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Density oscillations in a classical multi-component plasma

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Abstract

The excitation spectrum of the density oscillations is computed for a classical multi-component plasma with Coulomb and short-range interactions. The dielectric function and structure factor are calculated. It is shown that in the limit of vanishing Coulomb coupling an additional, fast, "anomalous" sound appears in the spectrum, beside the ordinary hydrodynamic sound and the sound-like excitations.

We consider a classical multi-component plasma consisting of several ionic species labelled by i, each with N_i particles in volume V, mass m_i and electric charge ez_i, where $-e$ is the electron charge and z_i is a reduced effective charge, interacting through Coulomb potentials and a short range potential χ, the latter being the same for all species. The ensemble is subjected to the neutrality condition $\sum_i n_i z_i = 0$, where $n_i = N_i/V$ is the density of the i-th species. The interaction energy is written as

$$U = \frac{1}{2}\sum_{ij}\int d\mathbf{r}d\mathbf{r}'\left[\varphi_{ij}(\mathbf{r}-\mathbf{r}')+\chi(\mathbf{r}-\mathbf{r}')\right]\delta n_i(\mathbf{r})\delta n_j(\mathbf{r}') \ \ , \tag{1}$$

where $\varphi_{ij} = e^2 z_i z_j/\left|\mathbf{r}-\mathbf{r}'\right|$ is the Coulomb interaction and $\delta n_i(\mathbf{r})$ denotes a small density disturbance which preserves the neutrality. It can be represented by $\delta n_i = -n_i div\mathbf{u}_i$, where $\mathbf{u}_i$ is a displacement field. We introduce the Fourier transforms

$$\delta n_i(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\delta n_i(\mathbf{q})e^{i\mathbf{qr}} \ , \ \varphi(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{q}}\varphi(\mathbf{q})e^{i\mathbf{qr}} \ \ , \tag{2}$$

where $N = \sum_i N_i$ is the total number of particles, $\varphi(\mathbf{r}) = e^2/r$ and $\varphi(\mathbf{q}) = \varphi(q) = 4\pi e^2/q^2$. A similar Fourier transform is employed for the displacement field $\mathbf{u}_i$, which leads to $\delta n_i(\mathbf{q}) = -i\mathbf{q}\mathbf{u}_i(\mathbf{q})$. We emphasize that the representation $\delta n_i = -n_i div\mathbf{u}_i$ for the small disturbances of the particle density is valid for $\mathbf{q}\mathbf{u}_i(\mathbf{r}) \ll 1$. We can see that only the longitudinal components $u_i(\mathbf{q})$ of the displacement field are relevant, so we may write $\mathbf{u}_i(\mathbf{q}) = (\mathbf{q}/q)u_i(\mathbf{q})$, $\delta n_i(\mathbf{q}) = -iqu_i(\mathbf{q})$, with $\delta n_i^*(-\mathbf{q})$=$\delta n_i(\mathbf{q})$, $\mathbf{u}_i^*(-\mathbf{q}) = \mathbf{u}_i(\mathbf{q})$ and $u_i^*(-\mathbf{q}) = -u_i(\mathbf{q})$. Making use of the Fourier transforms introduced above, the interaction U given by equation (1) can be written as

$$U = -\frac{1}{2n}\sum_{ij\mathbf{q}}n_i n_j q^2\left[\varphi_{ij}(q)+\chi(q)\right]u_i(\mathbf{q})u_j(-\mathbf{q}) \ \ , \tag{3}$$

where $\varphi_{ij}(q) = z_i z_j\varphi(q)$.

Similarly, the kinetic energy associated with the coordinates u_i is given by

$$T = -\frac{1}{2n}\sum_{i\mathbf{q}} m_i n_i \dot{u}_i(\mathbf{q})\dot{u}_i(-\mathbf{q}) \ . \tag{4}$$

In addition, we introduce an external field $\phi(\mathbf{r})$ which gives rise to the interaction

$$V = -i\frac{e}{n}\sum_{i\mathbf{q}} n_i z_i q\phi(\mathbf{q})u_i(-\mathbf{q}) \ . \tag{5}$$

The equations of motion corresponding to the lagrangian $L = T - U - V$ are given by

$$m_i\ddot{u}_i + 4\pi e^2 z_i \sum_j z_j n_j u_j + q^2\chi\sum_j n_j u_j = -iqez_i\phi \ , \tag{6}$$

where we dropped out the argument $\mathbf{q}$ in $u_i(\mathbf{q})$ and $\phi(\mathbf{q})$. We consider first the homogeneous system of equations given by (6), and introduce the notations $a = 4\pi e^2$, $b = \chi q^2$,

$$S_1 = \sum_i \frac{z_i^2 n_i}{m_i} \ , \ S_2 = \sum_i \frac{n_i}{m_i} \ , \ S_3 = \sum_i \frac{z_i n_i}{m_i} \ , \tag{7}$$

and

$$x = \frac{1}{n}\sum_i z_i n_i u_i \ , \ y = \frac{1}{n}\sum_i n_i u_i \ , \tag{8}$$

where $n = N/V$ is the total density of particles. Making use of these notations, the homogeneous system of equations (6) can be written as

$$\begin{aligned} &(-\omega^2 + aS_1)\,x + bS_3 y = 0 \ , \\ &aS_3 x + (-\omega^2 + bS_2)\,y = 0 \ . \end{aligned} \tag{9}$$

In addition, we have

$$\omega^2 u_i = \frac{anz_i}{m_i}x + \frac{bn}{m_i}y \ . \tag{10}$$

The spectrum of frequencies ω of the system of equations (9) can be obtained straightforwardly. It is given by

$$\omega_{1,2}^2 = \frac{1}{2}\left[aS_1 + bS_2 \pm \sqrt{a^2S_1^2 + 2ab\,(2S_3^2 - S_1S_2) + b^2S_2^2}\right] \ . \tag{11}$$

The ω_2-branch in equation (11) (corresponding to the minus sign) represents sound-like excitations. In the long wavelength limit it is given by

$$\omega_2^2 = \left(S_2 - S_3^2/S_1\right)b = v_s^2 q^2 \ , \ q \to 0 \ , \tag{12}$$

where

$$v_s = \sqrt{(S_2 - S_3^2/S_1)\,\chi} \tag{13}$$

is the sound velocity. We can see easily, by applying the Schwarz-Cauchy inequality to the vectors $a_i = \sqrt{n_i/m_i}$ and $b_i = z_i\sqrt{n_i/m_i}$, that v_s^2 is always positive ($S_2 - S_3^2/S_1) \geq 0$). For shorter wavelengths the ω_2-branch of the spectrum approaches an horizontal asymptote given by

$$\omega_2^2 \sim \left(1 - S_3^2/S_1S_2\right)\omega_p^2 \ , \ q \to \infty \ , \tag{14}$$

where

$$\omega_p^2 = aS_1 = 4\pi e^2 \sum_i \frac{z_i^2 n_i}{m_i} \tag{15}$$

gives the plasma frequency ω_p. It is worth noting that in the limit of vanishing Coulomb coupling ($a \rightarrow 0$) the sound-like branch of the spectrum disappears completely, according to equation (11).

The ω_1-branch of the spectrum given by equation (11) (corresponding to the plus sign) gives the plasmonic excitations. In the long wavelength limit we get

$$\omega_1^2 = aS_1 + bS_3^2/S_1 = \omega_p^2 + bS_3^2/S_1 \ , \ \ q \rightarrow 0 \ . \tag{16}$$

For shorter wavelengths or in the limit of vanishing Coulomb interaction the ω_1-branch approaches an asymptote given by

$$\omega_1^2 \sim bS_2 + aS_3^2/S_2 \ . \tag{17}$$

One can see that in these limits the ω_1-branch behaves like an "anomalous" sound given by

$$\omega_a = \sqrt{bS_2} = v_a q \ , \tag{18}$$

propagating with velocity

$$v_a = \sqrt{S_2 \chi} = \frac{1}{\sqrt{1 - S_3^2/S_1 S_2}} v_s \tag{19}$$

(which is always a positive qauntity). This additional sound is always faster than the ordinary sound, since

$$\frac{v_a}{v_s} = \frac{1}{\sqrt{1 - S_3^2/S_1 S_2}} > 1 \ . \tag{20}$$

We emphasize that this additional sound holds in the limit of vanishing Coulomb interaction. For a finite Coulomb coupling it holds for shorter wavelengths.

Such a "two-sounds anomaly" seems to be pretty well documented in liquid water.[1] If we assume that the dynamics of liquid water has a plasma component consisting of H^{+z} cations, with density $2n$ and mass m (proton mass), and O^{-2z} anions with density n and mass $M = 16m$, where n is the water density, then we get $v_a/v_s = (1 - S_3^2/S_1 S_2)^{-1/2} \simeq (2M/9m + 5/9)^{1/2} \simeq 2$, which is precisely the ratio of the two sound velocities determined experimentally.[2] If we note that the characteristic frequency determined in these experiments is of the order of $\omega \simeq 10^{131} s^{-1}$ then we can estimate the reduced effective charge z from $\omega \simeq \omega_p = 16\pi n e^2 z^2/\mu$ given by equation (15), where $\mu = 2mM/(M + 2m)$ is the reduced mass. We get $z \simeq 3 \times 10^{-2}$, which is a very small value. One may say indeed that liquid water is in the limit of vanishing Coulomb coupling. We note also that for deuterated water we get from equation (20) $v_a/v_s = \sqrt{2}$, while the experimental value seems to be closer to 2.[3] The excitation spectrum given by equations (11) for the $O^{-2z} - H^z$ plasma is shown in Fig. 1.

[1] See, for instance, S. C. Santucci, D. Fioretto, L. Comez, A. Gessini and C. Masciovecchio, Phys. Rev. Lett. **97** 225701 (2006) and references therein; F. Sette, G. Ruocco, M. Krisch, C. Masciovecchio, R. Verbeni and U. Bergmann, Phys. Rev. Lett. **77** 83 (1996). It is worth noting that the interaction employed here (Coulombian plus short-range) is similar with the interaction used in previous studies of molecular dynamics, where such an "anomalous" sound was first suggested (A. Rahman and F. H. Stillinger, Phys. Rev. **A10** 368 (1974)).

[2] The velocity of the ordinary sound in water is $v_s \simeq 1500 m/s$, while the velocity of the "anomalous" sound is $v_a \simeq 3000 m/s$.

[3] J. Teixeira, M. C. Bellissent-Funel, S. H. Chen and B. Dorner, Phys. Rev. Lett. **54** 2681 (1985); C. Petrillo, F. Sacchetti, B. Dorner and J.-B. Suck, Phys. Rev. **E62** 3611 (2000). The velocity of the "anomalous" sound given by equation (20) is $v_a \simeq 2200 m/s$.

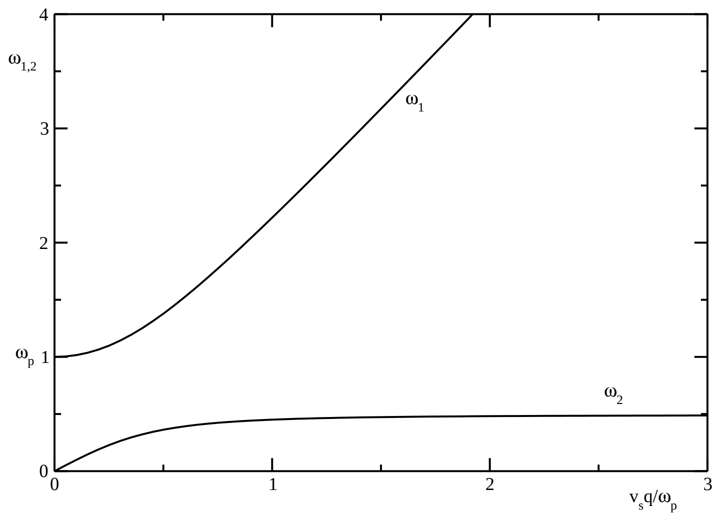

Figure 1: Spectrum of density excitations given by equation (11) for the $O^{-2z} - H^{+z}$ plasma.

We emphasize that sound-like excitations given by equation (12) are different from the ordianry hydrodynamic sound. Indeed, the former are non-equilibrium elementary excitations while the latter proceeds by equilibrium, adiabatic motion. It is easy to see that the velocity of the ordinary sound is given by $v_0 = 1/\kappa \sum_i n_i m_i$, where κ is the adiabatic compressibility (the correspoding interaction reads $U = (2\kappa)^{-1} \int d\mathbf{r} \left[div\mathbf{u}(\mathbf{r}) \right]^2 = -(2\kappa n)^{-1} \sum_{\mathbf{q}} q^2 u(\mathbf{q}) u(-\mathbf{q})$). For the $H^{+z} - O^{-2z}$ plasma we get $v_0 = 1/\sqrt{\kappa n(M+2m)}$ and (12) gives $v_s = \sqrt{9n\chi/(M+2m)}$. We may assign the additional fast sound to the sound-like excitations propagating with velocity $v_s = 3000 m/s$ and compare them with the ordinary sound propagating with velocity $v_0 = 1500 m/s$. We can see that the ratio $v_s/v_0 = 3n\sqrt{\kappa\chi}$ does not exhibit an isotopic effect, in agreement with experiments. the interaction with the movements of the individual particles gives a finite lifetime for the sound-like excitations, which exist beyond a certain threshold wavevector (where the hydrodynamic sound ceases to exist, being absorbed by such individual movements).

Equation $\delta n_i = -n_i div\mathbf{u}_i$ is equivalent with Maxwell equation $div\mathbf{E}_i = 4\pi q_i \delta n_i$, where the electric field is given by $\mathbf{E}_i = -4\pi q_i n_i \mathbf{u}_i$, where $q_i = ez_i$ is the electric charge of the i-th species of ions. It follows that the internal field is given by

$$E_{int} = -4\pi e \sum_i z_i n_i u_i \tag{21}$$

We get easily this field from equations (6) with an external electric field,

$$E_{int} = -iq\phi \frac{\omega_p^2}{\omega^2 - \omega_p^2} \tag{22}$$

in the long wavelength limit (it is proportional to x given by equation (8)). The dielectric function is defined by $D = \varepsilon E = e(D + E_{int})$, where $D = -iq\phi$ is the external field (electric displacement). We get the dielectric function

$$\varepsilon = 1 - \omega_p^2/\omega^2 \ , \tag{23}$$

as expected. This dielectric function exhibits an absorption edge (ω_p) for very low frequencies. In this static limit it is very likely to admit the existence of an additional internal field of intrinsic polarizability which changes the above dielectric function into $\varepsilon = (\omega^2 - \omega_p^2)/(\omega^2 + \omega_0^2)$, where ω_0 is a frequency parameter accounting for such an internal field.

From equation (10) we can see that the displacement u_i is a superposition of the two eigenvectors of the system of equations (9), which oscillates with eigenfrequencies $\omega_{1,2}$, respectively. It follows that these coordinates are those of linear harmonic oscillators with the potential energy of the form $m_i\omega^2u_i^2/2$. The statistical distribution of the coordinates u_i in the classical limit is given by $dw \sim \exp(-m_i\omega^2u_i^2/2T)du_i$, where T denotes the temperature. We get the thermal averages

$$\langle u_i u_j \rangle = \frac{T}{m_i\omega^2}\delta_{ij} \ . \tag{24}$$

On the other hand the structure factor, defined as

$$\begin{gathered} S(q,\omega) = \frac{1}{2\pi}\int d\mathbf{r}d\mathbf{r}'dt \left\langle \delta n(\mathbf{r},t)\delta n(\mathbf{r}',0)\right\rangle e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')-i\omega t} = \\ = \frac{N}{2\pi n^2}\int dt \left\langle \delta n(\mathbf{q},t)\delta n(-\mathbf{q},0)\right\rangle e^{-i\omega t} \end{gathered} \tag{25}$$

can be written as

$$S(q,\omega) = \frac{Nq^2}{2\pi n^2}\int dt \sum_{ij} n_i n_j \left\langle u_i(t)u_j(0)\right\rangle e^{-i\omega t} \ . \tag{26}$$

Writing

$$u_i = u_i^{(1)}e^{i\omega_1 t} + u_i^{(2)}e^{i\omega_2 t} \tag{27}$$

and making use of equation (24) we get the structure factor

$$S(q,\omega) = NTq^2\left(\sum_i n_i^2/n^2m_i\right)\left[\frac{1}{\omega_1^2}\delta(\omega-\omega_1) + \frac{1}{\omega_2^2}\delta(\omega-\omega_2)\right] \tag{28}$$

We can see that the relevant sound contributions read

$$S(q,\omega) \simeq \frac{NT}{v_{s,a}^2}\left(\sum_i n_i^2/n^2m_i\right)\delta(\omega - v_{s,a}q) \ . \tag{29}$$

The short-range interaction χ can be generalized to a short-range interaction χ_{ij} distinct for each pair of species. In this case, the excitation spectrum of the density oscillations may exhibit multiple branches in general, for a multi-component plasma. In addition, it may have special features, like a dip in the plasmonic branch, or negative velocity for the ordinary sound, which may indicate either an anomalous behaviour or unphysical situations.

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