LOCAL MAXWELLIAN DISTRIBUTION IN FLUIDS

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The spatial and temporal intervals playing the role of hydrodynamic scales for fluids have been analyzed. Those intervals are identified with the dimensions of a region, in which the local Maxwellian distribution is established, and a time interval, for which this distribution is established. The Maxwellian distribution is shown to arise in fluids owing to the interaction between the localized thermal vibrations of fluid particles. For the spatial and temporal hydrodynamic scales, the estimates of 100 nm and 10^{-10} s, respectively, are obtained.

1. Introduction

The fluid is known to be considered in hydrodynamics [1] as a continuous medium. Accordingly, the fluid state is determined by the fields of physical quantities. One of them is the temperature field $T(\mathbf{r},t)$, where $\mathbf{r}=(x,y,z)$ is the radius-vector of a point in the volume occupied by the fluid, and t is the time. The behavior of fluids is described with the use of the derivatives of mentioned the physical quantities with respect to the spatial coordinates and the time. For this purpose, the following infinitely small quantities are introduced into consideration: the infinitesimal spatial – dx, dy, and dz – and time – dt – intervals. The notion of mathematically infinitely small volume – a region located around the point $\mathbf{r}$ and characterized by the volume $d\mathbf{r}=dxdydz$ – is also introduced.

It is evident that the notion of infinitely small quantity is a mathematical abstraction. Actually, infinitely small intervals are associated with finite ones: the spatial, Δr, and, time, Δt, intervals. It is the latter quantities that play the roles of spatial and time scales in hydrodynamics. There is no mathematically infinitely small volume as well. Actually, this notion is associated with a region characterized by a finite volume Δr^3, which is referred to as a physically infinitesimal volume (PIV) [1].

Hence, the temperature $T(\mathbf{r},t)$ that is ascribed to the region $d\mathbf{r}$ is, in effect, the temperature in the PIV that surrounds the point $\mathbf{r}$. It is known [2] that the temperature of the region can be talked about only provided that the Maxwellian distribution for the velocities of the thermal motion of particles in this region is established. This distribution is referred to as a local one.

It is evident that the finite size of PIV imposes restrictions on the upper limit of velocities for the thermal motion of particles that are contained in this region. Therefore, in this case, one may talk only about an incomplete, approximate Maxwellian distribution. Hence, Δr is a dimension of the region, in which the mentioned distribution is established. For the same reason, Δt is the time interval needed for the indicated distribution to be established in the region.

In this work, we propose a mechanism that governs the establishment of a local Maxwellian distribution in fluids. On the basis of the proposed mechanism, we determined the orders of magnitude for the quantities Δr and Δt. To our knowledge, this issue has not been discussed in the literature earlier.

2. Calculation Model

Consider a system consisting of N identical unstructured particles. As the own volume of a particle, we adopt the volume v_0 per particle in the case where the system is in the crystalline state. The particle dimension a is defined by the expression

$$a=v_0^{1/3}. \tag{1}$$

In the case where the system is not in the crystalline state, the volume per particle will be denoted as v_1. Let us also consider a characteristic linear dimension u defined by the formula

$$v_1^{1/3}-a=u. \tag{2}$$

The both introduced dimensions are connected with characteristic time intervals, τ_0 and τ_1, which will be calculated by the formulas

$$\tau_0=a/c, \tag{3}$$

$$\tau_1=u/c, \tag{4}$$

where c is a definite characteristic velocity.

3. Small Parameter in the Physics of Fluids

In comparison with other physical systems, the theory describing the establishment of a local Maxwellian distribution seems to be most completely developed for a rarefied gas [2]. This circumstance promoted us to address this theory and to recall some of its results, which may expectedly be applied to the case of fluids.

For the rarefied gas, the following hierarchy of spatial scales is valid:

$$a \ll u \ll l, \tag{5}$$

where l is the mean free path of a particle, which is calculated by the formula

$$l \sim u(u/a)^2. \tag{6}$$

The spatial hierarchy (5) is coupled with the time hierarchy

$$\tau_0 \ll \tau_1 \ll \tau, \tag{7}$$

where τ is the mean free time of a particle, which is calculated by the formula

$$\tau \sim l/c, \tag{8}$$

where c is the average thermal velocity of particles.

The local Maxwellian distribution is known [2] to be established within the length of a mean free path, and the time needed for its establishment equals the free-run time of a particle. Therefore, in the case of the rarefied gas, for the size Δr of PIV and the time interval Δt needed for establishing the Maxwellian distribution in the PIV, we have

$$a \ll u \ll \Delta r, \tag{9}$$

$$\tau_0 \ll \tau_1 \ll \Delta t, \tag{10}$$

$$\Delta r \sim u(u/a)^2, \tag{11}$$

$$\Delta t \sim \tau_1 (u/a)^2. \tag{12}$$

Formulas (9)–(12) demonstrate that, for the rarefied gas, there exists a small parameter,

$$\beta = a/u, \tag{13}$$

which, in essence, is responsible for the existence of both mentioned hierarchies. Really, substituting equality (13) into formulas (9)–(12), we obtain

$$\beta^3 \ll \beta^2 \ll 1 \tag{14}$$

instead of relations (9) and (10). Then, equalities (11) and (12) read

$$\Delta r \sim u\beta^{-2}, \tag{15}$$

$$\Delta t \sim \tau_1 \beta^{-2}. \tag{16}$$

Does a small parameter exist, which could be used to construct the spatial and time hierarchies for fluids by analogy with those for the rarefied gas? In the literature [3], the existence of such a parameter is denied. However, in our opinion, it does exist.

Really, contrary to the rarefied-gas case, the spatial and time hierarchies for the fluid look like

$$u \ll a \ll \Delta r, \tag{17}$$

$$\tau_1 \ll \tau_0 \ll \Delta t. \tag{18}$$

In expressions (17) and (18), we see a small parameter

$$\phi = u/a. \tag{19}$$

Hence, the introduction of a small parameter for the fluid is still possible. However, the following question arises in this case: Are the relations analogous to those, which are obeyed for the rarefied gas, namely,

$$\Delta r \sim a\phi^{-2}, \tag{20}$$

$$\Delta t \sim \tau_0 \phi^{-2}, \tag{21}$$

valid for the fluid as well? The reasonings given below, in our opinion, give an affirmative answer to this question.

4. Mechanism Governing the Establishment of a Local Maxwellian Distribution in the Fluid

It is known [4] that two types of thermal motion of particles – vibrations and random wanderings – are realized in fluids. The latter type comprises a sequence of elementary movements, which occur, on the average, in a time interval called the dwell time,

$$\tau' = \tau_0' \exp\left(\frac{\Delta F}{k_\mathrm{B} T}\right), \tag{22}$$

where k_B is the Boltzmann constant; ΔF is a free energy barrier, which should be overcome by the particle at every elementary movement; and τ_0' is identified with the period of particle thermal vibrations. For our speculations, crucial is the fact that formula (22) includes the temperature T. Whence, the following evident conclusion follows: for an elementary movement of the given particle to take place, the Maxwellian distribution has to be established in its vicinity. This statement is valid, provided that the inequality

$$\Delta t \ll \tau' \tag{23}$$

is satisfied. Inequality (23) means that the random wanderings do not participate in the establishment of the Maxwellian distribution, and, hence, the mentioned distribution is formed exclusively due to the interaction between thermal vibrations. Therefore, the quantity c corresponds to the propagation velocity of vibrational excitations, i.e. it can be identified with the sound speed.

Owing to inequality (23), the equilibrium positions of particles can be considered constant within the time interval τ'. As a result, the fluid can be regarded as a quasicrystal within this time interval so that the methods of solid state physics can be applied to the analysis [5].

Let $\mathbf{R} = \{R_1, R_2, \ldots, R_{3N}\}$ denote a $3N$-dimensional vector, where the components R_j are the coordinates of particles. The vector $\mathbf{R}$ evidently describes a configuration of the system, i.e. the spatial arrangement of particles composing the system. In the case where the system is in the crystalline state, let the configuration of equilibrium particle positions be described by the vector $\mathbf{R}_0$. Let the notation $E(\mathbf{R})$ stand for the potential energy and $\mathbf{S} = \mathbf{R} - \mathbf{R}_0$ for the particle displacements. We expand $E(\mathbf{R})$ in a series in particle displacements,

$$E(\mathbf{R}) = E(\mathbf{R}_0) + \mathbf{QS} + \mathbf{BSS} + \mathbf{GSSS} + ..., \tag{24}$$

where the following notations are introduced:

$$\mathbf{Q} = \{q_j\} \left.\frac{\partial E}{\partial \mathbf{S}}\right|_{\mathbf{R}=\mathbf{R}_0},$$

$$\mathbf{B} = \{b_{jk}\} = \left.\frac{1}{2}\frac{\partial^2 E}{\partial \mathbf{S}^2}\right|_{\mathbf{R}=\mathbf{R}_0},$$

$$\mathbf{G} = \{g_{jkl}\} = \left.\frac{1}{3!}\frac{\partial^3 E}{\partial \mathbf{S}^3}\right|_{\mathbf{R}=\mathbf{R}_0}. \tag{25}$$

Let the displacement $\mathbf{S}$ be represented in the form of a sum

$$\mathbf{S} = \mathbf{U} + \mathbf{W}, \tag{26}$$

where $\mathbf{U} = \{u_j\}$ is the difference between the equilibrium coordinates of particles in the crystalline and amorphous states (the "static" displacement), and $\mathbf{W} = \{w_j\}$ describes the displacement of particles owing to their thermal vibrations (the vibrational displacement). The adjective "static" was quoted to emphasize the conditional character of this term, because the matter actually concerns the particle immobility within the time interval τ' only.

Substituting expression (26) into formula (24) and retaining terms up to quadratic ones in $\mathbf{W}$, we obtain

$$H = H_0 + H', \tag{27}$$

where

$$H = E(\mathbf{R}) - (E(\mathbf{R}_0) + E_1 + E_2), \tag{28}$$

$$E_1 = \mathbf{Q}\,\boldsymbol{.}\,\mathbf{W} + \mathbf{B} : \mathbf{UU} + \mathbf{GUUU} + ..., \tag{29}$$

$$\begin{aligned} E_2 = {} & \mathbf{Q}\,\boldsymbol{.}\,\mathbf{W} + \mathbf{B} : \mathbf{UW} + \mathbf{G} : \mathbf{UUW} + \\ & + \mathbf{G} : \mathbf{UWU} + \mathbf{G} : \mathbf{WUU} + ..., \end{aligned} \tag{30}$$

$$H_0 = \mathbf{B} : \mathbf{WW}, \tag{31}$$

$$H' = \mathbf{G} : \mathbf{UWW} + \mathbf{G} : \mathbf{WUW} + \mathbf{G} : \mathbf{WWU}. \tag{32}$$

According to equalities (28) and (29), the energy of thermal vibrations in the fluid is reckoned from the value of $E(\mathbf{R}_0)+E_1$. From expression (31), one can see that H_0 is the energy of thermal vibrations in the crystal in the harmonic approximation. According to formulas (30) and (32), the quantities E_2 and H' describe the energy of interaction between thermal vibrations and "static" displacements in the first- and second-order, respectively, approximations in $\mathbf{W}$. Since every term in sum (30) is a linear function of $\mathbf{W}$, the quantity E_2 evidently does not describe the interaction between thermal vibrations. In the selected approximation, such a possibility is reserved only for the quantity H'.

Bearing in mind the known estimate [4]

$$g \sim b/a, \tag{33}$$

we arrive at a conclusion about the existence of the small parameter in the physics of fluids

$$\phi = \frac{H'}{H_0} \sim u/a. \tag{34}$$

As one can see from expressions (27)–(32), these formulas can be used to reduce the solution of the problem of the vibrational motion of particles in the fluid to the classical scheme of perturbation theory. Namely, we have a nonperturbed Hamiltonian H_0 and a small correction to it, the perturbation H'. According to this theory [3], the perturbation invokes a relaxation process, which is characterized by the relaxation time

$$\theta = \theta_0 \phi^{-2}, \tag{35}$$

where θ_0 is the time scale for the process concerned.

The choice of a time scale for that or another relaxation process is based on the time hierarchy. For instance, suppose that we analyze a process characterized by the relaxation time $\theta = \Delta t$ from expression (21). The inequality $\tau_0 \ll \Delta t$ stimulate us to examine the zeroth-order approximation in the small parameter $\tau_0/\Delta t$. In this approximation, the physical parameters are supposed to undergo no changes. However, just this feature is characteristic of the time interval adopted for the time scale. Hence, in this case, the equality $\theta_0 = \tau_0$ turns out valid so that formula (35) coincides with formula (21). Then, it follows that, in the case where the Maxwellian distribution is established due to the interaction between thermal vibrations, formula (20) is also valid. It means that the mentioned Maxwellian distribution is established in the region with the dimension Δr determined by this formula.

Thus, our previous assumptions concerning the applicability of formulas (20)–(21) to the description of the fluid behavior, in our opinion, can be consider as verified.

5. Numerical Estimates

Let us introduce the notation $\Delta v = v_1 - v_0$. Then formulas (1)–(3) and 19) yield

$$\phi = \frac{1}{3}\frac{\Delta v}{v_0}, \tag{36}$$

where the ratio $\frac{\Delta v}{v_0}$ corresponds to a relative variation of the volume, when the crystalline system melts. Let us calculate the quantities Δr and Δt for liquid argon. According to the handbook data, $v_0 = 43 \times 10^{-30}$ m^3 and $\frac{\Delta v}{v_0} = 0.15$. Using the quoted data and formulas (1)–(4), (20), (31), and (36), we obtain $\Delta r \sim 10^{-7}$ m and $\Delta t \sim 10^{-10}$ s.

6. Localization of High-Frequency Vibrations in the Fluid

The fact that the Maxwellian distribution is established in a certain region evidently means that vibrations, whose interaction results in the establishment of a local Maxwellian distribution, are localized in this very region. It is also clear that the wave vector $\mathbf{k}$ of vibrations that take part in this process should satisfy the condition

$$k\Delta r \gg \pi. \tag{37}$$

Let us designate vibrations that obey this condition as high-frequency ones. Vibrations that satisfy the inverse inequality

$$k\Delta r \ll \pi \tag{38}$$

will be referred to as low-frequency. Hence, using the accepted terms, we can say that, contrary to low-frequency–delocalized–vibrations, high-frequency thermal vibrations in the fluid are localized in regions of the dimension Δr.

Let us express the vibrational displacement as a sum of normal crystal vibrations,

$$w_j = \sum_k w_{jk} \exp(-i\omega_k t)\exp(i\mathbf{kr}), \tag{39}$$

where ω_k are the characteristic frequencies of the crystal, and the wave vector components $k_j = \pi p/L$, where L is the dimension of the system, and p are integers. Let us also expand the "static" displacement in a trigonometric series

$$u_j = \sum_k u_{jk} \exp(i\mathbf{kr}). \tag{40}$$

Below, the terms of this series will be conditionally referred to as "static" vibrations.

Substituting expressions (39) and (40) into formula (32), we obtain a sum of terms, each of which corresponds to the interaction of two normal and one "static" vibration. Let us designate their wave vectors by $\mathbf{k}'$, $\mathbf{k}''$, and $\mathbf{k}'''$, and the corresponding frequencies of first two vibrations by ω' and ω''. In formula (32), the summation is carried out over $\mathbf{r}$. In addition, the energy averaged over the time is usually dealt with. Therefore, each of the mentioned terms in the expression for the energy has to be integrated over t and summed up over $\mathbf{r}$.

From the classical solid state theory [5], it is known that, after such operations having been fulfilled, each of the mentioned terms substantially differs from zero only provided that two following conditions are satisfied:

$$\mathbf{k}' + \mathbf{k}''' - \mathbf{k}'' = 0, \tag{41}$$

$$\omega' + \omega'' = 0. \tag{42}$$

It is clear that, under such conditions, any energy exchange between thermal vibrations is out of the question, which means that the proposed mechanism seems to be not able to provide the establishment of a Maxwellian distribution.

However, the classical theory considers vibrations that propagate in the ideal lattice, and those are delocalized vibrations. In our case, the matter concerns vibrations that are localized in a region of the dimension Δr. Therefore, the wave number can be determined only with an error $\sim \pi/\Delta r$, and the frequency with an error $\sim \pi c/\Delta r$. In this case, equalities (41) and (42) should be replaced by the inequalities

$$|\mathbf{k}' + \mathbf{k}''' - \mathbf{k}''| < \pi/\Delta r, \tag{43}$$

$$|\omega' + \omega''| < \pi c/\Delta r. \tag{44}$$

According to expression (44), two normal thermal vibrations interact, if the difference between their frequencies is smaller than $\pi c/\Delta r$. Now, if we remember that the wave number changes by steps equal to π/L, and the frequency by corresponding steps equal to $\pi c/L$, it turns out that the frequency interval $\pi c/\Delta r$ contains a significant number of frequencies. It is the interaction between thermal vibrations with such frequencies that provides the establishment of a Maxwellian distribution.

As one can see from expression (44), "static" vibrations do not participate directly in the energy exchange. Nevertheless, they play an important role in the establishment of a local Maxwellian distribution. It is due to "static" vibrations that the localization of thermal vibrations is attained: the latter become localized as a result of the scattering by the former. A definite contribution to the scattering of thermal vibrations is also made by the processes that are described by the terms of the first order in $\mathbf{W}$ in sum (30).

Accordingly, the quantity Δr is, in effect, the damping length for thermal vibrations l_1, with the damping being associated with the indicated scattering. One may get convinced in it at least basing on the following approximate estimations. Roughly speaking, the "static" displacements of particles from their equilibrium positions can be regarded as the appearance of defects in the crystal structure. Those defects are obstacles for thermal waves. The scattering cross-section σ for such an obstacle can be roughly evaluated according to the relation $\sigma \sim u^2$. The concentration of obstacles, n, has the order of about $1/a^3$. Defining the damping length by the expression $l_1 \sim 1/n\sigma$ and substituting the n- and δ-values into this expression, we arrive at formula (20).

After high-frequency vibrations having been localized, they cannot be distinguished any more from one another, if the difference between their frequencies, $\Delta\omega$, is smaller than $\pi c/\Delta r$. Therefore, this difference becomes a frequency scale for the indicated vibrations. Accordingly, the quantity $\pi/\Delta r$ becomes a wave-number scale for them.

The number of regions with the dimension Δr in the whole system is equal to $(L/\Delta r)^3$. Vibrations localized in an arbitrary region do not interact with vibrations localized in the other regions. Therefore, the high-frequency vibrations are degenerate, and their degeneration degree amounts to $(L/\Delta r)^3$.

For the sake of definiteness, let us specify inequality (37) by rewriting it, e.g., in the form

$$k\Delta r \geqslant 10 \tag{45}$$

and, hence, having introduced the lower limit for the wave numbers of localized vibrations, $k_m = 10\pi/\Delta r$. The frequency of this vibration equals $\omega_m = 10\pi/\Delta t$. With regard for the numerical estimate for Δt obtained above, the magnitude of the frequency ω_m turns out to be of the order of 10 cm^{-1}. Should absorption bands be revealed in fluids in this range of Raman spectra, they will evidence the reality of localized vibrations and, at the same time, provide an opportunity to experimentally determine the PIV parameters in fluids.

7. Conclusions

High-frequency thermal vibrations in fluids are localized owing to their scattering by fluctuations of equilibrium particle positions. The dimensions of localization regions are approximately equal to the damping length for the mentioned vibrations, being of the order of 100 nm. The localized vibrations may induce the emergence of absorption bands in the Raman spectrum at frequencies of the order of 10 cm^{-1}

The local Maxwellian distribution is established in the fluid due to the interaction between the localized vibrations. Accordingly, the region, in which this distribution exists, is the localization region for those vibrations, and the distribution establishment time is equal to the time interval needed for the thermal equilibrium to be established in the system of mentioned vibrations. By the order of magnitude, this time interval equals 10^{-10} s.

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ЛОКАЛЬНИЙ МАКСВЕЛЛІВСЬКИЙ РОЗПОДІЛ У РІДИНАХ

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Резюме

Розглянуто просторовий та часовий інтервали, що слугують для рідин масштабами в гідродинаміці. Ці інтервали ототожнюються із розміром області, де встановлюється локальний максвеллівський розподіл, і часом, за який цей розподіл встановлюється. Показано, що максвеллівський розподіл виникає у рідинах завдяки взаємодії між локалізованими тепловими коливаннями частинок рідини. Для просторового та часового масштабів гідродинаміки отримано оцінки – відповідно, 100 нм та 10^{-10} с.