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NON-LOCAL EQUATION OF STATE: CRITICAL PHENOMENA AND COLLECTIVE EXCITATIONS

Non-local properties of the thermal equation of state of a fluid system are observed for the wide range of changes of thermodynamic parameters. Density profiles of a fluid, which are constructed by the non-local equation of state, show that significant changes of system's density occur in a significant part of the volume in the case of approaching the critical liquid-vapor point. The application of the non-local thermal equation of state as a closure of the equations of classical hydrodynamics allowed us to obtain the spectrum of collective excitations which is similar to the spectrum of excitations in liquid helium.

Keywords: equation of state, non-local properties, collective excitations.

1. Introduction

An opportunity to make the quantitative description of uniform liquid systems is an important result of the statistical physics in recent years [1]. The Gibbs thermodynamic potential G and the Helmholtz free energy F are the most convenient quantities for the thermodynamic consideration of this issue. However, according to the numerous experiments, any real liquid systems are non-uniform ones due to the influence of limiting surfaces, as well as due to the influence of external fields. The heterogeneity caused by the presence of walls and obtained in the process of calculation of the thermodynamic properties of real systems is considered quite localized in the domain, where surface forces act. For this reason the marginal non-uniformity can be neglected in the calculations of bulk properties of sufficiently large systems. The heterogeneity caused by the presence of a gravitational field for molecular distances is small enough in most cases. Therefore, the fluid is considered as a system composed of uniform subsystems with different

intensive parameters. Both approximations allow one to calculate the properties of thermodynamic systems within the range of permissible errors. However, according to some experimental results, the mentioned approach does not allow one to make a satisfactory description of the experiment in some cases – for example, in the case of an external field that varies in space or in the vicinity of the critical points [2–4]. Due to this reason, in order to describe the properties of the real system, its non-uniformity must be taken into account. In general, the free energy of a non-uniform system is no longer a function of the variables T and n . It is a functional $F = N F [T(\mathbf{r}), n(\mathbf{r})]$ of functions of the spatial coordinates \mathbf{r} : $T(\mathbf{r})$ and $n(\mathbf{r})$. The calculation of physical quantities' spatial distribution using a statistical operator is an extremely difficult task in this case [5]. Therefore, the behavior of the system is usually considered under the local approximation. Using this approach, the system might be regarded as one that consists of “physically small” cells – space regions that are sufficiently small to be considered uniform, and the thermodynamics of uniform systems can be applied to each of these small space regions. Moreover, the mentioned “physically small”

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cells contain enough particles to have an opportunity to use the thermodynamics methods to describe them. The density of the corresponding potential, for example, the free energy density $f(\mathbf{r})$, is introduced to calculate the behavior of the system in an external field [6]:

$$F = \int_V d\mathbf{r} f(n(\mathbf{r})). \quad (1)$$

In this case, the free energy is a function of T and n , but those, in turn, are functions of the coordinates \mathbf{r} . Within this approach, the relationship between the chemical potential $\mu(\mathbf{r})$ of a heterogeneous liquid system and the external field $u(\mathbf{r})$ is described by the well-known expression:

$$u(\mathbf{r}) = \mu_0 - \mu(\mathbf{r}), \quad (2)$$

where μ_0 – chemical potential of a uniform system. But, as noted in [7], this approach is useful just for the areas of changes of thermodynamic parameters far from the limit of the system stability. Due to this reason, the possibility of introducing a local free energy density in the immediate vicinity of the critical point requires a separate consideration. The introduction of the densities of thermodynamic potentials for heterogeneous systems was considered in [8]. In particular, the obtained expression for the entropy S can be presented in the form of a series [9]:

$$\begin{aligned} TS = TS_0 - \frac{kTN}{V} \int_V d\mathbf{r}_1 F_1(\mathbf{r}_1) \ln F_1(\mathbf{r}_1) + \\ + 2 \frac{kTN(N-1)}{2V^2} \int_V d\mathbf{r}_1 \ln F_1(\mathbf{r}_1) \int_V d\mathbf{r}_2 F_2(\mathbf{r}_1, \mathbf{r}_2) - \\ - \frac{kTN(N-1)}{2V^2} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 F_2(\mathbf{r}_1, \mathbf{r}_2) \ln F_2(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (3)$$

Here, S_0 – the entropy of an ideal gas, $F_1(\mathbf{r}_1)$ and $F_2(\mathbf{r}_1, \mathbf{r}_2)$ – partial distribution functions of the non-uniform system of the first order and the second one, respectively.

According to the analysis of expression (3) in [8], the entropy can be represented as the integral of a function far from the critical point, where the function $F_2(\mathbf{R}, \mathbf{r})$ is short-range. However, with approaching the critical point, the correlation functions become long-range, and the integration of the last

term of expression (3) of the inner integral gives a function that has the infinite range of its action (in the case of unlimited systems) or the range reaching a characteristic size L of the system. For this reason, the entropy cannot be represented in the form of a volumetric integral of a local function in the vicinity of the critical point. Consequently, the concept of appropriate spatial density cannot be introduced for the Helmholtz free energy and thermodynamic Gibbs potential near the critical point. This leads to the consequence that the regarded system no longer has local properties, but has the properties peculiar to the whole system. Sufficiently far from the critical point, the susceptibility of any system to external fields is small, so they have little effect on the physical properties of the system. Moreover, the susceptibility of the system to external fields tends to infinity with approaching the critical point. In this case, the sharp spatial distribution of the physical properties of a substance, including the liquid density or concentration and density of a solution in a gravitational field (gravitational effect), is generated by external forces [10, 11]. The further development of the theoretical approach has been associated with the construction of a consistent theory of the fluid density $n(\mathbf{r})$ as a functional $\mu(\mathbf{r})$. According to the free energy density functional method, the evaluation of the local density profile $n(\mathbf{r})$ in an external field $u(\mathbf{r})$ requires one to solve the task of a free energy minimization, considering it to be a function of the functional $n(\mathbf{r})$ [12]. An expression for the free energy density $f(\mathbf{r})$ of fluids as a density functional was obtained by J.W. Cahn and J. Hilliard in the smooth inhomogeneity approximating [13]:

$$f(\mathbf{r}) = f_0(n(\mathbf{r})) + \frac{A}{2} [\nabla n(\mathbf{r})]^2 + (u(\mathbf{r}) - \mu(\mathbf{r})) n(\mathbf{r}), \quad (4)$$

where $f_0(n(\mathbf{r}))$ – the free energy density in the local approximation, $A = \xi^2 / \chi$, ξ – the correlation radius and $\chi = \left(\frac{\partial \mu}{\partial n}\right)_T$ – compressibility.

For the construction of a consistent thermodynamic theory, which will describe the behavior of one-component heterogeneous system, the fundamental approach based on the calculation of the contribution of each layer between equipotential surfaces not in the corresponding thermodynamic potentials, but in the Hamiltonian of the system was proposed [15]. In this case, expression (5) should be taken instead of (2):

$$u(\mathbf{r}) = \mu_0 - \mu(\vec{r}) + \Delta\mu_{\text{cor}}(\mathbf{r}), \quad (5)$$

where $\Delta\mu_{\text{cor}}$ – the contribution of correlation effects for which the following expression in the form of an infinite series was obtained:

$$\begin{aligned} \frac{1}{kT}\Delta\mu_{\text{cor}}(\mathbf{r}) &= \frac{1}{2}\nabla^2\Delta n(\mathbf{r})\int_V d\mathbf{r}_1 C_2(\mathbf{r},\mathbf{r}_1)(\mathbf{r}_1-\mathbf{r})^2 + \\ &+ \frac{1}{2}(\nabla\Delta n(\mathbf{r}))^2\int_V d\mathbf{r}_1\int_V d\mathbf{r}_2 C_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)(\mathbf{r}_1-\mathbf{r})\times \\ &\times(\mathbf{r}_2-\mathbf{r}) + \nabla\Delta n(\mathbf{r})\left\{\int_V d\mathbf{r}_1 C_2(\mathbf{r},\mathbf{r}_1)(\mathbf{r}_1-\mathbf{r}) + \right. \\ &\left. + \Delta n(\mathbf{r})\int_V d\mathbf{r}_1\int_V d\mathbf{r}_2 C_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)(\mathbf{r}_1-\mathbf{r})\right\} + \dots \quad (6) \end{aligned}$$

In this expression, $C_2(\mathbf{r},\mathbf{r}_1)$ and $C_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)$ are direct correlation functions of the second order and the third one, respectively, and T is system’s temperature.

This non-local equation of state can be used, for example, for calculating the density profile and the concentration of a binary solution in a wide range of variation of the thermodynamic variables, including the neighborhood of the critical points of evaporation or stratification, as well as for obtaining the spectrum of collective excitations in the liquid by means of classical hydrodynamics.

2. Distribution of the Concentration of a Binary Solution Near the Critical Point of Stratification

To illustrate the application of the obtained expressions – nonlocal equation of state – we will evaluate the distribution of the first component concentration $\Delta x(z)$ of a binary solution in a non-ideal pore (pore, in which it is impossible to ignore the influence of forces at the wall surface) in the gravitational field near the critical point of stratification. Let us consider the case where the system includes an infinite flat-parallel pore (layer) $2L$ in thickness. The forces of the gravitational field are directed along the z direction (axis z is normal to the pore-limiting surfaces). The potential of these forces can be written in form:

$$\begin{aligned} u_A(z) &= -m_{0A}gz, \\ u_B(z) &= -m_{0B}gz, \end{aligned} \quad (7)$$

where $u_A(z)$ and $u_B(z)$ – potential of the gravity field acting on particles of A and B types, respectively, m_{0A} and m_{0B} – mass of particles of A and B

types, respectively, and g – gravity acceleration. In addition, near the walls, there are forces of attraction (repulsion), whose potential has an exponential form and can be written as

$$\begin{aligned} u_A(z) &= B_{A1}e^{-k(L+z)} + B_{A2}e^{-k(L-z)} = \\ &= (B_{A1} + B_{A2})e^{-kL}\text{ch } kz + (B_{A1} - B_{A2})e^{-kL}\text{sh } kz, \\ u_B(z) &= B_{B1}e^{-k(L+z)} + B_{B2}e^{-k(L-z)} = \\ &= (B_{B1} + B_{B2})e^{-kL}\text{ch } kz + (B_{B1} - B_{B2})e^{-kL}\text{sh } kz, \end{aligned} \quad (8)$$

where B_{A1} (B_{B1}) and B_{A2} (B_{B2}) – amplitudes of exponential surface potentials at the left ($z = -L$) and right ($z = L$) borders of the system for components A and B , respectively, and k – parameter of the exponential decay potential.

Solving Eq. 5, we obtain the profile of a binary solution in the form [21]:

$$\begin{aligned} \Delta x(z) &= -A m_{0BA}g\left(\frac{1}{\kappa\text{ch } \kappa L} - z\right) - \\ &- A(B_{BA1} + B_{BA2})e^{-kL}\frac{k}{\kappa}\frac{1}{k^2 - \kappa^2}\frac{\text{sh } kL}{\text{sh } \kappa L}\text{ch } \kappa z - \\ &- A(B_{BA1} - B_{BA2})e^{-kL}\frac{k}{\kappa}\frac{1}{k^2 - \kappa^2}\frac{\text{ch } kL}{\text{ch } \kappa L}\text{sh } \kappa z + \\ &+ A(B_{BA1} + B_{BA2})e^{-kL}\frac{1}{k^2 - \kappa^2}\text{ch } kz + \\ &+ A(B_{BA1} - B_{BA2})e^{-kL}\frac{1}{k^2 - \kappa^2}\text{sh } kz + \\ &+ A(B_{BA1} + B_{BA2})e^{-kL}\frac{1}{k\kappa^2 L}\text{sh } kL. \end{aligned} \quad (9)$$

where $B_{BA1} = B_{B1} - B_{A1}$, $B_{BA2} = B_{B2} - B_{A2}$, $A = A(\xi)$ – value depending on the parameters of the critical point of a solution, and $k = \frac{1}{\xi}$.

The spatial distribution of the concentration of a binary model solution $\Delta x(z)$ for different values of the correlation radius ξ and a fixed value m_{0BA} for systems with different values of constants B_{BA1} and B_{BA2} is shown in Figs. 1 and 2. From the analysis given above, the concentration profiles give evidence that if the system is sufficiently far from the critical point, the concentration profiles are determined exclusively by the external gravitational field at any constant values of B_{BA1} and B_{BA2} . The local approximation in this case also leads to the emergence of concentration profiles that match the density profile of the system with ideal walls and are determined by the presence of the gravitational field only. The

existence of the walls in this case leads to a deformation of the profiles on the boundaries of the system at the distances, where the wall surface forces effectively act, i.e. these effects cannot be observed experimentally at the present time. The spatial distributions shown in Figs. 1 and 2 indicate that, in the middle of the system (in the layer bounded by the planes with coordinates $z \approx \pm 0.3L$), the gravitational field leads to minor ($\approx 2\%$) concentration variations that, by sign, match the ones calculated in the local approximation. A significant deviation occurs near the walls of the system with the value of the deviation being determined only by the intensity of the wall potential [14]. Furthermore, the analysis of data indicates that, although the overall behavior of the system is determined by the concentration of the gravitational field (solution concentration increases with coordinates), the distribution of the concentration throughout the volume of the system significantly deviates from the classical gravitational effects, especially near the walls.

So, in general, the presence of imperfect walls leads to the fact that the concentration profiles are losing properties of a coordinate odd function that must be considered in the experimental study of the critical properties of the fluid and in the calculation of the corresponding critical amplitudes in the scaling equations [16]. In addition, such walls substantially change the spatial distribution of the concentration gradient, which should influence the results of experiments on the scattering of light and neutrons in the vicinity of the critical point of separation.

3. Thermodynamic Theory of Collective Excitations in Classical Liquids

Consider the collective excitations in the fluid in terms of the classical equations of hydrodynamics. We note that the experimental studies by means of the neutron scattering in atomic, molecular and ion-electron (liquid metals) liquids made in the 1960s–1970s gave evidence on the existence of the spectrum of collective excitations of the phonon and roton types, the explicit form of which is given on Fig. 3. Before that, it was considered that the spectrum of this kind is typical not of classical liquids [17], but exclusively of quantum liquids, in particular of liquid helium. But in the 1970s, the quantum-mechanical calculations in [18] have shown that the spectrum of this kind really corresponds to the collective mo-

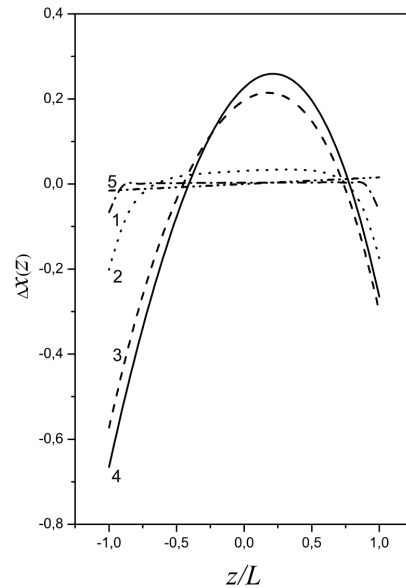


Fig. 1. Spatial distribution of the concentration $\Delta x(z)$ of a binary solution in a flat non-ideal pore in the gravitational field for the the system with $L = 10^{-5}$ m, $k^{-1} = 3 \times 10^{-10}$ m, $B_{BA1} = 10^{-24}$ J, $B_{BA2} = 10^{-24}$ J, $C_1 = 2 \times 10^5$, $C_2 = 0$, at different values of ξ : 1 – 10^{-7} , 2 – 10^{-6} , 3 – 5×10^{-6} , 4 – 10^{-5} , 5 – local approximation

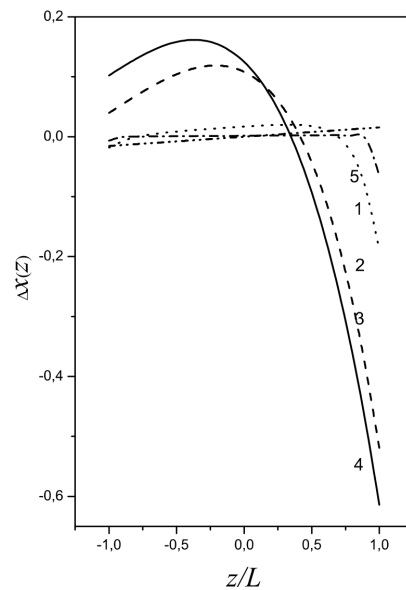


Fig. 2. Spatial distribution of the concentration $\Delta x(z)$ of a binary solution in a flat non-ideal pore in the gravitational field for the system with $L = 10^{-5}$ m, $k^{-1} = 3 \times 10^{-10}$ m, $B_{BA1} = 10^{-24}$ J, $B_{BA2} = 10^{-24}$ J, $C_1 = 2 \times 10^5$, $C_2 = 0$, at different values of ξ : 1 – 10^{-7} , 2 – 10^{-6} , 3 – 5×10^{-6} , 4 – 10^{-5} , 5 – local approximation

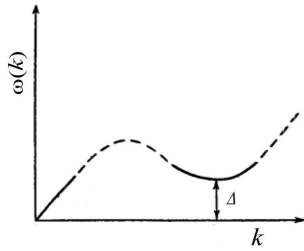


Fig. 3. Landau energy spectrum of elementary excitations [19]

tions in non-quantum liquids (argon, lead, classical helium). In those works, the quantum calculations were made by means of two-time Green functions in the quasiharmonic approximation. This approximation corresponds to the description of a phonon in the self-consistent field of other phonons. The drawback of the calculations made is that the averaging by the probabilities of coordinates of two particles was made twice. In order to study the collective excitations in liquids, an unproblematic hydrodynamic approach was proposed. This method has no above-mentioned drawback because there is no averaging with the radial distribution function. Instead, the non-local equation of state of non-uniform system is used.

Let us consider the hydrodynamic continuity equations and the Euler equation for a one-component liquid [20]:

$$\begin{cases} \frac{\partial \rho}{\partial t} = -\text{div } \rho \mathbf{v}, \\ \rho \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \text{ grad}) \mathbf{v} \right) = -\text{grad } p. \end{cases} \quad (10)$$

Using (10), let us consider the dynamics of density fluctuations in the regarded system. In order to do it, we will represent the time-spatial variables of local density, velocity, and pressure in the following form:

$$\begin{aligned} \rho(\mathbf{r}, t) &= \rho_0 + \rho_1(\mathbf{r}, t), \\ \mathbf{v}(\mathbf{r}, t) &= \mathbf{v}_0 + \mathbf{v}_1(\mathbf{r}, t), \\ p(\mathbf{r}, t) &= p_0 + p_1(\mathbf{r}, t), \end{aligned} \quad (11)$$

where $\rho_0, v_0,$ and p_0 – density, velocity, and pressure of a system without the fluctuations, which are, in this case, considered to be constants. By $\rho_1, v_1,$ and $p_1,$ we denote the fluctuations of these variables, which will be considered small and dependent on both spatial and time variables:

$$\left| \frac{\rho_1}{\rho_0} \right| \ll 1, \quad \left| \frac{p_1}{p_0} \right| \ll 1. \quad (12)$$

In the case where there are no fluctuations, v_0 is equal to zero. Then the elementary excitations are regarded in terms of classical hydrodynamics as fluctuations of the density. Substituting (11) into (10) and keeping only the terms linear in fluctuations, we get a system of linearized hydrodynamic equations, which describe the dynamics of fluctuations:

$$\begin{cases} \frac{\partial \rho_1}{\partial t} = -\text{div}(\rho_0 \mathbf{v}_1), \\ \frac{\partial(\rho_0 \mathbf{v}_1)}{\partial t} = -\nabla p(\mathbf{r}). \end{cases} \quad (13)$$

Differentiating the first equation with respect to the time and acting by the divergence operator on the second one, we get

$$\frac{\partial^2 \rho_1}{\partial t^2} = \nabla^2 p_1. \quad (14)$$

In order to build the solution of the incomplete system of classical hydrodynamic equations, in particular, Eq. (13), the ordinary local equation of state of a uniform finite system at fixed density and temperature is used:

$$p = p(\rho, T). \quad (15)$$

In the case of fixed density ρ and entropy $S,$ we can use another equation of state:

$$p = p(\rho, S). \quad (16)$$

In the local case, the variation of the pressure is given by the expressions:

$$\delta p = \left(\frac{\partial p}{\partial \rho} \right)_T \delta \rho, \quad (17)$$

$$\delta p = \left(\frac{\partial p}{\partial \rho} \right)_S \delta \rho. \quad (18)$$

Regarding the shape of acoustic waves at small magnitudes of the wave vector, it becomes clear that Eq. (17) or (18) can be used. In this case, we get $\omega(k) = c_s k$ for the dispersion curve, where c_s is the adiabatic sound velocity.

Alongside with the transition to high-frequency acoustic waves, the wavelength in a classical liquid may decrease from meters to nanometers, which causes an increase of the density gradient by nine orders. It is obvious, that, in this case, the local equations (15)–(18) cannot be used, and it is required

to regard the pressure not as a function of the density, but as a functional of the whole density curve [21, 22]. It is the usage of the non-local dependence between $\delta p(\mathbf{r})$ and $\delta \rho(\mathbf{r}')$, where \mathbf{r}, \mathbf{r}' – spatial coordinates. Hence, the classic hydrodynamic equations give the opportunity to calculate the spectrum of collective excitations qualitatively similar to Fig. 4.

In this case of large values of the density gradient, Eqs. (17) and (18) should be replaced by

$$\delta \rho(\mathbf{r}) = \int G(\mathbf{r} - \mathbf{r}') \delta p(\mathbf{r}') d\mathbf{r}', \quad (19)$$

where $G(\mathbf{r} - \mathbf{r}')$ – a binary correlation function with the δ -singularity defined in the corresponding ensemble or in the k -space

$$\delta \rho_1(k) = G(k) \delta p(k) = (a + bk^2 + ck^4 + \dots) \delta p, \quad (20)$$

where a, b, c – correlation function moments of the 0th, 2nd, and 4th order, correspondingly:

$$\begin{aligned} a &= 4\pi \int_0^\infty G(r) r^2 dr = \left(\frac{\partial p}{\partial \rho} \right)_s, \\ b &= \frac{4\pi}{2!} \int_0^\infty G(r) r^4 dr, \\ c &= \frac{4\pi}{4!} \int_0^\infty G(r) r^6 dr. \end{aligned} \quad (21)$$

In the case of small k , Eq. (21) allows evaluating the sound dispersion law in the standard form:

$$\omega^2 = \beta_S^{-1} \rho k^2. \quad (22)$$

In the general case in view of the non-locality of the equation of state, the dispersion relation can be presented in a more complicated form:

$$\omega^2 = \frac{k^2}{a + bk^2 + ck^4 + \dots}. \quad (23)$$

The dispersion relation (23) is valid in the case where the reciprocal value of the absolute value of the wave vector k is larger than the effective distance, on which the external field changes (and as a consequence, system's local density changes as well) [3].

Under the condition $c = 0$ the dispersion curve has a form presented in Fig. 4. With regard for the 4th moment of the correlation function c , the dispersion curve has a form given in Fig. 5. Thus, considering

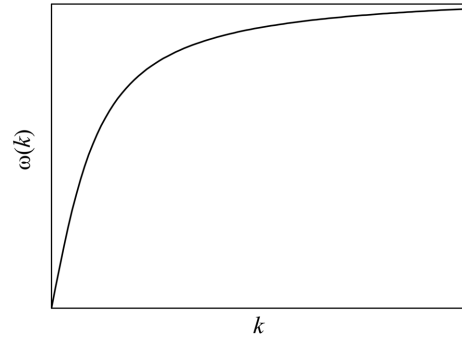


Fig. 4. Dependence $\omega(k)$ in the case where the fourth moment of the correlation function is zero, as well as all aspects of higher order for classical fluids

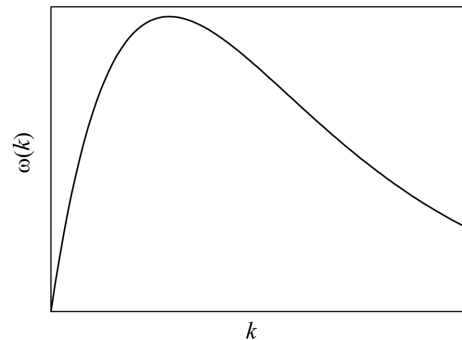


Fig. 5. Dependence $\omega(k)$ in the case where the sixth moment of the correlation function is zero, as well as all aspects of higher order for classical fluids

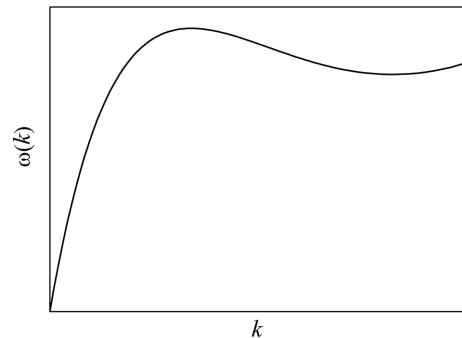


Fig. 6. Dependence $\omega(k)$ of classical fluids provided vanishing eighth time correlation functions, as well as all aspects of a higher order, the sixth moment is negative

the 6th moment of the correlative function, we get the dispersion curve shown in Fig. 6, which is qualitatively similar to the dispersion curve of helium in Fig. 3.

The proposed method of the description of the phonon spectrum of liquid systems is similar to the

one proposed by L.D. Landau and E.M. Lifshitz and used to get the spectrum of magnons in magnetic materials. They constructed the phenomenological (“hydrodynamic”) Landau–Lifshitz equations that describe the local magnetization of the system, $\mathbf{M}(\mathbf{r})$, in the external magnetic field $\mathbf{H}(\mathbf{r}')$ and the non-local connection between $\mathbf{M}(\mathbf{r})$ and $\mathbf{H}(\mathbf{r}')$ is used [23].

4. Conclusion

The usage of the non-local equation of state, the theory of which was developed to study the spatial distribution of the density and concentration of binary solutions, leads to the conclusion that this spatial distribution caused by the presence of the external field in the case of spatially limited systems strongly depends on the geometry and size of the system. Moreover, the different nature of the walls of a container causes significant deflections of the concentration found in the local approximation. This influences, in turn, the values of critical amplitudes calculated with regard for experimental results. The non-local equation of state makes a closure of the classical hydrodynamic equations and allows one to evaluate a spectrum of collective excitations in liquid systems, which is similar to the one of liquid helium obtained earlier in the frame of quantum statistics.

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НЕЛОКАЛЬНЕ РІВНЯННЯ СТАНУ: КРИТИЧНІ ЯВИЩА ТА КОЛЕКТИВНЕ ЗБУДЖЕННЯ

Показано, що в широкому інтервалі зміни термодинамічних параметрів термічне рівняння стану рідинної системи набуває нелокальних властивостей. Побудовані на основі нелокального рівняння стану профілі густини рідини дозволяють визначити, що при наближенні до критичної точки рідина–пара суттєва зміна густини системи має місце у значній частині об’єму. Застосування нелокального термічного рівняння стану для замикання рівнянь класичної гідродинаміки дозволяє одержати спектр колективних збуджень, подібний до спектра збуджень у рідинному гелії.

Ключові слова: рівняння стану, нелокальні властивості, колективне збудження.