LIGHT SCATTERING BY THE SURFACE OF A LIQUID UNDER A TEMPERATURE GRADIENT

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Hydrodynamic fluctuations of the surface of a liquid considered as a continuous medium with a constant temperature gradient have been analyzed. The calculated asymmetry of the capillary wave spectrum agrees well with experimental data.

1. Introduction

In work [1], as well as in earlier work [2], the theory of thermal hydrodynamic fluctuations in a stationary nonequilibrium continuous medium has been developed. The theory is based on Onsager's regression hypothesis and the assumption of a local equilibrium in such a medium. The nonequilibrium fluctuation-dissipation theorem (FDT) for Langevin sources (Langevin random forces) formulated in those works, which is also referred to as the second FDT or, simply, the Langevin FDT, differs essentially – by the presence of cross-correlations among sources – from the branch of modern statistical physics that became widespread since the middle of the 1980s and called nonequilibrium fluctuation hydrodynamics. In the latter, the Langevin approach to the description of fluctuations in nonequilibrium states is adopted as a postulate. As the Langevin forces, the forces found by Landau and Lifshitz for a liquid at equilibrium [3] are used, with the thermodynamic parameters in formulas for intensities being substituted by their local values. Therefore, the nonequilibrium fluctuation hydrodynamics can also be coined as fluctuation hydrodynamics with Landau–Lifshitz local forces. The simultaneous correlation functions calculated in the framework of this approach turn out different from the locally equilibrium ones.

The viewpoint expressed in work [1] is completely opposite. It consists in that the nonequilibrium hydrodynamic state is considered to be locally equilibrium *a priori*, as it takes place in the nonequilibrium hydrodynamics of continuous media (the hypothesis of local equilibrium). Respectively, the simultaneous correlation functions of fluctuations are locally equilibrium, whereas the Langevin forces determined from them differ from the Landau–Lifshitz ones. The Langevin approach with such forces is equivalent to the Einstein approach associated with obtaining the dynamical solution and the following averaging of locally equilibrium initial fluctuations. This means that there exists a distinct split of the problem into the static and dynamic parts, whereas the nonequilibrium fluctuation hydrodynamics refuses a similar separation from the very beginning [4].

In work [5], a comparison of theory [1] with experiment was carried out for a simple case of nonequilibrium stationary state – a bulk liquid with a temperature gradient. The Mandelshtam–Brillouin doublet caused by fluctuation waves is asymmetric for a medium with a temperature gradient, because the numbers of phonons, which propagate along and against the temperature gradient, are different. The nonequilibrium fluctuation hydrodynamics gives an overestimated value for asymmetry, whereas the proposed theory provides a satisfactory result.

Below, there will be considered the surface fluctuations of a liquid, in which the temperature changes linearly in space. This problem is easy enough to illustrate the ideas concerning the local equilibrium in a nonequilibrium liquid, the equivalency of the Einstein and Langevin approaches, and the cross-correlations between Langevin forces. Nowadays, the nonequilibrium fluctuation hydrodynamics serves as a basis for the theory of light scattering by capillary fluctuation waves [6], and a large body of experimental material has been accumulated [7, 8], which reveals a discrepancy with the theory [6]. The aim of our work consists in finding the structure factor for surface displacements and its asymmetry, as well as in comparing our results with those of works [6–8].

An importance of carrying out experiments on the Mandelshtam–Brillouin scattering in a continuous nonequilibrium medium with a temperature gradient for testing the theory should be emphasized. This makes it possible to study the range of small temperature gradients. Just this range has a predominant interest from the viewpoint of studying the hydrodynamic fluctuations. It is so, because hydrodynamics is efficient, first of all, if the gradients of macroscopic fields of the temperature, velocity, and so on are small.

2. Simultaneous Correlation Functions of Displacements and Displacement Velocities for a Nonequilibrium Surface

To calculate the light scattering by a liquid surface, it is necessary to find the structure factor, i.e. the space-time Fourier transform of the autocorrelation function of displacements,

$$S_{\xi,\xi}(\mathbf{k},\omega)=\frac{1}{TS}\int\limits_S d\mathbf{r}\int\limits_S d\mathbf{r}'\int\limits_{-T/2.}^{T/2} dt\int\limits_{-T/2.}^{T/2} dt'\times$$

$$\times\left\langle\xi(\mathbf{r},t)\,\xi(\mathbf{r}',t')\right\rangle e^{i\omega(t-t')-i\mathbf{k}(\mathbf{r}-\mathbf{r}')} \quad (1)$$

where the surface area S and the time of experiment T are large, and $\xi(\mathbf{r},t)$ is the surface displacement at a point determined by the radius-vector $\mathbf{r}$ at the time moment t. The angle brackets $\langle\ldots\rangle$ denote the locally equilibrium averaging. Taking into account what was said in Introduction, the determination of the structure factor requires the knowledge of simultaneous fluctuation correlation functions and the time evolution of fluctuations, irrespective of which approach we prefer. Consider now the first part of the problem, assuming further that the liquid depth is infinite.

For a liquid in equilibrium, the simultaneous correlation function of surface displacements was found by Mandelshtam in the $\mathbf{k}$-representation [9] and Leontovich in the $\mathbf{r}$-representation [10]. Actually, the starting point for its determination was an expression for the equilibrium distribution function of liquid surface displacements,

$$f(\xi)\propto\exp\left(-\frac{\sigma}{T_0}\int\limits_S d\mathbf{r}\left(\sqrt{1+(\boldsymbol{\nabla}\xi)^2}-1\right)\right), \quad (2)$$

where T_0 is the liquid temperature, and σ the coefficient of surface tension. If the temperature is not constant along the liquid surface, the initial locally equilibrium distribution function should be taken in the form

$$f(\xi)\propto\exp\left(-\sigma\int\limits_S d\mathbf{r}\frac{1}{T(\mathbf{r})}\left(\sqrt{1+(\boldsymbol{\nabla}\xi)^2}-1\right)\right). \quad (3)$$

Below, we assume that the liquid parameters – such as the coefficient of surface tension σ, density ρ, shear η, and kinematic viscosity ν – do not depend on the temperature, being constant. Anyway, such an assumption is satisfied for water, for which the temperature dependences of those parameters are relatively weak. It considerably simplifies the problem, and its application in previous works [6–8] was rather natural. In addition, water also has essential advantages in comparison with other liquids, being therefore most often used in experiments. In particular, its coefficient of surface tension is not very high, as compared, for instance, with mercury; therefore, the amplitude of fluctuation capillary waves is larger. In addition, the temperature gradient does not induce the emergence of instabilities, as it takes place, for example, in octane.

From Eq. (3), we obtain

$$\left\langle\boldsymbol{\nabla}\xi(\mathbf{r})\,\boldsymbol{\nabla}'\xi(\mathbf{r}')\right\rangle=\frac{T(\mathbf{r})}{\sigma}\delta(\mathbf{r}-\mathbf{r}') \quad (4)$$

in the square-law approximation with respect to displacements. Making the expansion

$$\xi(\mathbf{r})=\frac{1}{\sqrt{S}}\sum_{\mathbf{k}}\xi_{\mathbf{k}}e^{i\mathbf{kr}} \quad (5)$$

for the temperature which changes linearly in space,

$$T(\mathbf{r})=T_0+\mathbf{r}\boldsymbol{\nabla}T, \quad (6)$$

we find the simultaneous correlation functions for the Fourier components of displacements:

$$\langle\xi_{\mathbf{k}}\xi_{\mathbf{k}'}\rangle=-\frac{T_0}{\sigma\mathbf{k}\mathbf{k}'}\Delta_{\mathbf{k},\mathbf{k}'}, \quad (7)$$

where

$$\Delta_{\mathbf{k},\mathbf{k}'}=\delta_{\mathbf{k},-\mathbf{k}'}+\frac{i}{2}\left(\delta_{\mathbf{k}+\mathbf{q},-\mathbf{k}'}-\delta_{\mathbf{k}-\mathbf{q},-\mathbf{k}'}\right) \quad (8)$$

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and

$$\mathbf{q} = \frac{\nabla T}{T_0}. \tag{9}$$

In a similar way, the locally equilibrium distribution function for displacement velocities, which is determined by the fluctuations of kinetic energy, can be used – just as it was made in work [11] – to obtain an expression for the simultaneous correlation function of displacement velocities,

$$\left\langle \dot{\xi}_{\mathbf{k}} \, \dot{\xi}_{\mathbf{k}'} \right\rangle = \frac{T_0}{\rho} \frac{k + k'}{2} \Delta_{\mathbf{k},\mathbf{k}'}. \tag{10}$$

Formula (10) can also be derived from expression (7) and an expression for the dispersion of capillary wave frequency [see Eq. (14) below].

It is evident that, in this problem, there are no correlations between displacements and their velocities. As a result, the corresponding matrix of simultaneous correlation functions looks like

$$\langle x_{i,\mathbf{k}} x_{j,\mathbf{k}'} \rangle = \begin{pmatrix} -\frac{1}{\sigma \mathbf{k}\mathbf{k}'} & 0 \\ 0 & \frac{k+k'}{2\rho} \end{pmatrix} T_0 \Delta_{\mathbf{k},\mathbf{k}'} \tag{11}$$

where $x_{i,\mathbf{k}} = \binom{\xi_{\mathbf{k}}}{\dot{\xi}_{\mathbf{k}}}$.

3. Fluctuation Dynamics and Nonequilibrium FDT for Langevin Sources

The equation of liquid surface oscillations for capillary waves preserves its form, provided that the liquid parameters are independent of the temperature. If the kinematic viscosity ν is low, this equation looks like [12]

$$\ddot{\xi}_{\mathbf{k}} + 2\delta \, \dot{\xi}_{\mathbf{k}} + \omega_c^2 \xi_{\mathbf{k}} = 0, \tag{12}$$

where the parameter

$$\delta = 2\nu k^2 \tag{13}$$

determines the wave damping, and

$$\omega_c = \sqrt{\frac{\sigma k^3}{\rho}} \tag{14}$$

is the cyclic frequency. Let us write down Eq. (12) in the form

$$\dot{x}_{i,\mathbf{k}} = -\lambda_{ij,\mathbf{k}} \, x_{j,\mathbf{k}} \tag{15}$$

where the matrix $\lambda_{ij,\mathbf{k}}$ is

$$\lambda_{ij,\mathbf{k}} = \begin{pmatrix} 0 & -1 \\ \omega_c^2 & 2\delta \end{pmatrix}. \tag{16}$$

Formulas (11) and (16) define the Ornstein–Uhlenbeck process. As was proved in work [1], it is this process that governs the stochastic properties of Langevin sources $y_{i,\mathbf{k}}$. Applying the relevant formulas, we find the kinetic coefficients

$$\gamma_{i,\mathbf{k};j,\mathbf{k}'} = \lambda_{im,\mathbf{k}} \langle x_{m,\mathbf{k}} x_{j,\mathbf{k}'} \rangle =$$

$$= \begin{pmatrix} 0 & -\frac{k+k'}{2} \\ -\frac{k^3}{\mathbf{k}\mathbf{k}'} & 2\nu k^2 (k + k') \end{pmatrix} \frac{T_0}{\rho} \Delta_{\mathbf{k},\mathbf{k}'}, \tag{17}$$

and the spectral distribution of random forces, which are no more than a white noise,

$$(y_{i,\mathbf{k}} y_{j,\mathbf{k}'})_\omega = \gamma_{i,\mathbf{k};j,\mathbf{k}'} + \gamma_{j,\mathbf{k}';i,\mathbf{k}} =$$

$$= \begin{pmatrix} 0 & -\left(\frac{k+k'}{2} + \frac{k'^3}{\mathbf{k}\mathbf{k}'}\right) \\ -\left(\frac{k+k'}{2} + \frac{k^3}{\mathbf{k}\mathbf{k}'}\right) & 2\nu \left(k^2 + k'^2\right)(k + k') \end{pmatrix} \frac{T_0}{\rho} \Delta_{\mathbf{k},\mathbf{k}'}. \tag{18}$$

The expression obtained represents the nonequilibrium FDT for Langevin sources and differs by the presence of crossed terms from the result of nonequilibrium fluctuation hydrodynamics, where non-zero is only the term at the intersection of the second row and the second column:

$$(y_{i,\mathbf{k}} y_{j,\mathbf{k}'})_\omega = \begin{pmatrix} 0 & 0 \\ 0 & 2\nu \left(k^2 + k'^2\right)(k + k') \end{pmatrix} \frac{T_0}{\rho} \Delta_{\mathbf{k},\mathbf{k}'}. \tag{19}$$

Formula (18) can be presented as an explicit sum of the equilibrium,

$$(y_{i,\mathbf{k}} y_{j,-\mathbf{k}})_\omega^{\mathrm{eq}} = \frac{T_0}{\rho} \begin{pmatrix} 0 & 0 \\ 0 & 8\nu k^3 \end{pmatrix}, \tag{20}$$

and nonequilibrium,

$$(y_{i,\mathbf{k}} y_{j,-\mathbf{k}\mp\mathbf{q}})_\omega^{\mathrm{noneq}} = i\frac{T_0}{\rho} \begin{pmatrix} 0 & \frac{3}{4}\frac{\mathbf{k}\mathbf{q}}{k^2} \\ -\frac{3}{4}\frac{\mathbf{k}\mathbf{q}}{k^2} & \pm 4\nu k^3 + 6\nu \mathbf{k}\mathbf{q} \end{pmatrix}, \tag{21}$$

contributions.

Hence, all the nonequilibrium features of Langevin forces stem from the nonequilibrium of simultaneous correlation functions, as it was in the bulk case. For the Rayleigh–Bénard problem, the nonequilibrium of simultaneous correlation functions also takes place; however, an important factor here is the nonequilibrium associated with fluctuation dynamics [2].

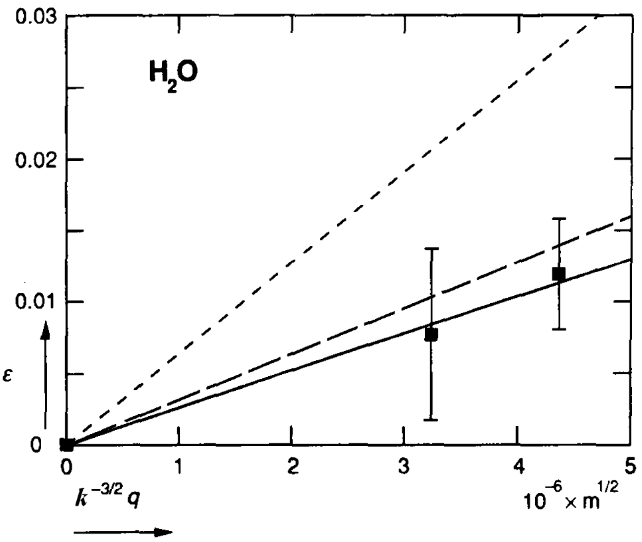

Fig. 1. Dependences of the asymmetry ε on the quantity $k^{-3/2}q$. The slopes are: 5.4×10^3 $\mathrm{m}^{-1/2}$ (nonequilibrium fluctuation hydrodynamics, short-dashed line), $(2.6\pm0.6)\times10^3$ $\mathrm{m}^{-1/2}$ (experiment, solid line), and 2.7×10^3 $\mathrm{m}^{-1/2}$ (this work, dashed line)

4. Structure Factor of Liquid Surface Displacements

To calculate expression (1), let us first use the Einstein method. The solution of the initial problem for Eq. (12) is

$$\xi_{\mathbf{k},\omega}=\Lambda^{\xi,\xi}_{\mathbf{k},\omega}\xi_{\mathbf{k}}+\Lambda^{\xi,\dot{\xi}}_{\mathbf{k},\omega}\dot{\xi}_{\mathbf{k}} \quad (22)$$

Since the correlations between displacements $\xi_{\mathbf{k}}$ and their velocities $\dot{\xi}_{\mathbf{k}}$ are absent, only the first term with

$$\Lambda^{\xi,\xi}_{\mathbf{k},\omega}=\frac{-i\omega+2\delta}{\omega_c^2-\omega^2-2i\delta\omega} \quad (23)$$

is of interest. The procedure of calculations is the same, as was described in work [1]. A distinction consists in that α_ξ depends, as is seen from Eq. (7), on the wave vectors:

$$\alpha_\xi=-\alpha\mathbf{p}\mathbf{p}'. \quad (24)$$

At the same time, carrying out the summation in the nonequilibrium contribution, $\mathbf{p}$ is replaced by $\mathbf{k}\pm\mathbf{q}/2$, and $\mathbf{p}'$ by $-\mathbf{k}\pm\mathbf{q}/2$. Then, the product $\mathbf{p}\mathbf{p}'$ does not include terms linear in $\mathbf{q}$, so that α_ξ becomes a constant which is equal to

$$\alpha_\xi=\sigma k^2. \quad (25)$$

Therefore, we may take advantage of formula (42) from work [1],

$$S_{\xi,\xi}(\mathbf{k},\omega)=\alpha_\xi T_0\left(2\mathrm{Re}+\mathbf{q}\nabla_{\mathbf{k}}\mathrm{Im}\right)\Lambda^{\xi,\xi}_{\mathbf{k},\omega} \quad (26)$$

Whence, taking Eqs. (23) and (25) into account, we find

$$S_{\xi,\xi}(\mathbf{k},\omega)=\frac{8T_0\nu k^3}{\rho\Delta}\left(1-\frac{6\nu\omega\omega_c^2\mathbf{kq}}{\Delta}\right), \quad (27)$$

where

$$\Delta=\left(\omega^2-\omega_c^2\right)^2+4\omega^2\delta^2. \quad (28)$$

Formula (27) can also be derived by the Langevin method, using the nonequilibrium FDT (18), as was done in work [1] for a bulk liquid with a temperature gradient. Therefore, both the Einstein and Langevin approaches to the description of nonequilibrium fluctuations bring about identical results. A main role in this equivalency is played by cross-correlations among Langevin forces.

For a liquid with low viscosity, $\omega_c\gg\delta$. Therefore, formula (27) can be expressed as a sum of two Lorentzians with different heights which correspond to the Stokes and anti-Stokes satellites of the Mandelshtam–Brillouin doublet at the frequencies $-\omega_c$ and ω_c:

$$S_{\xi,\xi}(\mathbf{k},\omega)=$$

$$=\frac{2\nu T_0}{\sigma}\left(\frac{1+\varepsilon(\mathbf{k},\omega)}{(\omega+\omega_c)^2+\delta^2}+\frac{1-\varepsilon(\mathbf{k},\omega)}{(\omega-\omega_c)^2+\delta^2}\right), \quad (29)$$

where

$$\varepsilon(\mathbf{k},\omega)=\frac{6\nu\omega_c^3\mathbf{kq}}{\Delta}. \quad (30)$$

Using the fluctuation hydrodynamics with local external forces introduced by Landau and Lifshitz, Grant and Desai [6] found a structure factor that differed from expression (27):

$$S_{\xi,\xi}(\mathbf{k},\omega)=\frac{8T_0\nu k^3}{\rho\Delta}\left(1-\frac{\left(8\omega^3+4\omega\omega_c^2\right)\nu\mathbf{kq}}{\Delta}\right). \quad (31)$$

This result, taking a low damping into consideration, can be transformed to

$$S_{\xi,\xi}(\mathbf{k},\omega)=\frac{8T_0\nu k^3}{\rho\Delta}\left(1-\frac{12\omega\omega_c^2\nu\mathbf{kq}}{\Delta}\right) \quad (32)$$

and, further, to expression (29) with the quantity $\varepsilon(\mathbf{k},\omega)$ twice as large as (30). Therefore, such a Langevin approach contradicts the Einstein one or the equivalent Langevin one with forces (18).

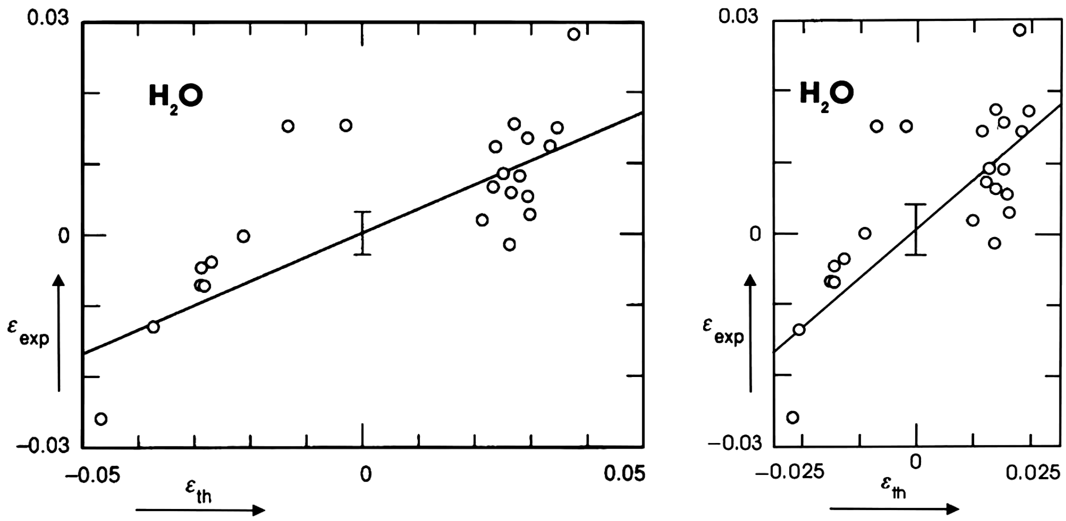

Fig. 2. Dependences of experimental asymmetry on theoretical one. The latter is (a) calculated on the basis of nonequilibrium fluctuation hydrodynamics (work [8]) and (b) determined by formula (34). The axis scales in both panels are identical

5. Comparison of Results

Let us introduce the spectrum asymmetry used in works [7, 8]:

$$\varepsilon = \frac{S_{\xi,\xi}(\mathbf{k}, -\omega_c) - S_{\xi,\xi}(\mathbf{k}, \omega_c)}{S_{\xi,\xi}(\mathbf{k}, -\omega_c) + S_{\xi,\xi}(\mathbf{k}, \omega_c)}. \tag{33}$$

This means that the asymmetry is determined by the heights of the Stokes and anti-Stokes peaks. Substituting expression (29) into formula (33), we obtain that, in our theory,

$$\varepsilon = \frac{3}{8}\frac{\omega_c \mathbf{kq}}{\nu k^4} = \frac{3}{8}\frac{\sqrt{\sigma\rho}}{\eta} k^{-3/2}\hat{k}\mathbf{q}, \tag{34}$$

where $\hat{k}$ is a unit vector directed along the vector $\mathbf{k}$. The nonequilibrium fluctuation hydrodynamics with structural factor (32) gives the asymmetry value that is twice larger. Below, we compare our results for the asymmetry with experimental data and the results of nonequilibrium fluctuation hydrodynamics, which does not require specific comments.

In Fig. 1, the plots from work [7] are reproduced, namely, the dependences of the asymmetry ε on the quantity $k^{-3/2}q$. The solid curve corresponds to experimental data, and the short-dashed one to the results of nonequilibrium fluctuation hydrodynamics. Our results [dependence (34)] are also depicted by the dashed line.

Figure 2,a reproduces the plot from work [8]. The experimental asymmetry is reckoned along the ordinate axis, and the theoretical one calculated in the framework of nonequilibrium fluctuation hydrodynamics along the abscissa axis. Figure 2,b exhibits the same dependence, but the theoretical asymmetry is determined by formula (34). The expected slope of the experimental line should be equal to 1. The fluctuation hydrodynamics with Landau–Lifshitz local forces gives rise to a value of 0.35, whereas our theory to 0.7.

6. Conclusions

The structural composition of a medium has no importance for low-frequency and long-wave hydrodynamic fluctuations. Therefore, in this limit, the medium should be considered as continuous. The results of this work, as well as those of some other ones [1, 2, 5], testify that, to construct the theory of thermal fluctuations in nonequilibrium stationary states of a continuous medium, it is sufficient to accept the hypothesis of local equilibrium in the medium and Onsager's regression hypothesis. Then, all probable approaches to the description of fluctuations become equivalent. It is important that, in the framework of the Langevin description of hydrodynamic fluctuations, the local equilibrium in a continuous medium cannot be taken into account by a simple substitution of constant thermodynamic parameters in the Landau–Lifshitz formulas by their local values. The comparison between the results of the developed theory of nonequilibrium thermal fluctuations and the experimental ones on the Mandelshtam–Brillouin light scattering looks satisfactorily good.

1. V.P. Lesnikov, Ukr. J. Phys. **49**, 279 (2004).

2. V.P. Lesnikov, Ukr. Fiz. Zh. **39**, 379 (1994); Ukr. Fiz. Zh. **41**, 181 (1996).
3. L.D. Landau and E.M. Lifshitz, Zh. Èksp. Teor. Fiz. **32**, 618 (1957).
4. A.M.-S. Tremblay, M. Arai, and E.D. Siggia, Phys. Rev. A **23**, 1451 (1981).
5. V.P. Lesnikov, Ukr. J. Phys. **53**, 23 (2008).
6. M. Grant and R.C. Desai, Phys. Rev. A **27**, 2577 (1983).
7. D.S. Chung, K.Y.C. Lee, and E. Mazur, Int. J. Thermodyn. **9**, 729 (1988).
8. D.S. Chung, K.Y.C. Lee, and E. Mazur, Phys. Lett. A **145**, 348 (1990).
9. L.I. Mandelshtam, *The Full Collection of Works* (AN SSSR, Moscow, 1947-1955), vol. 1 (in Russian).
10. M.A. Leontovich, *Statistical Physics* (Gostekhizdat, Moscow, 1944) (in Russian).
11. V.P. Lesnikov, Ukr. Fiz. Zh. **35**, 878 (1990).
12. V.G. Levich, *Physicochemical Hydrodynamics* (Prentice-Hall, Englewood Cliffs, N.J., 1962).

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РОЗСІЯННЯ СВІТЛА ПОВЕРХНЕЮ РІДИНИ ЗА НАЯВНОСТІ ГРАДІЄНТА ТЕМПЕРАТУРИ

В.П. Лесніков, Л.М. Васіліу

Р е з ю м е

Виходячи з уявлення про суцільне середовище, вивчено гідродинамічні флуктуації поверхні рідини, температура якої лінійно змінюється з відстанню вздовж поверхні. Розрахована асиметрія спектра капілярних флуктуаційних хвиль добре узгоджується з результатами експерименту.