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# Heat capacity and the number of instantaneous-normal modes of a simple liquid

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In the last decade, approaches to calculating the thermal properties of liquids have been actively developing. The most developed approaches are those based on the use of the „phonon“ theory, which was previously successfully applied to calculate the thermal properties of solids. The „phonon“ theory is based on the hypothesis that in addition to longitudinal acoustic waves of a wide range of frequencies, transverse high-frequency acoustic waves can propagate in a liquid. To find the heat capacity of a liquid, the Debye approach is used, which was modified by taking into account only high-frequency transverse waves in the excitation spectrum. Another approach is based on finding the frequency distribution of normal modes (instantaneous-normal modes) in a liquid and constructing the thermal and transport properties of the liquid using the found frequencies. In this paper, the equivalence of both approaches is shown in the harmonic approximation, and a simple one-parameter approximation formula is proposed for calculating the isochoric heat capacity of simple liquids.

**Keywords:** properties, heat capacity, instantaneous-normal modes, transverse waves, „phonon“ theory of liquid.

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## Introduction

The behavior of the molar isochoric heat capacity for simple solids is well described by the Debye model, which predicts a cubic increase of heat capacity at low temperatures $C_V \sim T^3$ and reaching a constant value corresponding to Dulong–Petit law $C_V = 3R$ at high temperatures. A monotonous decrease of heat capacity with the increase of temperature is experimentally observed in case of a simple liquid, for example, liquid metals, which is not the case for a solid (see, for example, [1] and Fig. 1 and 2). One of the urgent tasks today is to explain this behavior of the isochoric heat capacity of a liquid and to obtain analytical relations for predicting the dependence of heat capacity on temperature.

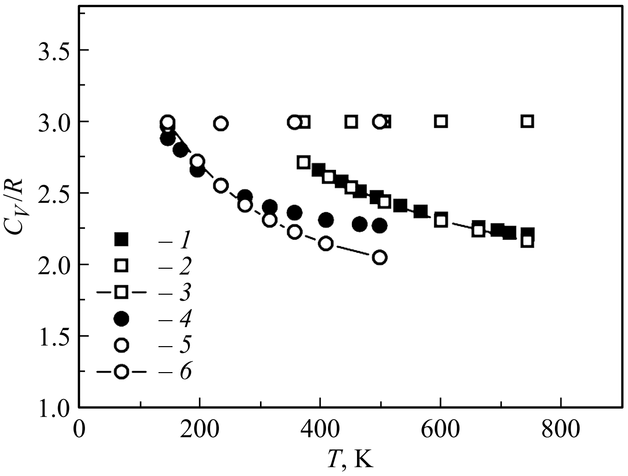

**Figure 1.** Heat capacity Xe: *1* — experimental data from Ref. [15], *2* — calculation according to formulas proposed in Ref. [15] (formulas (7)–(10)), *3* — calculation using the formula (23) with $U = 226.1\,\text{K}$ from Ref. [15] and $\alpha = 0.17$. Heat capacity Ar: *4* — experimental data from Ref. [15], *5* — calculation according to formulas proposed in Ref. [15] (formulas (7)–(10)), *6* — calculation using the formula (23) with $U = 116.7\,\text{K}$ from Ref. [15] and $\alpha = 0.18$.

## 1. Current state of research

Recently, significant progress has been made in the theoretical study of the thermal properties of liquids, which was largely attributable to a series of papers by Trachenko, Brazhkin and Bolmatov et al. [2–5]. In some of their papers, the authors proposed to modify Debye's approach with the hypothesis that in addition to longitudinal acoustic waves, transverse waves can also propagate in a liquid, but with frequencies greater than a certain boundary frequency $\omega_f$, called the Frenkel frequency:

$$\omega_f(T) = 2\pi/\tau_f.$$

Here $\tau_f$ is the relaxation time [6] equal to the characteristic time of the settled life of an atom in a liquid:

$$\tau_f = \mu(T)/G_\infty, \tag{1}$$

where $\mu$ is the dynamic viscosity of the liquid, $G_\infty$ is the shear modulus for waves with frequency tending to infinity.

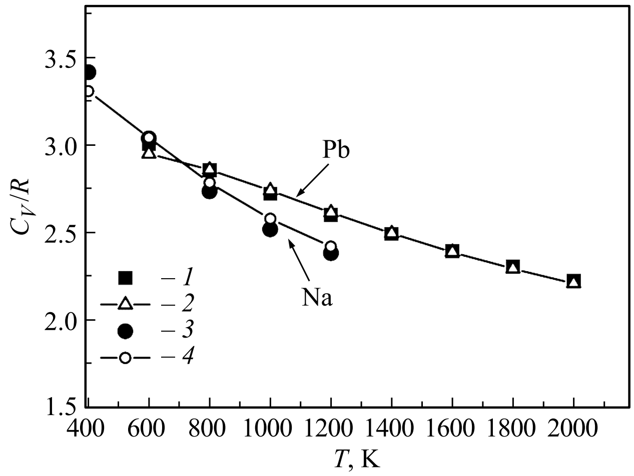

**Figure 2.** Comparison of heat capacity experimental data with approximation formula for sodium and lead from melting point to boiling point at $P = 1.01 \cdot 10^5$ Pa. *1* — experimental data for lead [26,27]; *2* — calculation according to (23) for lead, $U = 1069$ K from Ref. [27], $\alpha = 0$; *3* — experimental data for sodium [28]; *4* — calculation according to (23) for sodium, $U = 557$ K from Ref. [28], $\alpha = 0.15$.

When deriving the formula for heat capacity, the authors of Ref. [2] presented the total energy of the liquid as the sum of the energy of longitudinal acoustic waves $E_l$, the energy $E_t$ of transverse waves with frequencies greater than $\omega_f$, and the energy associated with diffusive motion of atoms $E_d$:

$$E = E_l + E_t(\omega > \omega_f) + E_d.$$

It was shown that the energy of the diffusion motion of atoms is equal to half the total energy of phonons corresponding to transverse waves with frequencies $\omega \le \omega_f$:

$$E_d = (E_t(\omega \le \omega_f)/2.$$

It should be noted that the representation of total energy as the sum of the energies of longitudinal and transverse waves and the energy associated with the diffusive motion of atoms is controversial, since the first two terms relate to processes occurring in momentum space ($\omega$, $\mathbf{k}$), and the last term pertains to processes in the coordinate space ($t$, $\mathbf{r}$). Such separation requires an additional substantiation.

The authors of Ref. [2] obtained the following final expression for the internal energy:

$$E = Nk_BT(1 + 0.5\alpha_T T)\big(3D(\hbar\omega_D/k_B/T) - (\omega_f/\omega_D)^3 D(\omega_f/\omega_D)\big), \tag{2}$$

where $\alpha_T$ — a coefficient equal in order to the coefficient of volumetric thermal expansion and taking into account the anharmonic contribution, $\omega_D$ — Debye frequency, $D(x)$ — Debye function close to unity with a small value of parameter $x = \hbar\omega_D/k_B/T$ (at high temperatures). One of the disadvantages of the formula is the presence of three parameters $\alpha_T$, $\omega_D$, $G_\infty$. (a part of the expression for $\omega_f$), which should be selected based on the conditions of the best match between the calculation formula and the experimental results.

The following equation can be obtained for the internal energy from (2) in the harmonic approximation (without taking into account the anharmonic correction $\alpha_T T/2$)

$$E = Nk_BT\big(3 - (\omega_f/\omega_D)^3\big). \tag{3}$$

The authors of Ref. [2–5] explain the monotonous decrease of heat capacity with the increase of the temperature by a decrease of the number of transverse waves due to an increase of the boundary frequency $\omega_f = 2\pi/\tau_f$, below which transverse waves cannot exist (the presence of a gap in the energy spectrum for transverse waves). At the maximum value of $\omega_f = \omega_D$, the heat capacity tends to its minimum value

$$C_V = 2NkB. \tag{4}$$

The line where $\omega_f = \omega_D$ was named the Frenkel line [7]. The question of the reality of the existence of this line and the minimum value of the heat capacity (4) is debatable [8,9].

The presence of a boundary wavenumber $k_g$ for transverse waves was shown for ordinary temperatures and pressures [8,10] and, as a result, a gap in the space of wavenumbers was demonstrated. No boundary frequency was detected.

A justification for the presence of a gap was given in later papers [11–13] based on the viscoelastic theory and the formula was derived (3) [14] using the dispersion relation for transverse waves

$$\omega^2 + \omega\tau_f^{-1} - c_t^2k^2 = 0, \tag{5}$$

, from which for transverse waves with wave vectors outside the gap ($k > k_g$) $\omega = \sqrt{c_t^2k^2 - \tau_f^{-2}}$, and for waves inside the gap ($k \le k_g$) $\omega = -(2\tau_f)^{-1} \pm \sqrt{(4\tau_f)^{-2} - c_t^2k^2}$.

Here

$$k_g = (c_t\tau_f)^{-1}, \tag{6}$$

where $c_t$ is the speed of sound for transverse waves.

Another area of analysis of the thermal properties of a liquid is analysis using the concepts of instantaneous normal modes developed in Ref. [15–22]. A relation is proposed in Ref. [15,16] for calculating the heat capacity of a liquid based on the derived ratio for the normalized density of instantaneous-normal modes:

$$g_{INM}(\omega) = C(\omega^2 + \Gamma^2(T))^{-1}\omega \cdot \exp(-\omega^2/\omega_D^2), \tag{7}$$

$$\Gamma(T) = \Gamma_0 \exp(-U/T), \tag{8}$$

$$C_V = k_B \int_0^\infty (\hbar\omega/2k_BT)^2 \operatorname{sh}^{-2}(\hbar\omega/2k_BT) g_{INM}(\omega)d\omega. \tag{9}$$

It was shown in Ref. [15] that the results of calculation of the heat capacity according to the proposed formulas are consistent with experimental data. However, the authors suggest using normalization for $g_{INM}(\omega)$ in their article to find the multiplier $C$ [15]

$$\int_0^\infty g_{INM}(\omega)d\omega = 3N. \tag{10}$$

This normalization at high temperatures leads to Dulong–Petit law:

$$C_V = 3Nk_B, \tag{11}$$

what was noted in the article [23] and what is inconsistent with the results of the calculation of the heat capacity given by the authors themselves in Ref. [15]. Indeed, Fig. 1 shows a comparison of data on heat capacity for liquefied gases from Ref. [15] with the results of calculations according to formulas (7)–(10) which were used for calculations, as stated in Ref. [15]. The figures show that the use of normalization (10) does not allow obtaining the necessary behavior of the heat capacity. In fact, the predicted value of the molar heat capacity is $C_V = 3R$. Changing the normalization to $3/2$, as recommended in Ref. [17], does not correct the situation, but only results in the shift of results from level 3 to level $3/2$.

Apparently, the authors did not perform normalization to find the parameter $C$, but adjusted the coefficient $C$ based on the results of experimental studies.

Despite this, the authors in this paper tried to apply a different approach to the problem of heat capacity compared to Ref. [2–5]— using the concepts of instantaneous-normal modes.

## 2. The relationship between internal energy and the number of stable instantaneous normal modes

Let us take a closer look at the concept of instantaneous-normal modes. To do this, let us decompose the potential energy of the system $N$ of interacting particles up to and including the second term in a series by atomic displacements.:

$$U = \Big[\sum_i U(R_{i0}) + \partial U/\partial R_i \cdot (R_i - R_{i0})$$

$$+ 0.5 \cdot \partial^2 U/\partial R_i \partial R_j)(R_i - R_{i0})(R_j - R_{j0})\Big].$$

Here $R_i$ are the coordinates of the particles of the system, $R_{io}$ are the coordinates of the particles in the equilibrium position. Let us introduce the notation $\partial^2 U/\partial R_i \partial R_j = D_{ij}$, $\sum_i U(R_{i0}) = U_0$ and take into account that $\partial U/\partial R_i = 0$.

The internal energy of the system consists of the sum of kinetic and potential energies:

$$E = U_0 + \sum\nolimits_i \frac{m\dot{R}_i^2}{2} + \sum\nolimits_{i,j} \frac{1}{2} D_{ij}(R_i - R_{i0})(R_j - R_{j0})$$

$$= U_0 + \sum\nolimits_i \frac{m\dot{r}_i^2}{2} + \sum\nolimits_{i,j} \frac{1}{2} D_{ij} r_i r_j, \quad r_i = R_i - R_{i0}. \tag{12}$$

Since the matrix of the second derivatives $\mathbf{D}$ is a symmetric matrix, there exists such an orthogonal transformation $\mathbf{O}$ that brings the matrix $\mathbf{D}$ to the diagonal form $\mathbf{\Lambda}$ with eigen numbers $\lambda$:

$$\mathbf{O}^T\mathbf{D}\mathbf{O} = \mathbf{\Lambda}.$$

The eigenvectors $\boldsymbol{\alpha}$ of the matrix $\mathbf{D}$ are equal to

$$\mathbf{O}^T\mathbf{r} = \boldsymbol{\alpha}.$$

Then (12) can be reduced to the form

$$E = \sum\nolimits_i \frac{m\dot{\alpha}_i^2}{2} + \sum\nolimits_i \frac{1}{2}\lambda_i \alpha_i^2 + U_0. \tag{13}$$

The presented expression takes into account that the internal energy is determined up to a constant, therefore $U_0$ is omitted. The positive eigenvalues of the matrix $\mathbf{D}\lambda \geq 0$ are denoted by $m\omega_i^2$. The negative eigenvalues of the matrix $\mathbf{D}(\lambda < 0)$ are denoted by $-m\Omega_i^2$. The eigenvectors corresponding to the given eigenvalues (modes) are called instantaneous-normal (hereinafter — just normal) modes. Modes with positive eigenvalues are called stable modes. They correspond to harmonic oscillations with frequencies $\omega_i^2$. Modes with negative eigenvalues are called unstable modes. They correspond to solutions that exponentially grow/decay with time. The total number of modes is equal to the total number of degrees of freedom of the system — $3N$. Only real frequencies are present in the spectrum of instantaneous normal modes in case of solids; a region of imaginary frequencies appears in case of liquids, the number of which increases with the increase of the temperature; the distribution is symmetrical for gases, i.e. the number of stable and unstable modes is the same [24].

Let us derive a formula relating the number of stable instantaneous-normal modes and internal energy using the concepts of instant-normal modes.

The total energy of the system can be written as follows from (13)

$$\langle E \rangle = \sum_{i=1}^{k} \left\langle \frac{m\dot{\alpha}_i^2}{2} + \frac{1}{2} m\omega_i^2 \alpha_i^2 \right\rangle + \sum_{i=k+1}^{3N} \left\langle \frac{m\dot{\alpha}_i^2}{2} - \frac{1}{2} m\Omega_i^2 \alpha_i^2 \right\rangle.$$

Here, the brackets indicate an average over all possible system configurations.

Let us consider the contribution of each type of mode, for which we write the equations:

$$\begin{cases} md^2\alpha_j/dt^2 = -m\omega_j^2\alpha_j, & j = 1\ldots k, \\ md^2\alpha_j/dt^2 = m\Omega_j^2\alpha_j, & j = k+1\ldots 3\cdot N. \end{cases}$$

The solution of the equations has the form

$$\begin{cases} \alpha_j = \alpha_{j1}\cos\omega_i t + \alpha_{j2}\sin\omega_i t, & j = 1\dots k, \\ \alpha_j = \alpha_{j3}\,\mathrm{ch}\,\Omega_j t + \alpha_{j4}\,\mathrm{sh}\,\Omega_j t, & j = k+1\dots 3\cdot N. \end{cases}$$

We obtain the average energy from here after transformations:

$$\langle E\rangle = \sum_{j=1}^{k}\frac{m}{2}\omega_j^2\langle\alpha_{j1}^2+\alpha_{j2}^2\rangle + \sum_{j=k+1}^{3N}\frac{m}{2}\Omega_j^2\langle(-\alpha_{j3}^2+\alpha_{j4}^2)\rangle. \tag{14}$$

The first term is responsible for the contribution of stable modes and has the form adopted for a conventional harmonic oscillator. Methods developed for a solid body can be used to calculate it. Averaging is possible at high temperatures using the Gibbs distribution to obtain the law of equidistribution over degrees of freedom.

The situation is more complicated with the last term, since the first term contains a minus sign, which leads to difficulties with averaging when using the Gibbs distribution. Apparently, the integration should be carried out within finite limits, the magnitude of which is not known.

Let us show that the last term is identically zero (at least in the harmonic case under consideration).

To do this, let us use the concept of the velocity autocorrelation function, which is important in fluid theory, and proceed to normal modes

$$S(t_1,t_2) = \frac{1}{3N}\sum_{i=1}^{3N}\langle v_i(t_1)v_i(t_2)\rangle = \frac{1}{3N}\sum_{j=1}^{3N}\langle\dot\alpha_j(t_1)\dot\alpha_j(t_2)\rangle,$$

and let us take advantage of the fact that it depends only on the time difference

$$S(t_1,t_2) = S(|t_2-t_1|).$$

Let us find the sum for stable modes

$$\sum_{j=1}^{k}\langle\dot\alpha_j(t_1)\dot\alpha_j(t_2)\rangle = \left\langle\sum_{j=1}^{k}\alpha_{j1}(0)\alpha'_{j1}(0)\omega_j^2\sin\omega_j t_1\sin\omega_j t_2\right\rangle$$

$$-\left\langle\sum_{j=1}^{k}\alpha_{j1}(0)\alpha'_{j2}(0)\omega_j^2[\sin\omega_j t_1\cos\omega_j t_2+\sin\omega_j t_2\cos\omega_j t_1]\right\rangle$$

$$+\left\langle\sum_{i=1}^{k}\alpha_{j2}(0)\alpha'_{j2}(0)\omega_j^2\cos\omega_j t_1\cos\omega_j t_2\right\rangle.$$

And for unstable modes

$$\sum_{j=1}^{3N-k}\langle\dot\alpha_j(t_1)\dot\alpha_j(t_2)\rangle\!\rangle = \left\langle\sum_{j=1}^{3T-k}\alpha_{j1}(0)\alpha'_{j1}(0)\Omega_j^2\,\mathrm{sh}\,\Omega_j t_1\,\mathrm{sh}\,\Omega_j t_2\right\rangle$$

$$+\left\langle\sum_{j=1}^{3N-k}\alpha_{j3}(0)\alpha'_{j4}(0)\Omega_j^2[\mathrm{sh}\,\Omega_j t_1\,\mathrm{ch}\,\Omega_j t_2+\mathrm{sh}\,\Omega_j t_2\,\mathrm{ch}\,\Omega_j t_1]\right\rangle$$

$$+\left\langle\sum_{j=1}^{3N-k}\alpha_{j4}(0)\alpha'_{j4}(0)\Omega_j^2\,\mathrm{ch}\,\Omega_j t_1\,\mathrm{ch}\,\Omega_j t_2\right\rangle.$$

It is taken into account here that the initial conditions for the same modes, but related to different times, may be different. The initial conditions in the above expressions refer to time $t_1$ without a stroke, to $t_2$ with a stroke.

Let us take into account the independence of $\alpha_{j1}$, $\alpha_{j2}$, $\alpha_{j3}$, $\alpha_{j4}$, as well as the fact that the average value for the ensemble is zero for each of them (all initial conditions, both positive and negative — are equally probable). Then

$$\sum_{j=1}^{k}\langle\dot\alpha_j(t_1)\dot\alpha_j(t_2)\rangle =$$

$$= \sum_{j=1}^{k}\langle\alpha_{j1}(0)\alpha'_{j1}(0)\rangle\omega_j^2\frac{1}{2}\big(\cos\omega_j(t_1-t_2)-\cos\omega_j(t_1+t_2)\big)$$

$$+\sum_{j=1}^{k}\langle\alpha_{j2}(0)\alpha'_{j2}(0)\rangle\omega_j^2\frac{1}{2}\big(\cos\omega_j(t_1-t_2)+\cos\omega_j(t_1+t_2)\big),$$

$$\sum_{ij=1}^{3N-k}\langle\dot\alpha_j(t_1)\dot\alpha_j(t_2)\rangle =$$

$$= \sum_{j=1}^{3N-k}\langle\alpha_{j3}(0)\alpha'_{j3}(0)\rangle\Omega_j^2\frac{1}{2}\big(\mathrm{ch}\,\Omega_j(t_1-t_2)-\mathrm{ch}\,\Omega_j(t_1+t_2)\big)$$

$$+\sum_{j=1}^{3N-k}\langle\alpha_{j4}(0)\alpha'_{j4}(0)\rangle\Omega_j^2\frac{1}{2}\big(\mathrm{ch}\,\Omega_j(t_1-t_2)+\mathrm{ch}\,\Omega_j(t_1+t_2)\big).$$

Since the autocorrelation function should depend only on the time difference $(t_2-t_1)$, it means $\langle\alpha_{j3}(0)\alpha'_{j3}(0)\rangle = \langle\alpha_{j4}(0)\alpha'_{j4}(0)\rangle$. If $t_1=t_2$, then $\langle\alpha_{j3}^2\rangle = \langle\alpha_{j3}^2\rangle$, $\langle\alpha_{j1}^2\rangle = \langle\alpha_{j2}^2\rangle$, hence the proof that the last term in the expression (14) is zero.

Thus, only stable vibrational modes make a non-zero contribution to the internal energy, i.e. the average energy of the system is

$$\langle E\rangle = \sum_{j=1}^{k}\frac{m}{2}\langle\omega_j^2\alpha_{j1}^2+\omega_j^2\alpha_{j2}^2\rangle. \tag{15}$$

In contrast to the approach in Ref. [15] , the number of stable instantaneous-normal modes in the ratio (15) is not fixed, but decreases with temperature, which leads to a decrease of the heat capacity of the liquid.

At high temperatures, for which the law of equal distribution of energy in degrees of freedom $\frac{m}{2}\langle\omega_j^2\alpha_{j1}^2+\omega_j^2\alpha_{j2}^2\rangle=k_BT$ is valid, it is possible to write

$$\langle E\rangle=k_BTN_s,\quad N_s+N_u=3N. \tag{16}$$

Here $N_s$, $N_u$ are the number of stable and unstable modes, respectively.

The type of dependence of the internal energy on the number of stable modes is in good agreement with the known behavior of the heat capacity during the transition from a solid for which $N_s=3N$ and $\langle E\rangle=3Nk_BT$ to a gas for which $N_s=(3/2)N$ and $\langle E\rangle=(3/2)Nk_BT$.

Let us introduce the proportion of unstable instantaneous normal modes $x=2N_u/(N_s+N_u)$ in accordance with Ref. [24], and rewrite (16) as $\langle E\rangle=(1-x)3Nk_BT+x(3/2)Nk_BT$, which coincides with the form of the expression from Ref. [24] and is justified by the results of moleculardynamic modeling.

Thus, a decrease of the heat capacity for liquids at high temperatures may be associated with the appearance of unstable modes in the spectrum $N_u(T)$ and, as a result, with a decrease in the number of stable modes.

## 3. Connection with the „phonon" theory of the heat capacity of a liquid

Stable modes correspond to real frequencies, unstable modes correspond to imaginary frequencies. In accordance with the dispersion relation (5), the imaginary frequencies correspond to the wave vectors of transverse waves from the range from 0 to $k_g$. Therefore, the number of unstable modes can be estimated as

$$N_u(T)=2(2\pi)^{-3}V\int_0^{k_g}4\pi k^2dk=V(3\pi^2)^{-1}k_g^3, \tag{17}$$

and the number of stable can be estimated as

$$N_s(T)=2(2\pi)^{-3}V\int_{k_g}^{k_D}4\pi k^2dk+V(2\pi)^{-3}\int_0^{k_D}4\pi k^2dk. \tag{18}$$

Two possible states of polarization of transverse waves are taken into account here, $V$ is the volume of the system.

We obtain from (16) and (18) that the total energy is equal to the sum of the energies of the transverse modes lying above $k_g$ and the longitudinal modes.

There is no term related to the diffusion of atoms, as suggested in Ref. [2].

We obtain the following from (17)

$$\langle E\rangle=3Nk_BT[1-V(N9\pi^2)^{-1}k_g^3]. \tag{19}$$

Introducing the maximum wave number $k_D=(6\pi^2NV^{-1})^{1/3}$, we obtain

$$\langle E\rangle=3Nk_BT[1-(2/3)\cdot(k_g/k_D)^3]. \tag{20}$$

Introducing the notation $\omega_D=ck_D$, $\omega_f=2^{1/3}ck_g\sim\tau_f^{-1}$, we obtain an analog of the formula (3).

Formulas (20) and (3) are similar up to a factor of 2. The difference is attributable to the consideration of the diffusion motion of particles in (3). There is no contribution of the diffusion term, at least in the harmonic approximation, in accordance with the arguments of the previous section, when moving from the pattern of the motion of individual particles to the pattern of the propagation of collective excitations.

Thus, the use of the concept of instant-normal modes allows obtaining a formula developed in the framework of the „phonon" theory of heat capacity. Based on the results of the analysis, it can also be concluded that the total energy, and hence the heat capacity, in accordance with (20) depends on the size of the gap $k_g$, which was demonstrated, for example, by the results of molecular dynamic modeling in Ref. [25].

## 4. A simple approximation formula for calculating the isochoric heat capacity

It may seem that according to (20) the minimum heat capacity is $C_{V\,\mathrm{min}}=Nk_B$ at $k_{g\,\mathrm{max}}=k_D$. This is not entirely true. The minimum value of the heat capacity corresponds to the case when the number of stable and unstable modes are equal: $N_u=N_s=3N/2$. The ratio $N_u=V(3\pi^2)^{-1}k_{g\,\mathrm{max}}^3=3N/2$ should be fulfilled to ensure this condition.

We obtain $(k_{g\,\mathrm{max}}/k_D)^3=3/4$ using the formula for $k_D$, i.e. according to (20):

$$\langle E\rangle=3/2Nk_BT, \tag{21}$$

as it should be. Let us write the following using formulas (1), (6), (19)

$$\langle E\rangle=3Nk_BT[1-2/3(G_\infty/(c_tk_D\mu(T)))^3]$$

$$=3Nk_bT[1-2/3(G_\infty/(c_tk_D\mu_0)^3\exp(-3U/T)].$$

For deriving the approximation formula let us pay attention to the fact that in the high temperature range, the internal energy should tend to the expression (21). Therefore, since $\exp(-3U/T)\to1$, the product $2/3(G_\infty/c_tk_D\mu_0)^3$ can be replaced by $(1/2)$ for simplification, and the formula can be rewritten in a simpler form:

$$\langle E\rangle=3Nk_BT[1-0.5\exp(-3U/T)].$$

Then the heat capacity is

$$C_V=3Nk_B[1-d(Te^{-3U/T})/dT]. \tag{22}$$

Let us introduce an additional coefficient $\alpha$ to adjust to the experimental data at the melting point:

$$C_V=3(1+\alpha)R[1-d(Te^{-3U/T})/dT]. \tag{23}$$

Fig. 1 shows a comparison of the heat capacity calculated using the formula (23) with experimental data for Ar and Xe, and Fig. 2 shows a comparison of calculations using the formula (23) with data for liquid lead and sodium. Isobaric heat capacity data from Ref. [26] were used to determine the experimental values of the heat capacity of lead. Density data, coefficient of thermal expansion, and velocity of sound from Ref. [27] were used to convert isobaric heat capacity to isochoric. Data from Ref. [28] were used for sodium. It is possible to see that the presented simple formula provides a good approximation of the calculation results.

## Conclusion

The approaches for calculating the internal energy and heat capacity of a liquid have been developed using the concepts of instantaneous-normal modes. It is shown that the internal energy in the harmonic approximation is determined by the contribution of stable modes only. The presence of a gap in the wavenumber spectrum of transverse waves is interpreted as a region occupied by unstable modes. Counting the number of normal modes in a gap with precision up to a multiplier 2 leads to the formula for calculating the internal energy proposed in the framework of the „phonon“ theory. The difference is attributable to the consideration of the contribution of diffusive particle motion in the framework of the „phonon“ theory, which is not detectable in the analysis of internal energy, at least in the harmonic approximation. A simple formula for estimating the heat capacity is proposed, containing one tuning parameter.

It is worth noting that all the results were obtained without taking into account the contribution of anharmonic additives to the internal energy of the liquid. As shown in Ref. [2], taking into account the anharmonic corrections $\Delta E_{anh}$ gives a contribution to the internal energy $\langle E \rangle$, equal in order of magnitude to $\Delta E_{anh}/E \sim \alpha_T T$, where $\alpha_T$ is the coefficient of volumetric thermal expansion of the liquid. This coefficient, for example, is in the order of $10^{-4}$ K for liquid lead from Ref. [27], i.e. the anharmonic correction becomes significant after the temperature $T \sim 10^4$ K, which is significantly higher than the temperatures representing someor a practical interest. The failure to account for anharmonic additives can lead to an error of about 10% at the temperatures of $T \sim 10^3$ K we are interested in.

### Conflict of interest

The author declares that he has no conflict of interest.

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