κ^0_T is the compressibility of the classical ideal gas

$$\kappa^0_T = 1/nk_BT. \tag{3.4}$$

In terms of the Fourier transform of the direct correlation function c(k) defined by

$$S(k) - 1 = c(k) + c(k)[S(k) - 1], \tag{3.5}$$

(3.2) is expressed as

$$c(k) = -(k_D/k)^2 + 1 - \kappa^0_T/\kappa_T + O(k^2). \tag{3.6}$$

3.2 Classical Ionic Mixtures

Eqs.(2.7) and (2.16) hold also for mixtures of charged particles in a uniform background. As in the case of one-component plasma, we note that $\langle e\rangle \neq 0$ and κ_T is the compressibility of mixtures in a uniform background which may become negative without causing the instability of the whole system. As a model of real systems, it is natural to regard electrons as a background and assume that the mixture is composed of ions. We may therefore expect that the mixture is classical. Eq.(2.7) is thus written as

$$\Sigma_{\alpha\beta}[\mu_{\alpha\gamma} + e_\alpha e_\beta v(k)](n_\gamma n_\beta)^{1/2}S_{\alpha\beta}(k) - k_BT\delta_{\alpha\beta} = O(k^2). \tag{3.7}$$

The Fourier transform of the direct correlation function $c_{\alpha\beta}(k)$ is related to the static form factor by

$$[S_{\alpha\beta}(k) - \delta_{\alpha\beta}] = c_{\alpha\beta}(k) + \Sigma c_{\alpha\gamma}(k)[S_{\gamma\beta}(k) - \delta_{\gamma\beta}]. \tag{3.8}$$

The long wavelength limit of the direct correlation function is thus given to the order of k^0 as

$$c_{\alpha\beta}(k) = -4\pi e_\alpha e_\beta(n_\alpha n_\beta)^{1/2}/k_BTk^2 + \delta_{\alpha\beta} - \mu_{\alpha\beta}(n_\alpha n_\beta)^{1/2}/k_BT. \tag{3.9}$$

This generalizes Eq.(3.6) to ionic mixtures. From (2.16) and (3.9), we have

$$\Sigma_{\alpha\beta}(x_\alpha x_\beta)^{1/2}[c_{\alpha\beta} + 4\pi ne_\alpha e_\beta(x_\alpha x_\beta)^{1/2}/k_BTk^2] = 1 - \kappa^0_T/\kappa_T. \tag{3.10}$$

For the charge density fluctuation spectrum, (3.7) gives the long-wavelength limit as

$$\Sigma_{\alpha\beta}e_\alpha e_\beta(n_\alpha n_\beta)^{1/2}S_{\alpha\beta}(k) = k_BT/v(k) + O(k^4). \tag{3.11}$$

For classical binary ionic mixtures (BIM), the structure factors are calculated as

$$n_1 S_{11}(k)/k_B T = e_2^{\,2}/A + O(k^2), \tag{3.12a}$$

$$(n_1 n_2)^{1/2} S_{12}(k)/k_B T = - e_1 e_2/A + O(k^2), \tag{3.12b}$$

$$n_2 S_{22}(k)/k_B T = e_1^{\,2}/A + O(k^2), \tag{3.12c}$$

where

$$A = e_2^{\,2}\mu_{11} + e_1^{\,2}\mu_{22} - 2e_1 e_2 \mu_{12}. \tag{3.12d}$$

We note that the terms of the order k^2 and k^4 cannot be determined from (3.7): Terms of these orders neglected in (2.7) or (3.7) should be taken into account.

To the total charge density fluctuation, however, careful calculations show that these neglected k^2 and k^4 terms do not contribute and we have

$$\Sigma_{\alpha\beta} e_\alpha e_\beta (n_\alpha n_\beta)^{1/2} S_{\alpha\beta}(k) = k_B T[1-C/Av(k)]/Av(k) + O(k^6), \tag{3.13}$$

where

$$C = \mu_{11}\mu_{22} - \mu_{12}^{\,2} . \tag{3.14}$$

When we use the temperature T, the concentration of 1-st species $x_1 = n_1/n$, and the total charge number density $(\Sigma e_\alpha/e)n$ (e being the unit charge) as independent variables, (3.13) reduces to the expression obtained earlier by the method of thermodynamic fluctuations.[3]

3.3 Two Component Plasma

We now consider the mixture of electrons and one species of ions, sometimes called two-component plasma (TCP). Electrons are denoted by the subscript 0 and ions are denoted by the subscript 1.

Taking the inverse of (2.7), we have for long wavelenghts

$$\chi_{ij} = n_i n_j \kappa_T + O(k^2), \tag{3.15}$$

where κ_T is the compressibility of the total system. Thus all the components of the density response function have the same long wavelength behavior and the system becomes thermodynamically unstable when the total compressibility vanishes.

This behavior of the response function has already been derived as a result of analyses based on temperature Green's functions.[4] The simple derivation shown above, however, seems to have not appeared in the literatures. We note that the relation (2.7) is accurate to the order of k^0 and the next order term has the order of k^2. Therefore the exact statement on the response function is limited to the order of k^0 in (3.15).

3.4. Ion System in Highly Incompressible Electrons

We here consider the mixtures of ions and electrons where electrons are highly degenerate and almost incompressible, simulating the role of the background charges. We thus assume that the Fermi energy of electrons E_F is much larger than the thermal energy of ions:

$$k_BT/E_F \ll 1. \tag{3.16}$$

In this case, the element μ_{00} may be estimated by the value for the ideal Fermi gas as

$$\mu_{00} = (2/3)E_F/n_0, \tag{3.17}$$

and we may assume that

$$\mu_{01}/\mu_{00},\ \mu_{11}/\mu_{00} \sim k_BT/E_F. \tag{3.18}$$

Let us first consider the case where the ions are of one species. Careful calculations lead to the density response functions as

$$\begin{aligned} -(k_BT/n_1)\chi_{11}(k,\omega=0) &= S_{11}(k) \\ &\left\{ \begin{array}{ll} = n_1k_BT\kappa_T + (k/k_D)^2 + O[(k/k_D)^2(k_BT/E_F)] & \\ \qquad\qquad \text{for } 1 \gg k_BT/E_F > (k/k_D)^2, & (3.19a) \\ = (k/k_D)^2 + n_1k_BT\kappa_T - (k/k_D)^4(n_1\mu_{11}/n_1k_BT) + O[(k/k_D)^2(k_BT/E_F)] & \\ \qquad\qquad \text{for } 1 \gg (k/k_D)^2 \gg k_BT/E_F, & (3.19b) \end{array} \right. \end{aligned}$$

$$-[k_BT/(n_0n_1)^{1/2}]\chi_{01}(k,\omega=0) = (n_0n_1)^{1/2}k_BT\kappa_T + O[(k/k_D)^2(k_BT/E_F)], \tag{3.19c}$$

$$-(k_BT/n_1)\chi_{00}(k,\omega=0) = n_1k_BT\kappa_T + O[(k/k_D)^2(k_BT/E_F)]. \tag{3.19d}$$

Here κ_T is the compressibility of the whole system

$$\kappa_T = n_0^2\mu_{00} + 2n_0n_1\mu_{01} + n_1^2\mu_{11}, \tag{3.20}$$

which can be approximated by the compressibility of electrons in Eqs.(3.19c) and (3.19d).

Eq.(3.19a) is consistent with the result (3.15) and gives the next order term for ions. In Eq.(3.19b), we note that $n_1\mu_{11}/n_1k_BT$ is the inverse compressibility of ions normalized by the ideal gas value n_1k_BT. We thus see how the aspect of the one-component plasma appears with the decrease of the electronic compressibility or the increase of μ_{00}.

When ions are composed of several species, we have

$$\begin{aligned}-[k_BT/(n_\alpha n_\beta)^{1/2}]\chi_{\alpha\beta}(k,\omega=0) &= S_{\alpha\beta}(k)\\ &= -[k_BT/(n_\alpha n_\beta)^{1/2}]\chi'_{\alpha\beta}(k,\omega=0) + O[(k/k_D)^2,\ (k_BT/E_B)]\end{aligned} \tag{3.21}$$

and

$$-(k_BT/n_0)\chi_{00}(k,\omega=0) = 1/\mu_{00} + O[(k/k_D)^2,\ (k_BT/E_B)]. \tag{3.22}$$

Here $\chi'_{\alpha\beta}$ is the density response function of the ionic mixture of the same composition in the uniform background. An example of such response functions is given in 3.2 for binary mixtures.

3.5 Screened One-Component Plasma and Ionic Mixtures

As a model of ions in highly degenerate electrons, there has been used the ion system interacting via the Coulomb interaction screened by the dielectric function of electrons $\varepsilon_e(k,\omega=0)$. The results in the foregoing sections hold also for these systems when the Coulomb potential is replaced by the screened Coulomb potential as

$$v(k) \to v(k)/\varepsilon_e(k,0). \tag{3.23}$$

In the case of one species of ions, the screened OCP, we thus have[5]

$$S(k) = -(k_BT/n)\chi = 1/[(k_D/k)^2/\varepsilon_e(k,0) + \kappa^0_T/\kappa_T], \tag{3.24}$$

As has been pointed out by Leger and Deutsch,[6] (3.24) is consistent with the results (3.15), (3.19a) and (3.19b), when the dielectric function of electrons satisfies the compressibility sum rule (of electron system).

Acknowledgements

The author thanks Professor C. Deutsch and Dr. D. Léger for discussions at Orsay supported by Japan Society for Promotion of Science and Centre National de la Recherche Scientique of France.

References

1. D. Pines and P. Nozières, The Theory of Quantum Liquids I (Benjamin, New York, 1966).
2. M. Baus and J. -P. Hansen, Phys. Rep. **59**, 1(1980):
   S. Ichimaru, Rev. Mod. Phys. **54**, 1017(1982).
3. J. -P. Hansen, G. M. Torrie, and P. Vieillefosse, Phys. Rev. **A16**, 2153(1977).
4. M. Watabe and M. Hasegawa, in The properties of Liquid Metals (Proceedings of the Second International Conference, Tokyo, 1972), edited by S. Takeuchi (Taylor and Francis, London, 1973), p.113.
5. H. Totsuji and K. Tokami, Phys. Rev. **A30**, 3175(1984).
6. D. Léger and C. Deutsch, J. Physique Lett. **46**, L475(1985).