STATISTICAL DESCRIPTION OF HYDRODYNAMIC PROCESSES IN IONIC MELTS WITH TAKING INTO ACCOUNT POLARIZATION EFFECTS

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Statistical description of hydrodynamic processes for ionic melts is proposed with taking into account polarization effects caused by the deformation of external ionic shells. This description is carried out by means of the Zubarev nonequilibrium statistical operator method, appropriate for investigations of both strong and weak nonequilibrium processes. The nonequilibrium statistical operator and the generalized hydrodynamic equations that take into account polarization processes are received for ionic-polarization model of ionic molten salts when the nonequilibrium averaged values of densities of ions number, their momentum, dipole momentum and total energy are chosen for the reduced description parameters. A spectrum of collective excitations is investigated within the viscoelastic approximation for ion-polarization model of ionic melts.

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I. INTRODUCTION

Study of equilibrium and nonequilibrium properties of ionic melts remains actual from the viewpoint of experimental[1–10], theoretical[11–26] as well as computer simulation[21,23–37] investigations. They are very important because of a wide range of applications in chemical, metallurgical and nuclear technologies[38–43]. It is important to notice the papers[1,2] where the binary distribution functions for a number of alkaline-chloride melts and some valence asymmetric ones were experimentally obtained for the first time by the method of neutron scattering in the systems with isotope replacement, developed by I.E. Enderby and colleagues. Dynamic structure factors of some ionic melts were received by means of an inelastic neutron scattering in works[3–5]. Moreover, diffusion, electroconductivity and viscosity coefficients were examined experimentally[9] as well. The recent X-rays inelastic scattering experiments on molten $NaCl$[6], $NaI$ and $CsCl$[7] have initiated study of collective excitations and dispersion laws of ionic melts. Theoretical investigations intended to explain observable phenomena in such systems were carried out on the basis of the kinetic equations for one-component plasma[44,45], the mode coupling theory[13,46,47], the generalized[12] and the extended[18,19] hydrodynamics, the Zubarev nonequilibrium statistical operator (NSO) approach[48,49], the generalized collective excitations approach[21,23–26,50] and others. It is important to note that in consequence of collective modes analysis for two-component plasma, five hydrodynamic modes (one heat, two sound and two mass and charge diffusion modes) and five relaxation modes were indicated based on the renormalized kinetics theory in papers[45,47]. Six of those modes describe properties of a system as neutral and four modes as a charged one. Correlation functions and corresponding response functions of mass and charge densities, temperature and momentum divergency fluctuations were considered in paper[12] using linear hydrodynamics equations, which takes into account thermoelectric and electrostriction effects. Statistical hydrodynamics of ionic systems were constructed in paper[18] with help of the nonequilibrium statistical operator method[48,49] based on the extended set of the reduced description parameters, including microscopic densities of particles number, their momentum, total energy and densities of generalized viscous stress tensor and energy flow. The obtained equations of extended hydrodynamics are valid for both strong and weak nonequilibrium processes. Moreover, in paper[19] this approach was reformulated on the basis of the generalized Fokker-Planck equation for the collective variables functional, considering nonlinear hydrodynamic fluctuations.
in ionic systems. The approach presented in paper 18 permitted to discover mutual influence of heat-viscosity processes in the time correlation functions “mass-mass”, “mass-charge”, “charge-charge” and their flows for weakly nonequilibrium processes in NaCl ionic melt. Theoretical study of dynamic structure factors, time correlation functions of longitudinal and transverse currents of mass and charge densities as well as transport coefficients11–18 obtained a qualitative agreement with the results of molecular dynamics calculations27–32 actively carried out in the mid 70s of the last century, starting from the paper27. In that time, the important results in investigations of structure and dynamical properties of ionic systems by means of the molecular dynamics method were obtained. In particular, the equilibrium binary distribution functions of ionic melts, calculated with the molecular dynamics method32 have a good agreement with the experimental data1,2. By means of the molecular dynamics simulations the dynamic structure factors for the model ionic melts of NaCl27,28 and RbBr29, time correlation functions of ionic velocities, diffusion and electroconductivity coefficients for ionic melts of NaCl, LiI, RbCl29,31 and others were received. An interesting fact is that the spectrum of charge density fluctuations of ionic melts in the long-wavelength limit has a characteristic peak like a spectrum of longitudinal optic phonons of ionic crystals. This was shown using the molecular dynamics simulations in paper22 and afterward in the theoretical studies11–14. Moreover, it was confirmed by Ab initio MD calculations in conjunction with the generalized collective mode approach24 and in real experiment10. Experimental investigations6–8, MD computer simulations35,36 and Ab initio MD simulations21,23–26 reveal an importance of taking into account polarization processes caused by electronic structure of ions. On the other hand, the theoretical study of collective modes dispersion for NaCl in the generalized collective mode approach21 showed that using the hard spheres ionic model yields too high values of optic modes frequencies. It is worth to mention that in theoretical studies and MD computer simulations of the equilibrium and nonequilibrium properties of ionic melts an effective ionic Haggings-Majer18,34 and Tosi-Fumi20,21 potentials which do not take into account polarization effects were used. However, in the real melts outer electrons shells can be polarized and so must contribute in an effective interaction. Today polarization effects are described within the three models: polarization point dipole models (PPDMs), shell models (SMs) and fluctuating charge models (FCMs). In PPDMs an induced point dipole is added to atomic or ionic positions, whereas in other two models dipole has a finite length. In SMs dipole is presented via a pair of point charges, namely with a positive nucleus
and a negative shell, linked with a harmonic connection; whereas in $FCMs$ point charges are fixed in certain positions and their values can fluctuate. In particular, influence of polarization effects on equilibrium properties of ionic melts $AgI$ were considered in study$^{51}$. In paper$^{35}$ polarization effects are described within $PPDM_s$ model when studying dynamical properties by means of MD simulations. In order to take into account electron shells deformations in works$^{23,24}$ a shell model was proposed in which electron shell is presented as an external electron cloud that interacts with nucleus through the harmonic potential and repulsive potential at small distance$^{44}$. Based on this model, the Car-Parrinello Ab initio simulations in which the dynamics of ionic subsystem was reduced to the pseudo-dynamics of electrons wave functions within the density functional formalism were carried out. This permits observation of polarization effects caused by deformations of external electron shells at the Ab initio level.

In present paper a statistical description of hydrodynamic processes in ionic melts with taking into account polarization effects caused by deformations of external electrons shells of ions is proposed. It is implemented by means of the Zubarev nonequilibrium statistical operator method$^{48,49}$ that permits to study both weak and strong nonequilibrium processes. In the second section the nonequilibrium statistical operator and the generalized hydrodynamic equations taking into account polarization effects are obtained for the ion-polarization model of ionic melts, when the nonequilibrium averaged values of densities of ions number $\hat{n}^a(r)$, their momentum $\hat{p}^a(r)$, angular momentum $\hat{s}^a(r)$, total energy $\hat{\varepsilon}(r)$ and dipole moment $\hat{d}^a(r)$ are chosen for the reduced description parameters. The generalized molecular hydrodynamics equations for ionic melts in the case of weak nonequilibrium are obtained in the third section. Section 4 contains analytic expressions for the collective excitations spectrum in the limit $k \rightarrow 0$, $\omega \rightarrow 0$ on the basis of the viscoelastic model for ionic melts with taking into account polarization processes.

II. HAMILTONIAN OF THE SYSTEM. NONEQUILIBRIUM STATISTICAL OPERATOR

Let us consider an ion-polarization model of ionic melts that classically describes ionic subsystem with taking into account polarization effects. We assume that both positively and negatively charged ions can be polarized, though in case of $NaI$ ionic melt, only negatively
charged jodine ions are polarized. In polarization processes related with electron transition between orbitals of an atom that turns to a positive ion and a negative atom of melt that turns to a negative ion, dipole moments of ions are induced. In consequence of interactions like “induced dipole - induced dipole”, “induced dipole - ion” and motion dynamics it leads to induced momenta of dipoles that in turn cause their rotational motion. Therefore, ions with induced dipole moments besides translational degrees of freedom possess rotational ones due to polarization processes. All these degrees of freedom of ions in melts must be accounted in the full Hamiltonian of the system. The latter can be presented in the following form:

\[ H = \sum_{a}^{N_a} \sum_{j=1}^{N_a} \left( \frac{p_j^2}{2m_a} + \frac{1}{2} \mathbf{J}_a : \mathbf{w}_j \mathbf{w}_j \right) + U_{\text{ion}}, \]  

which includes kinetic (translational and rotational energies) and potential parts; \( p_j \) denotes a momentum vector, \( m_a \) is a mass of ion of species \( a \), \( \mathbf{w}_j \) stands for an angular velocity and \( \mathbf{J}_a \) means an inertia tensor of the \( j \)-th polarized ion (ionic dipole) determined relatively its center of mass. \( U_{\text{ion}} \) we introduce as follows:

\[ U_{\text{ion}} = \frac{1}{2} \sum_{a,b}^{N_a N_b} \sum_{i,j=1}^{N_a} \Phi_{ab}(|r_{ij}|) - \sum_{a}^{N_a} d_j E_j^q - \frac{1}{2} \sum_{b}^{N_b} d_j E_j^d \] 

\[ + \sum_{a}^{N_a} \sum_{j=1}^{N_a} \frac{d_j^2}{2\alpha_j} + \sum_{a,b}^{N_a N_b} \sum_{i,j=1}^{N_a N_b} f_{ab}(r_{ij}) \frac{Z_a Z_b e^2}{r_{ij}^3} \mathbf{r}_{ij} \mathbf{d}_j, \]

where \( \sum' \) indicates that \( i \neq j \) when \( a = b \). \( \Phi_{ab}(|r_{ij}|) \) is an ion-ion interaction potential:

\[ \Phi_{ab}(|r_{ij}|) = \frac{Z_a Z_b e^2}{|r_{ij}|}, \]

\( Z_a, Z_b \) are the valences of the ions of a corresponding species, \( e \) denotes an electron charge, \( \sigma_a, \sigma_b \) are the radii of the ions of a corresponding species. \( \mathbf{d}_j \) means a dipole momentum of an ion with a distorted external shell

\[ \mathbf{d}_j = \alpha_j E_j = \alpha_j \sum_{b}^{N_b} f_{ab}(|r_{ij}|) \frac{Z_b e}{|r_{ij}|^3} \mathbf{r}_{ij}, \]

\( \alpha_j \) is a polarizability of the \( j \)-th ion in an electrical field

\[ E_j = E_j^d + E_j^q, \]

\[ E_j^q = \sum_{i \neq j}^{N_a} \frac{Z_b e}{|r_{ij}|^3} \mathbf{r}_{ij}, \]

\[ E_j^d = \sum_{i \neq j}^{N_a} \left( 3 \frac{(\mathbf{d}_i \cdot \mathbf{r}_{ij})}{|r_{ij}|^3} \mathbf{r}_{ij} - \frac{1}{|r_{ij}|^3} \mathbf{d}_i \right). \]
\(|r_{ij}| = |r_i - r_j|\) is a distance between ions. Damping dispersion functions \(f_{ab}(|r_{ij}|)\) can be determined according to paper 54. It is important to notice that interaction of polarized ions has a central-asymmetric character. Obviously, effects related with induced rotational degrees of freedom are expected to be small comparing to the induced dipoles processes in the general hydrodynamics picture of ionic melts.

Nonequilibrium states of the ion-polarization model of ionic melts are described by the nonequilibrium statistical operator \(\rho(x^N;t)\), which satisfies the Liouville equation

\[
\frac{\partial}{\partial t} \rho(x^N;t) + iL_N \rho(x^N;t) = 0, \tag{6}
\]

where \(iL_N\) stands for the Liouville operator, corresponding to Hamiltonian (1):

\[
iL_N = \sum_a \sum_{j=1}^{N_a} \left( \frac{p_j}{m_a} \cdot \frac{\partial}{\partial r_j} + (w_j \hat{d}_j) : \frac{\partial}{\partial \hat{d}_j} \right) + \sum_a \sum_{j=1}^{N_a} \left( \frac{\partial}{\partial r_j} U_{\text{ion}} \cdot \frac{\partial}{\partial p_j} + \hat{d}_j \cdot \frac{\partial}{\partial \hat{d}_j} U_{\text{ion}} \frac{\partial}{\partial \hat{d}_j} \right). \tag{7}
\]

\(\hat{d}_j = \frac{d_j}{|d_j|}\) is unit vector describing spatial orientations of ionic dipole.

To solve the Liouville equation (6) we use the Zubarev nonequilibrium statistical operator method, in which solutions are searched according to the N. Bogolyubov’s idea of a reduced description of nonequilibrium processes based on the set of observed variables \(\langle \hat{P}_n(r) \rangle^t\). Using this method, the solution of equation (6) can be present in a general form with taking into account the projection:

\[
\rho(x^N;t) = \rho_{\text{rel}}(x^N;t) - \int_{-\infty}^t e^{iL_N(t-t')}T_{\text{rel}}(t',t)(1 - P_{\text{rel}}(t'))iL_N \rho_{\text{rel}}(x^N;t') dt', \tag{8}
\]

where

\[
T_{\text{rel}}(t',t) = \exp_+ \left\{ - \int_{t'}^t (1 - P_{\text{rel}}(t''))iL_N dt'' \right\}
\]

is the evolution operator with taking into account Kawasaki-Gunton projection \(P_{\text{rel}}(t)\). Projection operator depends on a structure of relevant statistical operator \(\rho_{\text{rel}}(x^N;t)\)

\[
P_{\text{rel}}(t) \rho' = \left( \rho_{\text{rel}}(x^N;t) - \sum_n \int dr \frac{\partial \rho_{\text{rel}}(x^N;t)}{\partial \langle \hat{P}_n(r) \rangle^t} \langle \hat{P}_n(r) \rangle^t \right) \text{Sp}(\rho') \tag{9}
\]

\[
\quad + \sum_n \int dr \frac{\partial \rho_{\text{rel}}(x^N;t)}{\partial \langle \hat{P}_n(r) \rangle^t} \text{Sp}(\hat{P}_n(r) \rho')
\]
and possess the following properties
\[
P_{rel}(t)P_{rel}(t) = P_{rel}(t), \quad (1 - P_{rel}(t))P_{rel}(t') = 0, \quad P_{rel}(t)\rho(t) = \rho_{rel}(t), \quad P_{rel}(t)\rho_{rel}(t') = \rho_{rel}(t).
\]

Relevant statistical operator \(\rho_{rel}(t)\) is received from the conditions of an informational entropy extremum at fixed values of the reduced description parameters \(\langle \hat{P}_n(r) \rangle^t\) including the normalization condition \(\text{Sp}\rho_{rel}(x^N; t) = 1\). Within Gibbs approach one can obtain
\[
\rho_{rel}(x^N; t) = \exp \left\{ -\Phi(t) - \sum_n \int d\mathbf{r} F_n(\mathbf{r}; t) \hat{P}_n(\mathbf{r}) \right\},
\]
\[
\Phi(t) = \ln \text{Sp} \exp \left\{ -\sum_n \int d\mathbf{r} F_n(\mathbf{r}; t) \hat{P}_n(\mathbf{r}) \right\}.
\]
\(\Phi(t)\) is the Massieu-Planck functional, \(F_n(\mathbf{r}; t)\) are the Lagrange multipliers, which are determined from the self-consistency conditions
\[
\langle \hat{P}_n(\mathbf{r}) \rangle^t = \langle \hat{P}_n(\mathbf{r}) \rangle^t_{rel}
\]
and thermodynamic relations
\[
\frac{\delta \Phi(t)}{\delta F_n(\mathbf{r})} = \langle \hat{P}_n(\mathbf{r}) \rangle^t, \quad \frac{\delta S(t)}{\delta \langle \hat{P}_n(\mathbf{r}) \rangle^t} = -F_n(t).
\]

Here, \(S(t)\) denotes entropy of nonequilibrium state of the system determined according to Gibbs
\[
S(t) = \Phi(t) + \sum_n F_n(t)\langle \hat{P}_n(\mathbf{r}) \rangle^t.
\]

We will consider hydrodynamic state of ionic melt within the formulated ion-polarization model. For its description the averaged values of densities of ionic number \(\hat{n}^a(\mathbf{r}) = \sum_{j=1}^{Na} \delta(\mathbf{r} - \mathbf{r}_j)\), their momentum \(\hat{p}^a(\mathbf{r}) = \sum_{j=1}^{Na} \mathbf{p}_j \delta(\mathbf{r} - \mathbf{r}_j)\), angular momentum \(\hat{s}^a(\mathbf{r}) = \sum_{j=1}^{Na} \omega_j \delta(\mathbf{r} - \mathbf{r}_j)\), total energy \(\hat{\varepsilon}(\mathbf{r}) = \sum_a \sum_{j=1}^{Na} \left( \frac{p_j^2}{2m_a} + \frac{1}{2} \varepsilon_j \right) \mathbf{w}_j \cdot \mathbf{w}_j \delta(\mathbf{r} - \mathbf{r}_j) + \sum_a \sum_{j=1}^{Na} U_{ion}^a(\mathbf{r}_j) \delta(\mathbf{r} - \mathbf{r}_j)\) along with an induced dipole moment \(\hat{d}^a(\mathbf{r}) = \sum_{j=1}^{Na} \delta(\mathbf{r} - \mathbf{r}_j)\), which are observable variables and satisfy corresponding conservational laws, can be chosen for the reduced description parameters. For such a set of variables \(\rho_{rel}(x^N; t)\) can be written down as follows:
\[
\rho_{rel}(x^N; t) = \exp \left\{ -\Phi(t) - \int d\mathbf{r} \beta(\mathbf{r}; t) \left[ \hat{\varepsilon}(\mathbf{r}) - \sum_a \mathbf{v}^a(\mathbf{r}; t) \cdot \hat{p}^a(\mathbf{r}) - \sum_a \mathbf{v}^a(\mathbf{r}; t) \cdot \hat{s}^a(\mathbf{r}) \right] \right\},
\]
where the Lagrange multipliers $\beta(r; t)$, $v^a(r; t)$, $\nu^a(r; t)$, $E(r; t)$, $w^a(r; t)$ are determined from the self-consistency conditions

$$
\langle \dot{\xi}(r) \rangle^t = \langle \dot{\xi}(r) \rangle^t_{rel},
$$

$$
\langle \dot{p}^a(r) \rangle^t = \langle \dot{p}^a(r) \rangle^t_{rel},
$$

$$
\langle \dot{n}^a(r) \rangle^t = \langle \dot{n}^a(r) \rangle^t_{rel},
$$

$$
\langle \dot{d}^a(r) \rangle^t = \langle \dot{d}^a(r) \rangle^t_{rel},
$$

$$
\langle \dot{s}^a(r) \rangle^t = \langle \dot{s}^a(r) \rangle^t_{rel}
$$

and from the nonequilibrium thermodynamic relations (12), (13). They have the following meaning: $\beta(r; t) = 1/k_B T(r; t)$ is the inverse local temperature; $v^a(r; t)$ is the mean value of hydrodynamic velocity of ions; $w^a(r; t)$ denotes mean value of angular velocity of polarized ion, $\nu^a(r; t) = \mu^a_{el}(r; t) + \frac{m_a v^a(r; t)^2}{2} + \frac{\lambda^a_{el}(r; t) w^a(r; t)}{2}$; $\mu^a_{el}(r; t) = \mu^a(r; t) + Z_a e \varphi(r; t)$ stands for the electrochemical potential; $\mu^a(r; t)$ is the chemical potential of ions; $\varphi(r; t)$ denotes scalar potential of electric field $E(r; t)$ induced by ions and dipoles of the system. Electric field $E(r; t) = \langle \hat{E}(r) \rangle^t$ satisfies the averaged Maxwell equations:

$$
\nabla \times \langle \hat{E}(r) \rangle^t = -\frac{1}{c} \frac{\partial}{\partial t} \langle \hat{B}(r) \rangle^t,
$$

$$
\nabla \times \langle \hat{H}(r) \rangle^t = \frac{1}{c} \frac{\partial}{\partial t} \langle \hat{D}(r) \rangle^t
$$

$$
+ \frac{4\pi}{c} \left( \sum_a Z_a e \langle \hat{p}^a(r) \rangle^t + \sum_a \frac{1}{m_a} \mathbf{d}^a \cdot \nabla \langle \hat{p}^a(r) \rangle^t \right),
$$

$$
\nabla \cdot \langle \hat{B}(r) \rangle^t = 0,
$$

$$
\nabla \cdot \langle \hat{D}(r) \rangle^t = 4\pi \left( \sum_a Z_a e \langle \hat{n}^a(r) \rangle^t + \sum_a \mathbf{d}^a \cdot \nabla \langle \hat{n}^a(r) \rangle^t \right),
$$

Where, microscopic electric $\hat{E}(r)$ and magnetic $\hat{H}(r)$ fields and corresponding inductions $\hat{D}(r)$, $\hat{B}(r)$ satisfy the microscopic Lorenz-Maxwell equations. Known integral relations between $\langle \hat{D}(r) \rangle^t$ and $\langle \hat{E}(r) \rangle^t$ as well as between $\langle \hat{B}(r) \rangle^t$ and $\langle \hat{H}(r) \rangle^t$ determine spatially inhomogeneous dielectric function $\epsilon(r; r'; t, t')$ and magnetization $\chi(r; r'; t, t')$ which describe polarization processes in the system. Acting by the operators $(1 - P_{rel}(t))$ and $iL_N$ on $\rho_{rel}(t)$
in (8) we obtain

\[(1 - P_{\text{rel}}(t))iL_N\rho_{\text{rel}}(t) = \left\{ -\int d\mathbf{r}\beta(\mathbf{r}; t)I_\varepsilon(\mathbf{r}; t) + \sum_a \int d\mathbf{r}\beta(\mathbf{r}; t)v^a(\mathbf{r}; t)I_p^a(\mathbf{r}; t) + \sum_a \int d\mathbf{r}\nu^a(\mathbf{r}; t)I_n^a(\mathbf{r}; t) + \sum_a \int d\mathbf{r}\beta(\mathbf{r}; t)w^a(\mathbf{r}; t')I_s^a(\mathbf{r}; t') \right\}\rho_{\text{rel}}(t),
\]

where

\[I_\varepsilon(\mathbf{r}; t) = (1 - P(t))iL_N\varepsilon(\mathbf{r}), \tag{21}\]
\[I_p^a(\mathbf{r}; t) = (1 - P(t))iL_N\mathbf{p}^a(\mathbf{r}),\]
\[I_n^a(\mathbf{r}; t) = (1 - P(t))iL_N\mathbf{n}^a(\mathbf{r}),\]
\[I_d^a(\mathbf{r}; t) = (1 - P(t))iL_N\mathbf{d}^a(\mathbf{r}),\]
\[I_s^a(\mathbf{r}; t) = (1 - P(t))iL_N\mathbf{s}^a(\mathbf{r}),\]

are the generalized flows, and \(I_n^a(\mathbf{r}; t) = 0\). \(P(t)\) denotes the generalized Mori projection operator which in this case has the following structure

\[P(t)\hat{\mathbf{A}} = \langle \hat{\mathbf{A}} \rangle_{\text{rel}}^t + \int d\mathbf{r}\left\{ \frac{\delta(\hat{\mathbf{A}})_{\text{rel}}^t}{\delta(\mathbf{\varepsilon}(\mathbf{r}))^t}(\mathbf{\varepsilon}(\mathbf{r}) - \langle \mathbf{\varepsilon}(\mathbf{r}) \rangle^t) + \sum_a \frac{\delta(\hat{\mathbf{A}})_{\text{rel}}^t}{\delta(\mathbf{\hat{p}}^a(\mathbf{r}))^t}(\mathbf{\hat{p}}^a(\mathbf{r}) - \langle \mathbf{\hat{p}}^a(\mathbf{r}) \rangle^t) + \sum_a \frac{\delta(\hat{\mathbf{A}})_{\text{rel}}^t}{\delta(\mathbf{\hat{n}}^a(\mathbf{r}))^t}(\mathbf{\hat{n}}^a(\mathbf{r}) - \langle \mathbf{\hat{n}}^a(\mathbf{r}) \rangle^t) \right\}, \tag{22}\]

and properties \(P(t)(1 - P(t)) = 0, P(t)\hat{P}_\mathbf{\nu}(\mathbf{r}) = \hat{P}_\mathbf{\nu}(\mathbf{r})\).

Taking into account \((20)\) we obtain the nonequilibrium statistical operator of the ionic polarization model of ionic melt

\[\rho(t) = \rho_{\text{rel}}(t) + \int_{-\infty}^t e^{(t-t')T_{\text{rel}}(t, t') - \int d\mathbf{r}\beta(\mathbf{r}, t')I_\varepsilon(\mathbf{r}; t')} I_{\mathbf{v}}(\mathbf{r}; t') - \int d\mathbf{r}\beta(\mathbf{r}; t')I_{\mathbf{E}}(\mathbf{r}; t') I_{\mathbf{n}}^a(\mathbf{r}; t') - \int d\mathbf{r}\beta(\mathbf{r}; t')I_{\mathbf{w}}^a(\mathbf{r}; t') I_{\mathbf{s}}^a(\mathbf{r}; t') \right\}\rho_{\text{rel}}(t') dt', \tag{23}\]

in which the generalized flows of energy density \(I_\varepsilon(\mathbf{r}; t)\), momentum density \(I_{\mathbf{v}}^a(\mathbf{r}; t)\), angular momentum density \(I_{\mathbf{n}}^a(\mathbf{r}; t)\) and dipole moments density \(I_{\mathbf{s}}^a(\mathbf{r}; t)\) describe the dissipative
processes in the system. Using the NSO [23] we can obtain generalized hydrodynamics equations for the reduced description parameters \( \langle \hat{P}(\mathbf{r}) \rangle^t = \{ \langle \hat{n}^a(\mathbf{r}) \rangle^t, \langle \hat{p}^a(\mathbf{r}) \rangle^t, \langle \hat{s}^a(\mathbf{r}) \rangle^t, \langle \hat{d}^a(\mathbf{r}) \rangle^t, \langle \hat{\varepsilon}(\mathbf{r}) \rangle^t \} \) within the ion-polarization model of ionic melt. We present them in matrix form

\[
\frac{d}{dt} \langle \hat{P}(\mathbf{r}) \rangle^t = \langle \hat{P}(\mathbf{r}) \rangle^t_{rel} + \int dr' \int_{-\infty}^{t} e^{\varepsilon(t-t')} \tilde{\varphi}_{II}(\mathbf{r}, \mathbf{r}', t, t') \tilde{F}(\mathbf{r}', t') dt',
\]

where \( \tilde{P}(\mathbf{r}) \) is the column vector, \( \tilde{P}(\mathbf{r}) = iL_N \tilde{P}(\mathbf{r}), \tilde{F}(\mathbf{r}', t') = \{ -\beta(\mathbf{r}', t') \nu^a(\mathbf{r}', t'), -\beta(\mathbf{r}', t') \nu^a(\mathbf{r}', t'), -\beta(\mathbf{r}', t') \nu^a(\mathbf{r}', t'), -\beta(\mathbf{r}', t') \nu^a(\mathbf{r}', t') \} \) is the column vector of the nonequilibrium thermodynamic parameters, \( \tilde{\varphi}_{II}(\mathbf{r}, \mathbf{r}', t, t') \) is the matrix of the generalized transport kernels (memory functions):

\[
\tilde{\varphi}_{II}(\mathbf{r}, \mathbf{r}', t, t') = \langle \hat{I}(\mathbf{r}; t) T_{rel}(t, t') \hat{I}^{(+)\dagger}(\mathbf{r}', t') \rangle^t_{rel} =
\begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & \tilde{\varphi}_{pp} & \tilde{\varphi}_{ps} & \tilde{\varphi}_{pd} & \tilde{\varphi}_{pe} \\
0 & \tilde{\varphi}_{sp} & \tilde{\varphi}_{ss} & \tilde{\varphi}_{sd} & \tilde{\varphi}_{se} \\
0 & \tilde{\varphi}_{dp} & \tilde{\varphi}_{ds} & \tilde{\varphi}_{dd} & \tilde{\varphi}_{de} \\
0 & \tilde{\varphi}_{ep} & \tilde{\varphi}_{es} & \tilde{\varphi}_{ed} & \tilde{\varphi}_{ee}
\end{bmatrix}_{(\mathbf{r}, \mathbf{r}'; t, t')},
\]

\[
\tilde{\varphi}_{pp}(\mathbf{r}, \mathbf{r}', t, t') =
\begin{bmatrix}
\varphi_{pp}^{++} & \varphi_{pp}^{+-} \\
\varphi_{pp}^{-+} & \varphi_{pp}^{--}
\end{bmatrix}_{(\mathbf{r}, \mathbf{r}'; t, t')},
\]

\[
\varphi_{pp}^{ab}(\mathbf{r}, \mathbf{r}', t, t') = \langle \hat{I}_p^a(\mathbf{r}; t) T_{rel}(t, t') \hat{I}_p^b(\mathbf{r}', t') \rangle^t_{rel}
\]

are the generalized transport kernels describing viscous processes, herewith, \( \varphi_{pp}^{++} \) and \( \varphi_{pp}^{--} \) define generalized coefficients of viscosity caused by translational motion of positively and negatively charged polarized ions \( (a, b = \{+, -\}) \).

\[
\tilde{\varphi}_{ss}(\mathbf{r}, \mathbf{r}', t, t') =
\begin{bmatrix}
\varphi_{ss}^{++} & \varphi_{ss}^{+-} \\
\varphi_{ss}^{-+} & \varphi_{ss}^{--}
\end{bmatrix}_{(\mathbf{r}, \mathbf{r}'; t, t')},
\]

\[
\varphi_{ss}^{ab}(\mathbf{r}, \mathbf{r}', t, t') = \langle \hat{I}_s^a(\mathbf{r}; t) T_{rel}(t, t') \hat{I}_s^b(\mathbf{r}', t') \rangle^t_{rel}
\]

are generalized transport kernels describing viscous ionic processes caused by rotational motion of polarized ions, \( \varphi_{ss}^{++} \) and \( \varphi_{ss}^{--} \) define the generalized coefficients of angular viscosity of positively and negatively charged polarized ions,

\[
\tilde{\varphi}_{dd}(\mathbf{r}, \mathbf{r}', t, t') =
\begin{bmatrix}
\varphi_{dd}^{++} & \varphi_{dd}^{+-} \\
\varphi_{dd}^{-+} & \varphi_{dd}^{--}
\end{bmatrix}_{(\mathbf{r}, \mathbf{r}'; t, t')},
\]

\[
\varphi_{dd}^{ab}(\mathbf{r}, \mathbf{r}', t, t') = \langle \hat{I}_d^a(\mathbf{r}; t) T_{rel}(t, t') \hat{I}_d^b(\mathbf{r}', t') \rangle^t_{rel}
\]
\[ \varphi_{de}^{ab}(r, r'; t, t') = \langle I_d^a(r; t) T_{rel}(t, t') I_d^b(r'; t') \rangle_{rel}^{t'}, \tag{31} \]

denote the generalized transport kernels that describe transport processes of dipole moments of polarized ions of corresponding species, where
\[ I_d^a(r; t) = (1 - P(t)) i L_N d^a(r) = (1 - P(t)) \left( -\frac{1}{m_a} \partial_r \Pi_d^a(r) + \sum_{j=1}^{N_a} (\omega_j \cdot d_j) \delta(r - r_j) \right), \tag{32} \]
and \( \Pi_d^a(r) = \sum_{j=1}^{N_a} d_j p_j \delta(r - r_j) \).

\[ \tilde{\varphi}_{\xi\xi}(r, r'; t, t') = \langle I_{\xi}(r; t) T_{rel}(t, t') I_{\xi}(r'; t') \rangle_{rel}^{t'}, \tag{33} \]
is the generalized transport kernel of total energy, which determines the generalized coefficient of heat conductivity of ionic melt within the ion-polarization model. The matrix elements \( \tilde{\varphi}_{\rho\rho}, \tilde{\varphi}_{\rho\xi}, \tilde{\varphi}_{\rho\xi}, \tilde{\varphi}_{\xi\xi}, \tilde{\varphi}_{de} \) in (25) describe cross dissipative correlations between momenta, dipole moments and total energy flows of the system. The obtained nonequilibrium statistical operator (23) and the generalized hydrodynamics equations (24) together with the set of the generalized Maxwell equations (16)–(19) are valid for both weak and strong nonequilibrium processes in ionic melts with taking into account polarization processes. Set of equations (24) is unclosed and describe viscous, heat and polarization processes. The system of hydrodynamic equations can be significantly simplified and becomes closed for a weakly nonequilibrium processes, when the thermodynamic parameters \( \tilde{F}(r; t) \) and the reduced description parameters \( \langle \tilde{P}(r) \rangle^{t} \) slowly vary in time and space and slightly deviate from their equilibrium values \( \tilde{F}_0(r), \langle \tilde{P}(r) \rangle_0 \) respectively. In following section we will consider a weakly nonequilibrium processes in ionic melts within the ion-polarization model.

### III. GENERALIZED MOLECULAR HYDRODYNAMICS EQUATIONS FOR IONIC MELTS WITH TAKING INTO ACCOUNT POLARIZATION EFFECTS

In the case when the nonequilibrium thermodynamic parameters \( \tilde{F}(r; t) \) slightly deviate from their equilibrium values \( \tilde{F}_0(r) \), the relevant statistical operator (14) can be expanded in deviations \( \delta \tilde{F}(r; t) = \tilde{F}(r; t) - \tilde{F}_0(r) \) with taking into account linear terms only. Then, excluding \( \tilde{F}(r; t) \) from the relevant statistical operator by means of the self-consistency conditions (15) one can obtain
\[ \rho_{rel}^0(t) = \rho_0 \left( 1 + \sum_k \delta \tilde{P}(k; t) \tilde{\Phi}^{-1}(k) \tilde{P}(k) \right). \tag{34} \]
Here, $\rho_0$ is the equilibrium statistical operator of ionic melt, $\delta \tilde{P}(k; t) = \langle \tilde{P}(k; t) \rangle_t - \langle \tilde{P}(k; 0) \rangle_0$, $\tilde{P}(k)$ is a column vector whose elements are the Fourier-components of the reduced description parameters $\{\tilde{P}(k) = \int e^{ikr}\tilde{P}(r)dr\} = \{\hat{n}^a(k), \hat{p}^a(k), \hat{s}^a(k), \hat{d}^a(k), \hat{\varepsilon}(k)\}$. $\Phi^{-1}(k)$ is the inverse of the matrix of equilibrium correlation functions $\Phi(k)$

$$
\tilde{\Phi}(k) = \begin{bmatrix}
\tilde{\Phi}_{nn} & 0 & 0 & \tilde{\Phi}_{nd} & \tilde{\Phi}_{ne} \\
0 & \tilde{\Phi}_{pp} & 0 & 0 & 0 \\
0 & 0 & \tilde{\Phi}_{ss} & 0 & 0 \\
\tilde{\Phi}_{dn} & 0 & 0 & \tilde{\Phi}_{dd} & \tilde{\Phi}_{de} \\
\tilde{\Phi}_{en} & 0 & 0 & \tilde{\Phi}_{ed} & \tilde{\Phi}_{ee}
\end{bmatrix} \quad (35)
$$

Here,

$$
\tilde{\Phi}_{nn}(k) = \begin{bmatrix}
\Phi^{++}_{nn}(k) & \Phi^{+-}_{nn}(k) \\
\Phi^{-+}_{nn}(k) & \Phi^{--}_{nn}(k)
\end{bmatrix},
$$

(36)

is the matrix of static structure factors of ionic subsystem $\Phi_{ab}(k) = \langle \hat{n}^a(k)\hat{n}^b(-k) \rangle_0 = S_{ab}(k)$, where $\langle \ldots \rangle_0 = \int d\Gamma_N \ldots \rho_0$.

$$
\tilde{\Phi}_{pp}(k) = \begin{bmatrix}
\Phi^{++}_{pp}(k) & 0 \\
0 & \Phi^{--}_{pp}(k)
\end{bmatrix},
$$

(37)

with $\Phi_{pp}(k) = \langle \hat{p}^a(k)\hat{p}^a(-k) \rangle_0$, and

$$
\tilde{\Phi}_{ss}(k) = \begin{bmatrix}
\Phi^{++}_{ss}(k) & 0 \\
0 & \Phi^{--}_{ss}(k)
\end{bmatrix},
$$

(38)

whose elements $\Phi_{ss}(k) = \langle \hat{s}^a(k)\hat{s}^a(-k) \rangle_0$. Similarly,

$$
\tilde{\Phi}_{dd}(k) = \begin{bmatrix}
\Phi^{++}_{dd}(k) & \Phi^{+-}_{dd}(k) \\
\Phi^{-+}_{dd}(k) & \Phi^{--}_{dd}(k)
\end{bmatrix},
$$

(39)

where $\Phi_{dd}(k) = \langle \hat{d}^a(k)\hat{d}^b(-k) \rangle_0$ are the equilibrium correlation functions of Fourier-components of dipole moments densities for polarized ions $a$ and $b$.

$$
\tilde{\Phi}_{ee}(k) = \langle \hat{\varepsilon}(k)\hat{\varepsilon}(-k) \rangle_0
$$

(40)

is the equilibrium correlation Kubo-like function of Fourier-components of total energy density of ionic melt. Other matrix elements in (35) describe static correlations of variables $\hat{n}^a(k), \hat{p}^a(k), \hat{d}^a(k), \hat{\varepsilon}(k)$. 

12
In the approximation (34) the nonequilibrium statistical operator has the following structure

\[
\rho(t) = \rho^0_{rel}(t) - \sum_k \int_{-\infty}^{t} e^{\epsilon(t-t')} T^0_{rel}(t, t')
\]

\[
\times \left\{ I^0_d(k) (\bar{\Phi}^{-1}(k))_{\epsilon\epsilon} \delta \epsilon(k; t') + \sum_{ab} \left[ I^a_p(k) (\bar{\Phi}^{-1}(k))_{pp}^{ab} \delta p^b(k; t') \right. \right.
\]

\[
+ I^a_d(k) (\bar{\Phi}^{-1}(k))_{dd}^{ab} \delta d^b(k; t') \right] + \sum_{ab} I^a_s(k) (\bar{\Phi}^{-1}(k))_{ss}^{ab} \delta s^b(k; t') \right\} \rho_0 dt',
\]

where

\[
I^a_d(k) = (1 - P^0) i L_N \hat{d}^a(k), \quad I^a_p(k) = (1 - P^0) i L_N \hat{p}^a(k), \quad I^a_s(k) = (1 - P^0) i L_N \hat{s}^a(k), \quad I^a_{\epsilon}(k) = (1 - P^0) i L_N \hat{\epsilon}(k)
\]

are the generalized flows in a weakly nonequilibrium case. \( P^0 \) denotes Mori projection operator

\[
P^0 \hat{A} = \langle \hat{A} \rangle_0 + \sum_k \langle \hat{A} \hat{P}^{(+)}(-k) \rangle_0 \bar{\Phi}^{-1}(k) \hat{P}(k)
\]

that possesses the following properties: \( P^0(1 - P^0) = 0, P^0 \hat{P}(k) = \hat{P}(k) \). The set of the generalized hydrodynamics equations for ionic melt within the ion-polarization model with approximation (41) is now closed and can be presented in the matrix form

\[
\frac{d}{dt} \langle \hat{P}(k) \rangle^t - i \vec{\Omega}(k) \langle \hat{P}(k) \rangle^t + \int_{-\infty}^{t} e^{\epsilon(t-t')} \bar{\varphi}(k; t, t') \langle \hat{P}(k) \rangle^t' dt' = 0.
\]

Here,

\[
i \vec{\Omega}(k) = \langle i L_N \hat{P}(k) \hat{P}^{(+)}(-k) \rangle_0 \bar{\Phi}^{-1}(k)
\]

is the frequency matrix whose elements

\[
i \vec{\Omega}(k) = \begin{bmatrix}
0 & i \vec{\Omega}_{np} & i \vec{\Omega}_{ns} & 0 & 0 \\
0 & i \vec{\Omega}_{pn} & 0 & 0 & i \vec{\Omega}_{pe} \\
i \vec{\Omega}_{sn} & 0 & 0 & i \vec{\Omega}_{sd} & i \vec{\Omega}_{se} \\
0 & i \vec{\Omega}_{dp} & i \vec{\Omega}_{ds} & 0 & 0 \\
0 & i \vec{\Omega}_{ep} & i \vec{\Omega}_{es} & 0 & 0
\end{bmatrix}
\]
are the normalized static correlation functions.

\[ \tilde{\varphi}(\mathbf{k}; t, t') = \langle \tilde{I}(\mathbf{k}) T_0(t, t') \tilde{I}^+(\mathbf{-k}) \rangle_0 \Phi^{-1}(\mathbf{k}) \]

(47)

\[
\begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & \tilde{\varphi}_{pp} & \tilde{\varphi}_{ps} & \tilde{\varphi}_{pd} & \tilde{\varphi}_{p\varepsilon} \\
0 & \tilde{\varphi}_{sp} & \tilde{\varphi}_{ss} & \tilde{\varphi}_{sd} & \tilde{\varphi}_{s\varepsilon} \\
0 & \tilde{\varphi}_{dp} & \tilde{\varphi}_{ds} & \tilde{\varphi}_{dd} & \tilde{\varphi}_{d\varepsilon} \\
0 & \tilde{\varphi}_{ep} & \tilde{\varphi}_{es} & \tilde{\varphi}_{ed} & \tilde{\varphi}_{\varepsilon\varepsilon}
\end{bmatrix}
\]

is the matrix of transport kernels (memory function), which describe a weakly nonequilibrium transport processes including viscous, polarization and heat processes in ionic melts within the ion-polarization model. \( \tilde{I}(\mathbf{k}) = (I_a^d(\mathbf{k}), I_a^s(\mathbf{k}), I_a^e(\mathbf{k})) \) is the column vector, \( \tilde{I}^+(\mathbf{-k}) = (I_a^d(\mathbf{-k}), I_a^s(\mathbf{-k}), I_a^e(\mathbf{-k})) \) is the row vector. As can be shown, in the framework of the NSO method\(^{48,49} \), the time correlation functions of the basic set of the dynamic variables

\[ \Phi(\mathbf{k}; t) = \langle \tilde{P}(\mathbf{k}; t) \tilde{P}^+(\mathbf{-k}) \rangle_0 \]

(48)

satisfy the equation (44) as well

\[
\frac{d}{dt} \Phi(\mathbf{k}; t) - \tilde{\Omega}(\mathbf{k}) \Phi(\mathbf{k}; t) + \int_{-\infty}^{t} e^{\varepsilon(t-t')} \tilde{\varphi}(\mathbf{k}; t, t') \Phi(\mathbf{k}; t') dt' = 0 \]

(49)

which takes into account memory effects. In the Markovian approximation when these effects are negligible, in the limit \( k \to 0, \omega \to 0 \) and without taking into consideration cross dissipative correlations and rotational degrees of freedom, the set of equations (49) can be presented as follows:

\[
\frac{d}{dt} \Phi(\mathbf{k}; t) + \tilde{T}(\mathbf{k}) \Phi(\mathbf{k}; t) = 0, \]

(50)

where

\[
\tilde{T}(\mathbf{k}) = -i\tilde{\Omega}(\mathbf{k}) + \tilde{\varphi}(\mathbf{k}),
\]

(51)

is the generalized hydrodynamic matrix. Here,

\[
i\tilde{\Omega}(\mathbf{k}) = i\mathbf{k}
\]

\[
\begin{bmatrix}
0 & \tilde{\omega}_{np} & 0 & 0 \\
\tilde{\omega}_{pm} & 0 & \tilde{\omega}_{pd} & \tilde{\omega}_{p\varepsilon} \\
0 & \tilde{\omega}_{dp} & 0 & 0 \\
0 & \tilde{\omega}_{sp} & 0 & 0
\end{bmatrix}
\]

(52)
is the corresponding frequency matrix and

\[
\tilde{\phi}(k) = k^2 \begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & \tilde{\phi}_{pp} & 0 & 0 \\
0 & 0 & \tilde{\phi}_{dd} & 0 \\
0 & 0 & 0 & \tilde{\phi}_{ee}
\end{bmatrix}
\] (53)

the matrix of memory functions, in which the wave-vector dependence is extracted. The system of equations (49) permits to study the time correlation functions of partial dynamics in ionic melts. Though if the elements of the frequency matrix (46) can be calculated via equilibrium characteristics, in particular, the partial structure factors, the calculation of the transport kernels (47) is a well-known problem and it can be implemented only approximately with taking into account special feature of dissipative processes in the system. This issue accompanies the investigation of collective excitation spectrum for ionic melts with taking into account polarization effects, in particular in the hydrodynamics limit \( k \rightarrow 0, \omega \rightarrow 0 \). In the following section we use obtained above the generalized molecular hydrodynamics equations for ionic melts, in particular, within viscoelastic approximation, to investigate the spectrum of collective excitations in the hydrodynamic limit.

IV. COLLECTIVE MODES OF IONIC MELTS. VISCOELASTIC APPROXIMATION.

In order to study collective excitations within the ion-polarization model of ionic melts we will use viscoelastic approximation. We will not take into consideration total energy density as well as rotational degrees of freedom of induced dipoles and pass from the description in terms of partial dynamic variables \( \hat{n}^a(k), \hat{p}^a(k), \hat{d}^a(k) \) to the description based on total densities of ions mass \( \hat{n}(k) = m_+ \hat{n}^+(k) + m_- \hat{n}^-(k) \), total ions momentum \( \hat{p}(k) = \hat{p}^+(k) + \hat{p}^-(k) \), total charge \( \hat{\rho}(k) = Z_+ e \hat{n}^+(k) + Z_- e \hat{n}^-(k) \) and density of total current of charge \( \hat{j}(k) = \frac{Z_+ e}{m_+} \hat{p}^+(k) + \frac{Z_- e}{m_-} \hat{p}^-(k) \). In addition we consider only negatively charged atoms to be polarized, i.e. negative ions possess induced dipole moments. Thus, we include density of dipole moment of negatively charged ions \( \hat{d}^-(k) \) to the set of the reduced description parameters. However, it is more convenient to use the variable \( \hat{d}(k) \) orthogonal to the variables \( \hat{n}(k) \) and \( \hat{\rho}(k) \):

\[
\hat{d}(k) = \hat{d}^-(k) - A(k) \hat{n}(k) - B(k) \hat{\rho}(k).
\] (54)
Here, $A(k)$ and $B(k)$ are determined by the relations

$$A(k) = \langle \dot{\mathbf{d}}^{-}(k) \hat{n}(-k) \rangle_{0} \Phi^{-1}(k)_{nn} + \langle \dot{\mathbf{d}}^{-}(k) \hat{\phi}(-k) \rangle_{0} \Phi^{-1}(k)_{p},$$

$$B(k) = \langle \dot{\mathbf{d}}^{-}(k) \hat{n}(-k) \rangle_{0} \Phi^{-1}(k)_{n} + \langle \dot{\mathbf{d}}^{-}(k) \hat{\phi}(-k) \rangle_{0} \Phi^{-1}(k)_{q}.$$  

(55)  

(56)

In this case, the generalized hydrodynamic matrix has the following form

$$T(k) = \begin{pmatrix}
0 & \phi_{pp} & 0 & 0 & 0 \\
-\phi_{pn} & \phi_{pp} & \phi_{p} & \phi_{pd} & -\phi_{pd} \\
0 & 0 & \phi_{p} & \phi_{pd} & -\phi_{pd} \\
\phi_{p} & \phi_{p} & \phi_{p} & \phi_{pd} & -\phi_{pd} \\
0 & 0 & \phi_{p} & \phi_{pd} & -\phi_{pd}
\end{pmatrix}$$

(57)

with the corresponding elements of the frequency matrix and the memory functions matrix constructed on the generalized flows $\tilde{I}_{a}(k) = (1 - P_{0})iL_{N}\tilde{a}(k)$, where $\tilde{a}(k) = \{\hat{n}(k), \hat{\phi}(k), \hat{\phi}(k), \hat{\mathbf{d}}(k)\}$. $\phi_{pp} = \eta$ is a normalized viscosity coefficient of ionic melt, $\phi_{dd} = \phi_{d} = D_{-}$ stands for normalized dipole diffusion coefficient of negatively charged ions, $\phi_{jj} = \frac{\omega_{p}^{2}}{4\pi\sigma}$, $\sigma$ means an electroconductivity coefficient of ionic melt, where $\omega_{p}^{2} = \sum_{a} \omega_{a}^{2}$, $\omega_{a}^{2} = 4\pi \frac{n_{a}(Z_{a}e)^{2}}{m_{a}}$ is a squared plasma frequency of ions of species $a$. In the hydrodynamic matrix (57) the elements $\omega_{ls}$ is calculated applying the $|k| \rightarrow 0$ limit in $\omega_{ls}(k)$. Taking into account $\langle \hat{\mathbf{p}}^{+}\hat{\mathbf{p}}^{+} \rangle_{0} = \lim_{|k| \rightarrow 0} \langle \hat{\mathbf{p}}^{+}(k) \hat{\mathbf{p}}^{+}(-k) \rangle_{0} = \frac{n_{+}m_{+}}{\beta}$, $\langle \hat{\mathbf{p}}^{-}\hat{\mathbf{p}}^{-} \rangle_{0} = \lim_{|k| \rightarrow 0} \langle \hat{\mathbf{p}}^{-}(k) \hat{\mathbf{p}}^{-}(-k) \rangle_{0} = \frac{n_{+}m_{+}}{\beta}$, $n_{+} = \frac{N_{+}}{N}$, $n_{-} = \frac{N_{-}}{N}$, are the equilibrium average value of concentrations of negative and positive ions, we find for $\langle \hat{\mathbf{p}}^{+}\hat{\mathbf{p}}^{+} \rangle_{0}$ the following result

$$\lim_{|k| \rightarrow 0} \langle \hat{\mathbf{p}}^{+}(k) \hat{\mathbf{p}}^{+}(-k) \rangle_{0} = \frac{n_{+}m_{+}}{\beta},$$

or $\Phi_{pp} = \langle \hat{\mathbf{p}}^{+}\hat{\mathbf{p}}^{+} \rangle_{0} = \frac{m_{+}}{\beta}$, $m = n_{+}m_{+} + n_{-}m_{-}$ is the equilibrium value of the total mass density of ions of the system. Similarly, one can find $\Phi_{jj} = \langle \hat{\mathbf{j}} \hat{\mathbf{j}} \rangle_{0} = \lim_{|k| \rightarrow 0} \langle \hat{\mathbf{j}}(k) \hat{\mathbf{j}}(-k) \rangle_{0} = \frac{1}{4\pi\beta} \omega_{p}^{2}$. Cross-correlation function is equal to $\Phi_{pj} = \langle \hat{\mathbf{p}} \hat{\mathbf{j}} \rangle_{0} = \lim_{|k| \rightarrow 0} \langle \hat{\mathbf{p}}(k) \hat{\mathbf{j}}(-k) \rangle_{0} = \frac{1}{\beta} (Z_{+}en_{+} + Z_{-}en_{-})$, and taking into account the electroneutrality condition $(Z_{+}en_{+} + Z_{-}en_{-}) = 0$ one can get that $\Phi_{pj} = \Phi_{jp} = 0$. Considering the structure of the normalized static correlation functions $\omega_{ls}$ and values of the averages $\langle \hat{\mathbf{p}}^{+}\hat{\mathbf{p}}^{+} \rangle_{0}$, $\langle \hat{\mathbf{p}}^{-}\hat{\mathbf{p}}^{-} \rangle_{0}$, we find for $\omega_{ls}$ the following results:

$$\omega_{np} = 1, \quad \omega_{pn} = \frac{m_{+}}{\beta} \Phi^{-1}_{mn},$$

$$\omega_{nj} = 0, \quad \omega_{jn} = \frac{\omega_{p}^{2}}{4\pi\beta} \Phi^{-1}_{on},$$

(58)  

(59)
\[ \omega_{\eta \eta} = 0, \quad \omega_{\rho \rho} = \frac{m}{\beta} [\Phi^{-1}]_{\eta \eta}, \]  

(60)

\[ \omega_{\eta j} = 1, \quad \omega_{j \eta} = \frac{\omega_{\rho}^2}{4\pi \beta} [\Phi^{-1}]_{\eta \eta}, \]  

(61)

\[ \omega_{n j} = \omega_{\rho \rho} = 0 \] due to condition of electroneutrality of the system. In the expressions (58)–(61) the quantities \([\Phi^{-1}]_{\eta \eta}, \Phi^{-1}_{\eta \eta}, \Phi^{-1}_{\eta \eta}, \Phi^{-1}_{\eta \eta}\) are the elements of the matrix \(\Phi^{-1}\) inverse to the matrix of static correlation functions.

\[
\Phi = \begin{pmatrix}
\Phi_{\eta \eta} & 0 & \Phi_{\eta \rho} & 0 & 0 \\
0 & \Phi_{\rho \rho} & 0 & 0 & 0 \\
\Phi_{\eta \eta} & 0 & \Phi_{\eta \rho} & 0 & 0 \\
0 & 0 & 0 & \Phi_{\rho \rho} & 0 \\
0 & 0 & 0 & 0 & \Phi_{dd}
\end{pmatrix}.
\]  

(62)

Whereas, \(\Phi_{\eta \eta} = \lim_{|k| \to 0} \Phi_{\eta \eta}(k) = \lim_{|k| \to 0} \{m_+^2 S^{++}(k) + m_+ m_- [S^{+}(k) + S^{-}(k)] + m_- S^{--}(k)\} = m_+^2 S^{++}(0) + m_+ m_- [S^{+}(0) + S^{--}(0)] + m_- S^{--}(0)\), where we use \(S^{++}(k), S^{--}(k), S^{+}(k), S^{-}(k)\) for the partial static structure factors. In particular, \(S^{++}(0) = 1 + n_+ \int dr (g^{++}_2(r) - 1) = \frac{n_+}{\beta} \chi_T^+, S^{--}(0) = 1 + n_- \int dr (g^{--}_2(r) - 1) = \frac{n_-}{\beta} \chi_T^-, \) where \(g^{++}_2(r), g^{--}_2(r), \chi_T^+, \chi_T^-\) are the equilibrium pair distribution functions of ions and their isothermal susceptibilities. Similarly, one can calculate “charge-density” \(\Phi_{\eta \rho}\), “charge-charge” \(\Phi_{\rho \rho}\) correlation functions. We find \(\Phi_{\eta \rho} = Z_+ e [m_+ S^{++}(0) + m_- S^{--}(0)] + Z_- e [m_+ S^{+}(0) + m_- S^{--}(0)], \Phi_{\rho \rho} = (Z_+ e)^2 S^{++}(0) + Z_+ Z_- e^2 [S^{+}(0) + S^{--}(0)] + (Z_- e)^2 S^{--}(0)\).

Then the same way one can obtain the elements \(\omega_{pd}, \omega_{dp}, \omega_{dj}, \omega_{jd}\) of the frequency matrix

\[ \omega_{pd} = \left( \frac{n_+}{\beta} d^- - A(0) \frac{m}{\beta} \right) [\Phi^{-1}]_{dd}, \]  

(63)

\[ \omega_{dp} = \left( \frac{n_+}{\beta} d^- - A(0) \frac{m}{\beta} \right) [\Phi^{-1}]_{pp}, \]  

(64)

\[ \omega_{jd} = \left( \frac{Z_+ e n_+}{\beta} d^- - B(0) \frac{\omega_{\rho}^2}{4\pi \beta} \right) [\Phi^{-1}]_{dd}, \]  

(65)

\[ \omega_{dj} = \left( \frac{Z_- e n_-}{\beta} d^- - B(0) \frac{\omega_{\rho}^2}{4\pi \beta} \right) [\Phi^{-1}]_{jj}, \]  

(66)

where \([\Phi^{-1}]_{dd}\) is the element of the matrix \(\Phi^{-1}\) inverse to \(\Phi\), and \(\Phi_{dd} = \lim_{|k| \to 0} \langle \hat{d}(k) \hat{d}(-k) \rangle_0 \)
In order to obtain the collective excitation spectrum of ionic melt with taking into account polarization properties we will consider the elements $\omega_{ls}$ of the hydrodynamic matrix (57) and do not take into account dynamical cross correlations between flows of momentum, electric current and diffusive dipole flow which are described by the memory functions $\phi_{pd}$, $\phi_{dp}$, $\phi_{jd}$, $\phi_{dj}$. Thereby, the hydrodynamic collective modes can be found as the solution of the equation

$$
\begin{vmatrix}
  z(k) & -ik\omega_{np} & 0 & 0 & 0 \\
  -ik\omega_{pn} & z(k) + k^2\phi_{pp} & -ik\omega_{pj} & k^2\phi_{pj} & -ik\omega_{pd} \\
  0 & 0 & z(k) & -ik\omega_{pj} & 0 \\
  -ik\omega_{jm} & k^2\phi_{jp} & -ik\omega_{jp} & z(k) + k^2\phi_{jj} & -ik\omega_{jd} \\
  0 & -ik\omega_{dp} & 0 & -ik\omega_{dj} & z(k) + k^2D^{--}
\end{vmatrix} = 0.
$$

We will find the solutions as series in wave vector ($k = |\mathbf{k}|$)

$$
z(k) = z_1 k + z_2 k^2.
$$

Thus, one can get the set of equations for evaluation of the coefficients $z_1$ and $z_2$. After calculations we find that collective excitations spectrum contains two acoustic modes

$$
z_{s\pm} = \pm iC_s k - \Gamma_s k^2;
$$

(67)

two charge propagating modes

$$
z_{ch\pm} = \pm iC_{ch} k - \Gamma_{ch} k^2;
$$

(68)

and one diffusive polarization mode, related with dipole diffusion of negatively charged ions

$$
z_d = -D^{--} \frac{C_s^2 C_p^2 - \Lambda_{np}^j \Lambda_{pn}^j}{G} k^2.
$$

(69)

Here, we use the definitions

$$
C_s = \frac{1}{\sqrt{2}} \left[ C^2 + \sqrt{(C^4 - 4G)} \right]^{1/2},
$$

(70)

$$
C_{ch} = \frac{1}{\sqrt{2}} \left[ C^2 - \sqrt{(C^4 - 4G)} \right]^{1/2}
$$

(71)

that are sound and charge waves velocity respectively. $C^2 = C_1^2 + C_2^2 + C_3^2 + C_4^2$, where $C_1^2 = \omega_{np}\omega_{pn}$, $C_2^2 = \omega_{pj}\omega_{jp}$, $C_3^2 = \omega_{dp}\omega_{pd}$ and $C_4^2 = \omega_{dj}\omega_{jd}$. $G = C_1^2 C_2^2 + C_1^2 C_3^2 + C_2^2 C_3^2 - \Lambda_{np}^p \Lambda_{pn}^p - \Lambda_{dp}^j \Lambda_{pd}^j$, where we introduce $\Lambda_{ab}^c = \omega_{ac}\omega_{cb}$, for example $\Lambda_{np}^p = \omega_{np}\omega_{pn}$.
In equations (67)–(68) $\Gamma_s$ and $\Gamma_{ch}$ define the damping coefficients of corresponding waves determined by the relations

$$\begin{align*}
\Gamma_s &= \frac{1}{2} (\phi_{pp} + \phi_{jj} + D--) - \frac{1}{2(C_s^2C_2^2 - 2G)} \left\{ \phi_{pp} \left[ C_s^2 (C_2^2 + C_4^2) - G \right] \\
&\quad + \phi_{jj} \left[ C_s^2 (C_1^2 + C_3^2) - G \right] - D-- \left[ C_s^2 (C_1^2 + C_2^2) - G - C_1^2C_2^2 + \Lambda_{jp}^n\Lambda_{pj}^e \right] \\
&\quad + \phi_{jp} \left( \Lambda_{jp}^d + \Lambda_{jp}^n \right) + \phi_{jp} \left( \Lambda_{pj}^d + \Lambda_{pj}^e \right) \right\}, \\
\Gamma_{ch} &= \frac{1}{2} (\phi_{pp} + \phi_{jj} + D--) - \frac{1}{2(C_{ch}^2C_2^2 - 2G)} \left\{ \phi_{pp} \left[ C_{ch}^2 (C_2^2 + C_4^2) - G \right] \\
&\quad + \phi_{jj} \left[ C_{ch}^2 (C_1^2 + C_3^2) - G \right] + D-- \left[ C_{ch}^2 (C_1^2 + C_2^2) - G - C_1^2C_2^2 + \Lambda_{jp}^n\Lambda_{pj}^e \right] \\
&\quad + \phi_{pj} \left( \Lambda_{jp}^d + \Lambda_{jp}^n \right) + \phi_{jp} \left( \Lambda_{pj}^d + \Lambda_{pj}^e \right) \right\}.
\end{align*}$$

Perturbation theory

In the case when the cross correlations are sufficiently small one can get the simplest analytic expressions for collective modes. In order to do this we use the perturbation theory approach for collective modes developed in papers. Its idea is to present the generalized hydrodynamic matrix as the sum

$$T(k) = T_0(k) + \delta T(k),$$

where the first term corresponds to the “bare” modes that can be easily obtained analytically. The second is considered as perturbation and its contributions into collective modes can be found from the expansion of the perturbation theory

$$z_\alpha = z_\alpha^{(0)} + \delta z_\alpha^{(1)} + \delta z_\alpha^{(2)} + \ldots.$$

The following block matrix corresponds to the “bare” modes of the system

$$T_0(k) = \begin{pmatrix}
0 & -ik\omega_{np} & 0 & 0 & 0 \\
-ik\omega_{pn} & k^2\phi_{pp} & 0 & 0 & 0 \\
0 & 0 & 0 & -ik\omega_{ij} & 0 \\
0 & 0 & -ik\omega_{je} & k^2\phi_{jj} & 0 \\
0 & 0 & 0 & 0 & k^2D--
\end{pmatrix}.$$
Solving the eigenvalue problem in “zero” approximation, we obtain the collective modes spectrum together with the corresponding eigenvectors: two conjugated acoustic modes

\[ z_{s \pm}^{(0)} = \pm ikC_1 - k^2 \Gamma_{s}^{(0)}, \quad x_{s \pm} = \frac{1}{\sqrt{2}} (\pm 1, 1, 0, 0), \]  

(76)

two charge propagating modes

\[ z_{ch \pm}^{(0)} = \pm ikC_2 - k^2 \Gamma_{ch}^{(0)}, \quad x_{ch \pm} = \frac{1}{\sqrt{2}} (0, 0, \pm 1, 1), \]  

(77)

and the diffusive polarization mode, related with dipole diffusion of negative ions

\[ z_{d}^{(0)} = -k^2 D^{--}, \quad x_{d} = (0, 0, 0, 1). \]  

(78)

Here, the corresponding damping coefficients are determined as follows:

\[ \Gamma_{s}^{(0)} = \frac{1}{2} \phi_{pp}, \quad \Gamma_{ch}^{(0)} = \frac{1}{2} \phi_{jj}. \]  

(79)

The cross correlations define the perturbation matrix

\[
\delta T(k) = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & -i k \omega_{pg} & k^2 \phi_{pj} & -i k \omega_{pd} \\
0 & 0 & 0 & 0 & 0 \\
-i k \omega_{jn} & k^2 \phi_{jp} & 0 & 0 & -i k \omega_{jd} \\
0 & -i k \omega_{dp} & 0 & -i k \omega_{dj} & 0 & 0
\end{pmatrix}.
\]  

(80)

Now we can evaluate corrections for collective modes caused by the weak cross correlation. According to\textsuperscript{55,56}, such corrections are equal to zero in the first order in perturbation, while in the second order they are determined by the expression

\[
\delta z_{\alpha}^{(2)} = \sum_{\beta} \frac{\delta T_{\alpha \beta} \delta T_{\beta \alpha}}{z_{\alpha}^{(0)} - z_{\beta}^{(0)}},
\]  

(81)

where \( \beta \) runs over all possible values, except of \( \alpha \) subclass. \( \delta T_{\alpha \beta} \) are the perturbation matrix elements in the representation of matrix \( T_0(k) \) eigenvectors. \( \delta T_{\alpha \beta} = (x_{\alpha} \delta T x_{\beta}) = \sum_{i,j} x_{i,\alpha}^{*} \delta T_{ij} x_{j,\beta} \). After calculation of the necessary elements \( \delta T_{\alpha \beta} \) using the eigenvectors of matrix \( T_0(k) \) and taking into account the results of “zero” approximation (76)–(78) we receive the final expressions for the collective modes. For two acoustic modes we obtain

\[
z_{s \pm} = z_{s \pm}^{(0)} + z_{s \pm}^{(2)} = \pm ikC_1 \left( 1 + \frac{C_3^2}{2C_1^2} \right) - k^2 \left( \Gamma_{s}^{(0)} - \frac{(T_{s}^{(0)} - D^{--})C_3^2}{2C_1^2} \right);
\]  

(82)
for two charge propagating modes

\[ z_{\text{ch} \pm} = z_{\text{ch} \pm}^{(0)} + z_{\text{ch} \pm}^{(2)} \]

\[ = \pm ikC_2 \left( 1 + \frac{C_1^2}{2C_2^2} \right) - k^2 \left( \Gamma_{\text{ch}}^{(0)} - \frac{(\Gamma_{\text{ch}}^{(0)} - D^{--})C_1^2}{2C_2^2} \right) \]  

(83)

and for diffusive polarization mode related with the dipole diffusion of negatively charged ions

\[ z_d = z_d^{(0)} + z_d^{(2)} = -k^2 \left( D^{--} + \frac{(\Gamma_s^{(0)} - D^{--})C_3^2}{2C_4^2} + \frac{(\Gamma_{\text{ch}}^{(0)} - D^{--})C_4^2}{2C_5^2} \right) \].

(84)

One can see, that the acoustic and charge propagating modes calculated within the perturbation theory do not contain their cross-correlation contributions. This fact is caused by the asymmetry of the frequency matrix \( i\tilde{\Omega} \) due to the condition of electroneutrality of the system. Thus, the perturbation theory gives us the compact approximate expressions for the collective modes in which only the cross correlations related with the dipole moment are taken into account. On the other hand, when in expressions (67)–(68), that are explicit in \( k \to 0, \omega \to 0 \) limit we neglect the correlations with the dynamical variable of the dipole moment and the correlations between viscous and charge variables are also considered as small ones, we reproduce the results obtained within “zero” approximation of the perturbation theory (76)–(77).

V. CONCLUSIONS

We presented the statistical description of hydrodynamic processes of ionic melts with taking into account polarization effects caused by deformation of external electron shells of ions. It is implemented by means of the Zubarev nonequilibrium statistical operator method that enables to study both weak and strong nonequilibrium processes. As the result, the nonequilibrium statistical operator and the generalized hydrodynamics equations with taking into account polarization effects are received within the ion-polarization model of ionic melts, when the observable values such as the nonequilibrium averaged values of densities of ionic number \( \hat{n}^a(\mathbf{r}) \), their momentum \( \hat{\mathbf{p}}^a(\mathbf{r}) \), angular momentum \( \hat{\mathbf{s}}^a(\mathbf{r}) \), total energy \( \hat{\varepsilon}(\mathbf{r}) \) along with dipole moment \( \hat{\mathbf{d}}^a(\mathbf{r}) \) are chosen for the reduced description parameters. The generalized molecular hydrodynamics equations for ionic melts with taking into account polarization effects in weakly nonequilibrium case are obtained as well. Based on them within
the viscoelastic approximation for ionic melts in the limit $k \to 0, \omega \to 0$ for the spectrum of collective excitations we found two conjugated acoustic modes, two charge propagating modes and one diffusive mode, related with dipole diffusion of negatively charged ions. These modes where calculated using expansion in wave vector as well as perturbation theory. Here-with, in the limit of infinitesimal cross correlations from (67)–(68) the expressions of “zero” approximation can be reproduced. It is worth to mention that taking into consideration cross correlations described by memory functions $\phi_{pd}, \phi_{dp}, \phi_{jd}$ and $\phi_{dj}$ in both cases will renormalize the damping coefficients in propagating excitations and will not effect the shape of diffusive polarization mode. However perturbation theory yield approximate expressions for collective modes, it can be very useful as well. In particular, it permits to study the time correlation functions built on the basic dynamic variables (48) and investigate contributions caused by polarization effects in it within the generalized collective modes approach. Perturbation theory allow us to easily extend the model to thermoviscoelastic by taking into account the dynamic variable of total energy density in the region of small viscothermal correlations.

Investigations of transport processes in multi-component melts $LiF, BeF_2, ThF_4, UF_4$ for nuclear reactors with the uranium cycle and the melts $NaF, BeF_2, LiF, ZrF_4, Li_2BeF_4$ for the uranium and plutonium fuels are of great interest within the presented approach.

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