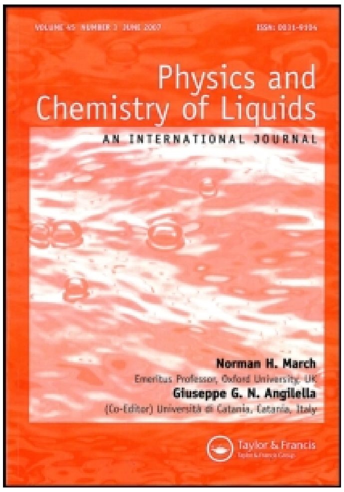

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Apostol, M.(2009)'Dynamics of collective density modes in multi-component molecular mixtures',Physics and Chemistry of Liquids,47:1,35 — 44

To link to this Article: DOI: 10.1080/00319100802428502

URL: http://dx.doi.org/10.1080/00319100802428502

Physics and Chemistry of Liquids
Vol. 47, No. 1, February 2009, 35–44

Dynamics of collective density modes in multi-component molecular mixtures

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(*Received 18 July 2008; final version received 23 August 2008*)

The excitation spectrum of the density collective oscillations is computed for multi-component molecular mixtures with both Coulomb and (repulsive) short-range interactions. Distinct sound-like excitations appear, governed by the short-range interaction, which differ from the ordinary hydrodynamic sound. The dielectric function and the structure factor are also calculated. The 'two-sounds phenomenon' can be understood by means of the predictions of this model.

Keywords: multi-component mixtures; density oscillations; sound waves; 'two-sounds anomaly'

This article is motivated by the 'two-sounds anomaly' persistently reported over the years in water, either in normal conditions or undercooled [1–6], as well as in other liquid molecular mixtures. Inelastic neutron, X-ray, Brillouin and, more recently, ultraviolet scattering, either in ordinary or in heavy water, seem to indicate an additional, faster, higher-frequency sound, propagating with velocity $\simeq 3000\,\mathrm{m\,s^{-1}}$ up to intermediate wavevectors (mean intermolecular distance in water is $\simeq 3$ Å), beside the ordinary hydrodynamic sound propagating with velocity $\simeq 1500\,\mathrm{m\,s^{-1}}$. A dispersionless mode ($\simeq 10^{13}\,\mathrm{s^{-1}}$) was also reported sometimes [3,5] (as well as no additional sound [7]). The phenomenon is also documented by both simulations of molecular dynamics and experimental data in binary mixtures with large mass difference (metallic alloys and rare-gas mixtures) [8–17].

We show herein that such a 'two-sounds anomaly' may appear in interacting molecular systems with (repulsive) short-range interaction. Such a model could reasonably be related to liquid water (or other physical systems as those indicated above). The velocity of the sound-like excitations is independent of temperature, in contrast with the velocity of the hydrodynamic sound which is governed by the adiabatic compressibility, and thus temperature dependent. In addition, the plasma-like branch of the spectrum due to the Coulomb interaction may appear as another sound-like mode for shorter wavelengths and weak Coulomb coupling. We report here also the computation of the dielectric function and the structure factor within such a model.

We start with the well-known representation of the particle density

$$n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) = \frac{1}{V}\sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \sum_i e^{-i\mathbf{q}\mathbf{r}_i} \tag{1}$$

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ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319100802428502
http://www.informaworld.com

for a collection of N particles enclosed in volume V, where $\mathbf{r}_i$ denotes the position of the ith particle. We consider a small displacement $\mathbf{r}_i \to \mathbf{r}_i + \mathbf{u}(\mathbf{r}_i)$ in these positions, as given by a displacement field $\mathbf{u}(\mathbf{r}_i)$, such that the particle density becomes

$$\tilde{n}(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{q}} e^{i\mathbf{qr}} \sum_i e^{-i\mathbf{q}[\mathbf{r}_i + \mathbf{u}(\mathbf{r}_i)]} = \frac{1}{V}\sum_{\mathbf{q}} e^{i\mathbf{qr}} \sum_i e^{-i\mathbf{qr}_i}[1 - i\mathbf{qu}(\mathbf{r}_i) + \cdots] \tag{2}$$

for $\mathbf{qu}(\mathbf{r}_i) \ll 1$. Now we employ a Fourier representation

$$\mathbf{u}(\mathbf{r}_i) = \frac{1}{\sqrt{N}}\sum_{\mathbf{q}} \mathbf{u}(\mathbf{q}) e^{i\mathbf{qr}_i} \tag{3}$$

as well as the well-known random-phase approximation

$$\sum_i e^{i(\mathbf{q}-\mathbf{q}')r_i} = N\delta_{\mathbf{q},\mathbf{q}'} \tag{4}$$

to get

$$\tilde{n}(\mathbf{r}) = n - in\frac{1}{\sqrt{N}}\sum_{\mathbf{q}} e^{i\mathbf{qr}}\mathbf{qu}(\mathbf{q}), \tag{5}$$

where $n = N/V$ is the particle density. By comparing Equations (1) and (5), we can see that the small change in the density can be represented as

$$\tilde{n}(\mathbf{r}) - n = \delta n(\mathbf{r}) = -n \operatorname{div} \mathbf{u}(\mathbf{r}), \tag{6}$$

and its Fourier transform $\delta n(\mathbf{q}) = -in\mathbf{qu}(\mathbf{q})$.

We apply this displacement-field approach to a multi-component molecular mixture consisting of several 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 φ_{ij} and short-range potentials χ_{ij}. The mixture is subjected to the neutrality condition $\sum_i n_i z_i = 0$, where $n_i = N_i/V$ is the particle density of the ith species. We consider elementary excitations of the particle density, whose interaction energy is given by

$$U = \frac{1}{2}\sum_{ij}\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\big[\varphi_{ij}(\mathbf{r}-\mathbf{r}') + \chi_{ij}(\mathbf{r}-\mathbf{r}')\big]\delta n_i(\mathbf{r})\delta n_j(\mathbf{r}'), \tag{7}$$

where $\varphi_{ij} = e^2 z_i z_j/|\mathbf{r}-\mathbf{r}'|$ and $\delta n_i(\mathbf{r})$ denotes a small density disturbance which preserves the neutrality. According to Equation (6) it can be represented as $\delta n_i = -n_i \operatorname{div} \mathbf{u}_i$, where $\mathbf{u}_i$ is the displacement field. We use the Fourier transforms

$$\delta n_i(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{q}} \delta n_i(\mathbf{q}) e^{i\mathbf{qr}}, \quad \varphi(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{q}} \varphi(\mathbf{q}) e^{i\mathbf{qr}}, \tag{8}$$

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 $\delta n_i(\mathbf{q}) = -in_i\mathbf{qu}_i(\mathbf{q})$. 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 (7) can be written as

$$U = -\frac{1}{2n}\sum_{ij\mathbf{q}} n_i n_j q^2 \big[\varphi_{ij}(q) + \chi_{ij}(q)\big] u_i(\mathbf{q}) u_j(-\mathbf{q}), \tag{9}$$

where $\varphi_{ij}(q) = z_i z_j \varphi(q)$ and $n = N/V$ is the total density of particles. We assume a weak q-dependence of $\chi_{ij}(q)$, as for short-range potentials.

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

$$T = -\frac{1}{2n}\sum_{i\mathbf{q}} m_i n_i \dot{u}_i(\mathbf{q}) \dot{u}_i(-\mathbf{q})\,. \tag{10}$$

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

$$V = -i\frac{e}{n}\sum_{i\mathbf{q}} n_i z_i q \phi(\mathbf{q}) u_i(-\mathbf{q})\,. \tag{11}$$

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

$$m_i \ddot{u}_i + 4\pi e^2 z_i \sum_j z_j n_j u_j + q^2 \sum_j \chi_{ij} n_j u_j = -iqez_i\phi, \tag{12}$$

where we dropped out the argument $\mathbf{q}$ in $u_i(\mathbf{q})$ and $\phi(\mathbf{q})$ and neglect the weak q-dependence of $\chi_{ij}(q) = \chi_{ij}$. In order to simplify these equations we take the same (repulsive) short-range potentials for all species, $\chi_{ij} = \chi > 0$, and analyse first the homogeneous system of equations given by (12). We introduce the notations $a = 4\pi e^2$, $b = q^2\chi$,

$$S_1 = \sum_i \frac{z_i^2 n_i}{m_i}, \quad S_2 = \sum_i \frac{n_i}{m_i}, \quad S_3 = \sum_i \frac{z_i n_i}{m_i}, \tag{13}$$

and

$$x = \frac{1}{n}\sum_i z_i n_i u_i, \quad y = \frac{1}{n}\sum_i n_i u_i. \tag{14}$$

Making use of these notations, the homogeneous system of Equation (12) can be written as

$$\begin{aligned} &\big(-\omega^2 + aS_1\big)x + bS_3 y = 0 \\ &aS_3 x + \big(-\omega^2 + bS_2\big)y = 0. \end{aligned} \tag{15}$$

In addition, we have

$$\omega^2 u_i = \frac{anz_i}{m_i}x + \frac{bn}{m_i}y. \tag{16}$$

The spectrum of frequencies, ω, of the system of Equations (15) can be obtained straightforwardly. It is given by

$$\omega_{1,2}^2 = \frac{1}{2}\left[aS_1 + bS_2 \pm \sqrt{a^2S_1^2 + 2ab\big(2S_3^2 - S_1S_2\big) + b^2S_2^2}\right]. \tag{17}$$

The ω_1-branch in Equation (17) (corresponding to the plus sign) represents the plasmonic excitations. In the long wavelength limit it reads

$$\omega_1^2 = aS_1 + \frac{bS_3^2}{S_1} = \omega_p^2 + \frac{bS_3^2}{S_1}, \quad q \to 0, \tag{18}$$

where ω_p, given by

$$\omega_p^2 = aS_1 = 4\pi e^2 \sum_i \frac{z_i^2 n_i}{m_i}, \tag{19}$$

is the plasma frequency. For shorter wavelengths the ω_1-branch approaches an asymptote given by

$$\omega_1^2 \simeq bS_2 + \frac{aS_3^2}{S_2}, \quad q \to \infty. \tag{20}$$

The ω_2-branch in Equation (17) (corresponding to the minus sign) represents sound-like excitations. In the long wavelength limit it is given by

$$\omega_2^2 = \left(\frac{S_2 - S_3^2}{S_1}\right)b = v_s^2 q^2, \quad q \to 0, \tag{21}$$

where

$$v_s = \sqrt{\left(\frac{S_2 - S_3^2}{S_1}\right)\chi} \tag{22}$$

is the corresponding 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 a horizontal asymptote, given by

$$\omega_2^2 \simeq \left(1 - S_3^2/S_1S_2\right)\omega_p^2, \quad q \to \infty\,. \tag{23}$$

In the limit of vanishing Coulomb coupling ($a \to 0$) the sound branch of the spectrum becomes $\omega_2^2 = bS_2 = v_s^2 q^2$, where

$$v_s^2 = \chi S_2 = \chi \sum_i \left(\frac{n_i}{m_i}\right), \tag{24}$$

an expression which holds also for the same mass $m_i = m$ for all particles (one component), due to the neutrality condition ($S_3 = 0$).

The above elementary excitations, which are governed by interaction, are non-equilibrium collective modes which might be termed density 'kinetic' modes [18]. The sound-like excitations (ω_2-branch in Equation (17)) may be called 'densitons', in order to distinguish them from plasmons (ω_1-branch in Equation (17)) and from the ordinary sound. They may correspond to the density collective modes suggested by Zwanzig for classical liquids [19]. We emphasise that these sound-like excitations are distinct from the ordinary hydrodynamic sound.

Indeed, the interaction corresponding to the latter can be written as

$$U=\frac{1}{2\kappa}\int d\mathbf{r}[\operatorname{div}\mathbf{u}(\mathbf{r})]^2=-\frac{1}{2\kappa n}\sum_{\mathbf{q}}q^2u(\mathbf{q})u(-\mathbf{q}), \tag{25}$$

where $\kappa=-(1/V)(\partial V/\partial p)_S$ is the adiabatic compressibility (p denotes the pressure and S stands for entropy). The above equation is derived by making use of the change $\delta V=-V(\delta n/n)=V\operatorname{div}\mathbf{u}$ in volume. We emphasise that for thermodynamic equilibrium we have only one displacement field $\mathbf{u}(\mathbf{r})$. Equation (25) together with the kinetic energy given by Equation (10) for $u_i(\mathbf{q})=u(\mathbf{q})$ leads to the sound branch $\omega_0^2=v_0^2q^2$, corresponding to the ordinary sound propagating with a velocity v_0 given by

$$v_0^2=\left(\kappa\sum_i n_im_i\right)^{-1}. \tag{26}$$

For $m_i=m$ (one component) the above equation gives the well known velocity $v_0=1/\sqrt{\kappa nm}$ of the ordinary sound. As is well known, it has a slight temperature dependence, through the compressibility, in contrast with the velocity v_s given above for the sound-like excitations. For an electrically neutral multi-component mixture it can be shown easily that $v_s^2/v_0^2\geq n^2\chi\kappa$.

If we apply Equations (24) and (26) to both ordinary and heavy water (one component, neutral molecule), and assume that interaction χ and, respectively, the compressibility κ are the same for the two kinds of water, we can see that the two sound velocities v_s and v_0 exhibit a slight isotopic effect, while their ratio $v_s/v_0=n\sqrt{\chi\kappa}$ does not exhibit such an isotopic effect, in agreement with experimental data. In this case, we may take $v_0=1500\,\mathrm{m\,s^{-1}}$ and $v_s=3000\,\mathrm{m\,s^{-1}}$ from experimental data and get the interaction parameter $\chi\simeq60\,\mathrm{eV\,Å^3}$ (for a mean inter-molecular spacing $\simeq3$ Å) . A similar picture, given by Equations (24) and (26), may apply to rare-gas mixtures, while for metallic alloys the Coulomb coupling must be taken into account (and Equation (22) employed).

If we assume the existence of a dispersionless mode in water, then we may consider that the water molecule is dissociated to some extent, and its components have an electric charge, such that the plasmonic mode given by Equation (19) can be identified with such a dispersionless mode. Various models of dissociation of the water molecule are known, like $OH^- - H^+$ or $OH^- - H_3O^+$. In all cases a certain mobility of the H^+ (hydrogen) cations and O^- (oxygen) anions is implied. We assume here that the dynamics of liquid water has a plasma-like 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 density of water. The excitation spectrum given by Equations (17) for such an $O^{-2z}-H^{+z}$ plasma is shown in Figure 1. Taking $\omega=10^{13}s^{-1}$ ($\simeq5\,m$eV) of the dispersionless mode [3,5,7] as the plasma frequency ω_p given by $\omega_p^2=16\pi ne^2z^2/\mu$ (Equation (19)), where $\mu=2mM/(M+2m)$ is the reduced mass, we get $z\simeq3\times10^{-2}$. The velocity of the hydrodynamic sound is given by $v_0=1/\sqrt{\kappa n(M+2m)}$ according to Equation (26) and the velocity of the sound-like excitations is given by $v_s=\sqrt{9n\chi/(M+2m)}$ from Equation (22). We can see that both velocities exhibit an isotopic effect, but their ratio $v_s/v_0=3n\sqrt{\chi\kappa}$ does not, in agreement with the experimental data. From $v_s=3000\,\mathrm{m\,s^{-1}}$ we derive the interaction $\chi\simeq7\,\mathrm{eV\cdot Å^3}$. Similar results are obtained for other forms of dissociation, like $OH^- - H^+$ or $OH^- - H_3O^+$. In this respect, the $O^{-2z}-H^{+z}$ plasma model can be viewed as an average, effective model for various plasma components that may exist in water.

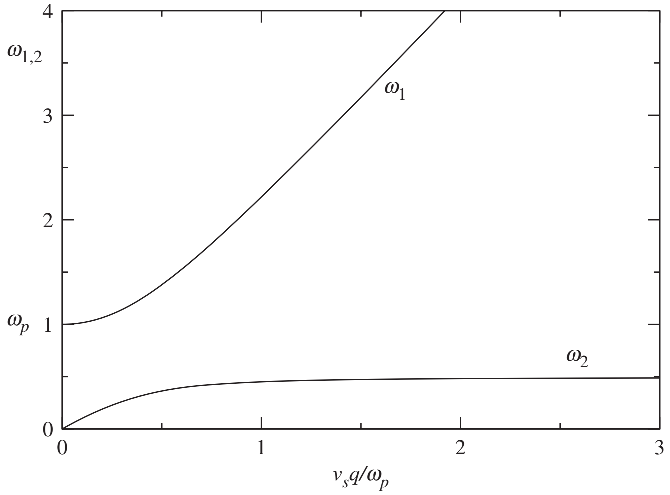

Figure 1. Spectrum of density excitations given by Equation (17) for the $O^{-2z} - H^{+z}$ plasma.

According to Equation (20), for shorter wavelengths the ω_1-branch approaches an asymptote given by $\omega_1^2 \sim bS_2 + aS_3^2/S_2$. In the limit of weak Coulomb coupling this ω_1-branch may appear as an 'anomalous' sound given by

$$\omega_a = \sqrt{bS_2} = v_a q, \tag{27}$$

propagating with velocity

$$v_a = \sqrt{S_2\chi} = \frac{1}{\sqrt{1 - S_3^2/S_1S_2}} v_s \tag{28}$$

(which is always a positive quantity). This additional, anomalous sound is always faster than the sound-like excitations propagating with velocity v_s, since

$$\frac{v_a}{v_s} = \frac{1}{\sqrt{1 - S_3^2/S_1S_2}} > 1. \tag{29}$$

It is worth noting that the molecular dynamics studies which originally predicted such a fast, anomalous sound [20] indeed employed a Coulomb interaction and a short-range one. We note, however, that the velocity v_a as given by (28) does not depend on the Coulomb coupling. In the plasma model for water discussed above, the ratio v_a/v_0 is ~ 2 ($\simeq \sqrt{2M/9m + 5/9}$), but it exhibits an isotopic effect, which does not seem to be supported by the experimental data.

It is easy to derive the dielectric function in the limit of long wavelengths from Equation (12). Indeed, for charged particles, the equation $\delta n_i = -n_i \operatorname{div} \mathbf{u}_i$ is equivalent to the Maxwell equation $\operatorname{div} \mathbf{E}_i = 4\pi q_i \delta n_i$, where the electric field is given by $\mathbf{E}_i = -4\pi q_i n_i \mathbf{u}_i$ and $q_i = ez_i$ is the electric charge of the ith species. It follows that the internal field is given by

$$E_{\text{int}} = -4\pi e \sum_i z_i n_i u_i. \tag{30}$$

We get this field easily from Equation (12),

$$E_{\text{int}} = -iq\phi \frac{\omega_p^2}{\omega^2 - \omega_p^2}, \tag{31}$$

in the long wavelength limit (it is proportional to x given by Equation (14)). The dielectric function is defined by $D = \varepsilon E = \varepsilon(D + E_{\text{int}})$, where $D = -iq\phi$ is the external field (electric displacement). We get the plasma dielectric function

$$\varepsilon = 1 - \omega_p^2/\omega^2, \tag{32}$$

as expected. It exhibits an absorption edge (ω_p) for very low frequencies. In the static limit it is reasonable to admit the existence of an additional internal field of intrinsic polarisability which removes the $\omega = 0$ singularity.

We pass now to the calculation of the structure factor. From Equation (16) we can see that the displacement u_i is a superposition of the two eigenvectors of the system of Equation (15), which oscillate with eigenfrequencies $\omega_{1,2}$, respectively. It follows that these coordinates are those of linear harmonic oscillators with the potential energy of the form $m_i\omega^2 u_i^2/2$. The statistical distribution of the coordinates u_i in the classical limit is given by $\mathrm{d}w \sim \exp(-m_i\omega^2 u_i^2/2T)\mathrm{d}u_i$, where T denotes the temperature. We get the thermal averages

$$\langle u_i u_j \rangle = \frac{T}{m_i \omega^2}\delta_{ij}. \tag{33}$$

On the other hand the structure factor defined by

$$\begin{aligned} S(q,\omega) &= \frac{1}{2\pi}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\,\mathrm{d}t\langle \delta n(\mathbf{r},t)\delta n(\mathbf{r}',0)\rangle e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')-i\omega t} \\ &= \frac{N}{2\pi n^2}\int \mathrm{d}t\langle \delta n(\mathbf{q},t)\delta n(-\mathbf{q},0)\rangle e^{-i\omega t} \end{aligned} \tag{34}$$

(we leave aside the central peak) can be written as

$$S(q,\omega) = \frac{Nq^2}{2\pi n^2}\int \mathrm{d}t \sum_{ij} n_i n_j \langle u_i(t) u_j(0)\rangle e^{-i\omega t}. \tag{35}$$

Writing

$$u_i = u_i^{(1)} e^{i\omega_1 t} + u_i^{(2)} e^{i\omega_2 t} \tag{36}$$

and making use of Equation (33) we get the structure factor

$$S(q,\omega) = NTq^2\left(\sum_i n_i^2/n^2 m_i\right)\left[\frac{1}{\omega_1^2}\delta(\omega-\omega_1) + \frac{1}{\omega_2^2}\delta(\omega-\omega_2)\right]. \tag{37}$$

We can see that the relevant sound contributions read

$$S(q,\omega) \simeq \frac{NT}{v_{s,a}^2}\left(\sum_i n_i^2/n^2 m_i\right)\delta(\omega - v_{s,a}q). \tag{38}$$

The relaxation and damping effects can be included in the above expressions of the structure factor. As it is well known, they amount to representing the δ-functions by Lorentzians.

The short-range interaction χ can be generalised to an interaction matrix χ_{ij} with distinct elements 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 mixture. In addition, it may have special features, like a dip in the plasmonic branch, or negative velocity for the sound-like excitations, which may indicate either an anomalous behaviour or unphysical situations, depending on the mutual magnitudes of the short-range potentials χ_{ij}.

It is worthwhile commenting upon the validity of the approach presented above. If we keep higher-order terms in the expansion given by Equation (2) (i.e. for moderate values of $\mathbf{qu}_i$) then additional interactions appear in Equation (9), which leads to finite lifetimes for the density excitations. This means that for larger wavevectors $\mathbf{q}$ these excitations are no longer well-defined excitations, as expected. Making use of Equation (33) we can estimate the mean product qu_i for the sound-like branch as $qu_i \sim \sqrt{T/m_i v_s^2}$, where the velocity v_s is given by Equation (22). This gives rather small values for qu_i. For instance, for water we get $qu \sim 0.5$ (at room temperature), which shows that the wavevector q may take reasonably large values providing the displacement u is sufficiently small. For the plasmonic branch, the condition $qu_i \ll 1$ gives a cutoff wavevector $q_c^i \simeq \sqrt{m_i \omega_p^2 / T}$ for large ω_p; for small values of the plasma frequency the condition becomes $qu_i \sim \sqrt{T/m_i v_a^2} \ll 1$.

Another source of finite lifetime for the density excitations arises from the kinetic term. Indeed, under the displacement $\mathbf{r}_{ik} \to \mathbf{r}_{ik} + \mathbf{u}_i(\mathbf{r}_{ik})$, where $\mathbf{r}_{ik}$ is the position of the kth particle in the ith species, a mixed term

$$H_{\text{int}} = \sum_{ik} m_i \mathbf{v}_{ik} \dot{\mathbf{u}}_i(\mathbf{r}_{ik}) \tag{39}$$

appears in the kinetic term, where $\mathbf{v}_{ik} = \dot{\mathbf{r}}_{ik}$ is the velocity of the ik-particle. It is easy to get an upper bound for this term, by using the Schwarz–Cauchy inequality. It is given by $N \langle m_i v_{ik}^2 \rangle^{1/2} \langle m_i \dot{u}_i^2 \rangle^{1/2}$ or, by making use of (33), $\sqrt{\varepsilon T}$ per particle, where ε represents the mean kinetic energy (which depends on temperature, in principle). This estimation can be taken as an uncertainty in energy, leading to a lifetime $\tau \simeq \hbar / \sqrt{\varepsilon T}$ and a corresponding meanfree path $\Lambda = v_s \tau$ for the sound-like excitations. For wavelengths λ much longer than the meanfree path, i.e. for wavevectors q such as $q \ll 1/v_s \tau$ we are in the collision-like regime ($\omega_2 \tau \ll 1$), and the collisions can establish the thermodynamic equilibrium (hydrodynamic regime). In this case the ordinary sound can be propagated (with velocity v_0). For $q \gg 1/v_s \tau$ we are in the collisionless regime, the ordinary sound is absorbed, and the non-equilibrium sound-like excitations ('densitons') can be propagated (with velocity v_s). Unfortunately, it is difficult to have a reliable estimation of the energy ε, and so of the threshold wavevector $q_t = 1/v_s \tau = \sqrt{\varepsilon T} / \hbar v_s$. For $\varepsilon = 10\,\text{meV}$ (and $v_s = 3000\,\text{m}\,\text{s}^{-1}$, $T = 300\,\text{K}$) we get $q_t \simeq 0.1\,\text{Å}^{-1}$, which is in a reasonable order-of-magnitude agreement with the experimental data [1–6,11,12,15]. It is interesting to note that if we apply this estimation to weakly interacting gases, where we may take $\varepsilon \sim T$, we get a high value of the threshold wavevector $q_t \sim T / \hbar v_s$, since v_s is very small (the short-range interaction is weak). We may say that sound-like excitations are very unlikely to exist in gases; it is only the ordinary sound that exists. On the contrary, the collision-like regime is quite unlikely in ordinary solids, so we have there sound-like excitations and to a much lesser extent ordinary sound.

Finally, we note that the collective excitations derived above contribute to the thermodynamics of liquids. Indeed, the free energy can be written as

$$F = F_0 + F_1 + F_2 = F_0 + T\sum_{\mathbf{q}} \ln\left(1 - e^{-\hbar\omega_1/T}\right) + T\sum_{\mathbf{q}} \ln\left(1 - e^{-\hbar\omega_2/T}\right), \tag{40}$$

where F_0 is the free energy associated with the particle movements and $\omega_{1,2}$ are given by Equation (17). The evaluation of integrals in Equation (40) depends on the particular magnitude of the excitation spectrum, but usually the integrals are rapidly convergent and their contribution to the thermodynamic properties of the liquid is small. For instance, the sound-like contribution is approximately given by $F_2 \simeq -\pi^2 VT(T/\hbar v_s)^3/90$, which is indeed a small correction to F_0 (the latter being governed mainly by the liquid cohesion).

In conclusion, we have shown that sound-like excitations may appear in interacting molecular systems, controlled by short-range interactions, distinct from the ordinary hydrodynamic sound. The former are non-equilibrium excitations, while the latter appear through equilibrium, adiabatic processes. The velocity v_s of the sound-like excitations is independent of temperature, while the velocity v_0 of the ordinary sound depends on temperature, through the adiabatic compressibility. In order to distinguish them we propose to call the former 'kinetic' modes of particle density, or 'densitons'. In addition, in the presence of Coulomb interaction, the well-known plasmonic branch is present in the spectrum of the density excitations, which, for shorter wavelengths and weak Coulomb coupling may look like another, anomalous, fast sound. We have shown that the 'two-sounds anomaly' reported in liquids like water, rare-gas mixtures, metallic alloys, etc., and documented by molecular dynamics studies, can be understood on this basis.

Acknowledgements

The author is indebted to E. Preoteasa for many fruitful discussions, and to his colleagues in the Department of Theoretical Physics, Magurele-Bucharest for kind support on various points of this research.

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