

# The effect of a gravitational field on dynamic processes in a material with near-critical state parameters

Yu. G. Leonenko

*S. S. Kutateladze Institute of Technology, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk, Russia*

(Submitted 13 June 1994)

Zh. Éksp. Teor. Fiz. **107**, 765–773 (March 1995)

The author investigates the influence of a gravitational field on certain dynamic processes in a material with near-critical state parameters: namely, the propagation of perturbations of the boundary between phases, the appearance of internal waves, and the kinetics by which the system reaches thermodynamic equilibrium. It is shown that the presence of gravitation is a decisive factor in these processes in the critical region. © 1995 American Institute of Physics.

## 1. INTRODUCTION

The experimental study of critical states of matter involves two fundamentally different kinds of difficulties. On one hand, the anomalous behavior of the properties of the medium requires operation of the measurement apparatus at the limits of its sensitivity; on the other hand, the reliability of the results is determined not by the accuracy with which the experiment is carried out, but rather by the physical state of the system under study. In a real experiment, a given process is always investigated in the presence of various types of perturbations; matter whose state parameters are close to critical is always sensitive to these. This fact, which is a consequence of the large susceptibility of the system, implies that even perturbations connected with the measurement process can turn out to be nonnegligible.<sup>1</sup>

For the physical processes discussed in this paper, perturbing factors such as gravitational field play a decisive role. The presence of this field not only strongly distorts the processes occurring in the medium, it also causes new phenomena to appear.

The influence of the gravitational field is unusually strong because of the anomalously high compressibility of matter in the vicinity of a critical point. The density of the medium begins to depend significantly on the vertical coordinate, which distorts the experimental measurements; in addition, it changes the state of the object under study to some extent.

## 2. PROPAGATION OF PERTURBATIONS OF THE INTERPHASE BOUNDARY BETWEEN LIQUID AND VAPOR

Near a critical point on the saturation curve, the difference in the liquid and vapor densities  $\rho_l - \rho_v$  is determined by the equation for the coexistence curve<sup>2</sup>

$$\frac{\rho_l - \rho_v}{\rho_c} = B \left( \frac{T_c - T}{T_c} \right)^\beta, \quad (1)$$

where  $\rho_c$ ,  $T_c$  are the critical density and temperature,  $T$  is the ambient temperature of the medium,  $\beta$  is a universal critical exponent, and  $B$  is a coefficient. Thus, there are two layers with uniform density. However, this picture is not always correct. For  $\varepsilon < \varepsilon_0$  (where  $\varepsilon = (T_c - T)/T_c$ , and  $\varepsilon_0 \sim 3 \cdot 10^{-3}$ ), the anomalous increase in compressibility of the material

begins to make itself felt (the coefficient of isothermal compressibility  $k_T \propto (\partial \rho / \partial P)_T \propto |\varepsilon|^{-\gamma}$ , with the universal critical exponent<sup>3</sup>  $\gamma \approx 1.2$ ), and the previously uniform phases become stratified with respect to density. As the critical temperature is approached, the stratification of the liquid and vapor first takes the form of a discontinuity in the density at the boundary between phases. As the temperature is further increased, the boundary is transformed into a meniscus, i.e., an abrupt but finite region over which the density changes.

Borisov *et al.*<sup>4</sup> carried out experimental and theoretical studies of the propagation of perturbations of the interphase boundary as a function of temperature.

The material (Freon-13, or  $\text{CClF}_3$ , with critical parameters  $P_c = 3.96 \cdot 10^6$  Pa,  $\rho_c = 0.58$  g/cm<sup>3</sup>, and  $T_c = 302.02$  K) was placed in a horizontal tube of length 3 m and inner diameter 5.7 cm. A perturbation of the boundary was generated mechanically, followed by observation of its propagation and evolution.

There are two regimes of propagation, depending on how close the system is to the critical point (Fig. 1). For  $\varepsilon > \varepsilon_0$  the propagation dynamics obey the Korteweg–deVries equation with weak dispersion and weak nonlinearity (the data from 1 and 2 are for different initial amplitudes of the perturbation  $h$ : 1 is for  $h/d \sim 0.12$ , 2 for  $h/d \sim 0.08$ , where  $d$  is the diameter of the tube). If Eq. (1) is used for the difference in densities, all the coefficients of the Korteweg–deVries equation depend on  $\varepsilon$ .<sup>4</sup> For  $\varepsilon < \varepsilon_0$  the wave processes deviate strongly from those of the two-layer model, and cannot be described without taking into account the distribution of density with respect to height.

Thus, the so-called gravitational effect, which begins to show up as a factor that affects the medium for  $\varepsilon < \varepsilon_0$ , must be taken into account in all of the measurements.

## 3. INTERNAL WAVES

In the immediate vicinity of the critical point, the gravitational field distorts the system so much that the class of observable phenomena is enlarged. For example, it becomes possible for internal waves to exist, i.e., oscillations of liquid particles that are displaced from their positions of equilibrium under the action of the gravitational and Archimedean forces.

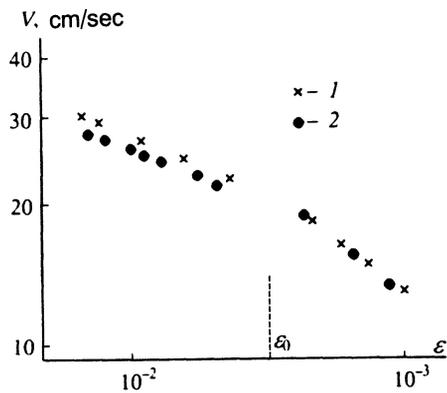


FIG. 1. Temperature dependence of the velocity of interphase perturbations.

A medium in which the density varies with height can be characterized<sup>5</sup> by its Väisälä–Brunt parameter  $N$ :

$$N = [-(g/\rho)(\partial\rho/\partial z)]^{1/2}, \quad (2)$$

where  $g$  is the free-fall acceleration,  $\rho$  is the equilibrium density distribution with respect to the vertical  $z$ , and  $N$  is the frequency of free oscillations of the liquid particles. For small perturbations of the medium with  $N = \text{const}$ , the following dispersion relation holds<sup>5</sup> (in the two-dimensional case):

$$\omega^2 = N^2 k_1^2 / (k_1^2 + k_2^2) = N^2 \cos^2 \theta, \quad (3)$$

which connects the frequency  $\omega$  with the horizontal  $k_1$  and vertical  $k_2$  components of the wave vector  $k$  for a wave whose state variables are proportional to  $\exp[i(k_1 x + k_2 y - \omega t)]$ . A fundamental feature of Eq. (3) is the fact that the frequency  $\omega$  depends only on the angle  $\theta$  that the wave vector  $\mathbf{k} = (k_1, k_2)$  makes with the horizontal, and does not depend on the fluid height. The liquid particles oscillate along rays that make an angle  $\theta$  with the vertical.

This interesting phenomenon, which is observed in salt water with stratified salinity,<sup>6</sup> was first observed in material near the critical point by Borisov *et al.*<sup>7</sup>

Figure 2(a) shows a Schlieren photograph of internal waves in a material near the critical point. The wave generator consisted of a horizontal cylinder 1 (Fig. 2b) whose axis was perpendicular to the plane of the figure. The cylinder was fastened to a mount 2 and executed horizontal harmonic oscillations with a frequency near 0.5 Hz. The liquid par-

ticles oscillate in accordance with Eq. (3) along the rays (dark regions), while the phase velocity (direction of  $\mathbf{k}$ ) is perpendicular to the particle motion.

Internal waves are one of the consequences of perturbing a medium by a gravitational field. Viewed another way, they constitute a new method for investigating critical phenomena. This will be demonstrated in the next section.

#### 4. RELAXATION PROCESSES

In this section it is demonstrated that the presence of a density gradient, which, as mentioned above, is a consequence of the perturbation of a material by a gravitational field, can play a decisive role in the process by which thermodynamic equilibrium is reached near the critical point.

The unusually intense development of density fluctuations as the system approaches the critical state is a fact of fundamental importance<sup>8</sup> that helps us to understand the reason for extremal behavior of equilibrium characteristics of matter such as the compressibility, thermal expansion, specific heat, etc. Although the patterns of behavior of these parameters have been rather well investigated within an extensive region around the critical point, there have been far fewer studies of the kinetic properties of the material, whose behavior leads to additional difficulties in carrying out quasistatic experiments.

Under ordinary conditions, relaxation of the density in a single-component liquid takes place rapidly; however, as the critical point is approached, the processes by which the equilibrium distribution is established are greatly slowed down. Lorentzen<sup>9</sup> investigated the time dependence of the density distribution by measuring the distance between the images of two thin vertical lines cast by light after it had passed through the material. They found that when the temperature was decreased from  $T - T_c = 0.09$  K to  $T - T_c = 0.02$  K, the density distribution versus height after three hours of thermal isolation differed considerably from the same distribution after 48 hours of thermal isolation. Under ordinary conditions, a local deviation from the equilibrium value is accompanied by the appearance of a pressure gradient, which leads to a matter flux that rapidly reestablishes equilibrium. The presence of randomly located gradients of the fluctuating parameters as the critical point is approached weakens the action of artificially created gradients, which slows equilibration.

In order to explain the slowing of the density relaxation time in the vicinity of the critical point, it is assumed that the

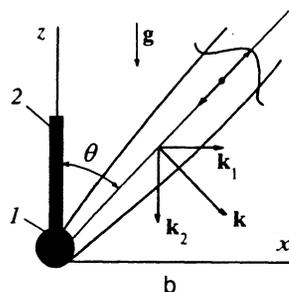


FIG. 2. Internal waves in a material with near-critical state parameters.

process is diffusive. To a first approximation, the equation for the matter flux  $j$  has the form

$$j = -L_1 \nabla T - L_2 \nabla \mu, \quad (4)$$

from which it is clear that the flux arises as a result of the presence in the medium of gradients in the temperature  $\nabla T$  and chemical potential  $\nabla \mu$ ;  $L_1$  and  $L_2$  are kinetic coefficients. In this case,  $\nabla \mu$  has the following meaning. It is assumed<sup>10</sup> that at each level  $z$  in the material the local chemical potential  $\mu(z)$  equals the chemical potential of a system with uniform density  $\rho$  (which is different for each  $z$ ) at the temperature  $T$  in the absence of gravitation. Consequently,  $\mu(z, T) = \mu(\rho(z), T)$  is the equilibrium distribution of chemical potential, implying that  $\nabla \mu$  appears whenever the density profile is out of equilibrium.

Thus, nonequilibrium behavior can arise from the presence of gradients in the temperature and chemical potential. In the first case ( $\nabla \mu = 0$ ) the characteristic time for establishing equilibrium can be written as  $\tau_T \sim \xi^2/a$ , where  $\xi$  is the characteristic scale of nonuniformity, and  $a$  is the thermal conductivity of the material. Since  $a \propto (T - T_c)^{0.6-0.7}$  (see Ref. 2), the equation for the temperature relaxation time takes the form

$$\tau_T \propto (T - T_c)^{-(0.6-0.7)}, \quad (5)$$

from which it is clear that the process slows down as the critical point is approached.

The mechanism for mass transfer near the critical point in the absence of a temperature gradient was investigated by Skripov *et al.*<sup>11</sup> When the system is in a weakly nonequilibrium state, the following expression is obtained for the matter flux:

$$j = -D_0 \text{grad}(\delta\rho),$$

where  $\delta\rho$  is the deviation of the density at a given place from its equilibrium value;  $D_0 = (L_1/\rho^2)k_T^{-1}$ , which has the dimensions  $\text{cm}^2 \cdot \text{s}^{-1}$ , is a coefficient of mass transfer analogous to the diffusion coefficient. As noted above,  $k_T \propto (T - T_c)^{-\gamma}$ ; therefore, we can write for the relaxation time

$$\tau_\mu \propto \xi^2/D_0 \propto (T - T_c)^{-\gamma}. \quad (6)$$

In this case the slowing of the system relaxation is also obvious as the critical point is approached.

There is a body of work in which relaxation of the density takes place according to one of the mechanisms described above. For example, Eremova *et al.*<sup>12</sup> investigated relaxation of nonuniformities in the density of  $^4\text{He}$  by converting the liquid from the two-phase to the one-phase regime near the critical point by rapid heating. The density measurement was based on the dielectric constant of helium placed in the gap of a capacitor with length 1.5 cm, diameter 2 cm; the size of the gap was  $6 \cdot 10^{-3}$  cm. The dependence of the relaxation time on  $(T - T_0)$  was a power law within the limits of the data scatter, with an exponent of 0.5 to 0.75:

$$\tau \propto (T - T_0)^{-(0.5-0.75)},$$

here  $T_0$  is the temperature of the phase transition. The authors proposed that the process was associated with relax-

ation of temperature nonuniformities in the medium surrounding the capacitor and was subject to Eq. (5).

Skripov *et al.*<sup>13</sup> also studied the kinetics of the approach to equilibrium of an initially two-phase system that passes through a critical point and enters a single-phase state. They tracked the relaxation of the density under isothermal conditions by measuring the intensity of scattered light. Except for an initial period during which the system was approaching thermal equilibrium, the time dependence of the scattered light intensity could be approximated by an exponential function. There is a connection between the intensity measured in the experiment and the relaxing parameter  $\rho - \rho_c$ . The temperature dependence of the relaxation time is well described by a power-law function:

$$\tau \propto (T - T_0)^{-\alpha}.$$

Values of  $\alpha$  obtained experimentally for various materials lie in the range 1.0 to 1.05. The authors explained their results by invoking the process of density relaxation under isothermal conditions (6). The difference in the exponents  $\alpha$  and  $\gamma$  was larger than the limits of error of the experiment. The authors explained this difference by noting that the experiments were not carried out on a critical isochor.

It is clear that the processes investigated in these two papers lead to quite different approaches to equilibrium. It would appear that Eremova *et al.*<sup>12</sup> eliminated the influence of the gravitational field by using a measurement cell with small dimensions.

In this paper we propose a new way to study the kinetics of approach to equilibrium near the critical point, in which the relaxation of the system density is determined by monitoring the evolution of internal wave propagation.

Our experiments were performed using a setup that was well described in Ref. 7. By using this setup, we were able to observe internal waves in a material near a critical point for the first time. Our initial results were published in Ref. 14. In these experiments, we first filled the working volume with material at a temperature below  $T_0$ . We then rapidly heated the walls to a temperature  $T$  above  $T_0$  (where  $T_0$  is the transition temperature to the single-phase state). Throughout the rest of the experiment, the temperature of the walls  $T$  was kept constant as we observed the relaxation of the Väisälä-Brunt parameter  $N$  in the working volume. This parameter was determined from Eq. (3) by choosing the frequency of oscillation  $\omega$  of the cylinder and measuring the angle  $\theta$  under these conditions (Fig. 2). This was possible because the times required to measure  $\theta$  as a function of  $\omega$  in this experiment ( $\sim 10$  s) at a given time were much smaller than the characteristic time over which the density profile changes ( $\sim 10^4$  s). Therefore, we can neglect the change in the density profile during a single measurement of  $N$ . Since we have the relation (2) between the value of  $N$  measured in the experiment and the relaxing parameter, we can determine the density profile as a function of time.

The experiments showed that at the end of the process of smearing out the density profile, the function  $N(t)$  had the form

$$N(t) = N(0) \exp(-t/\tau),$$

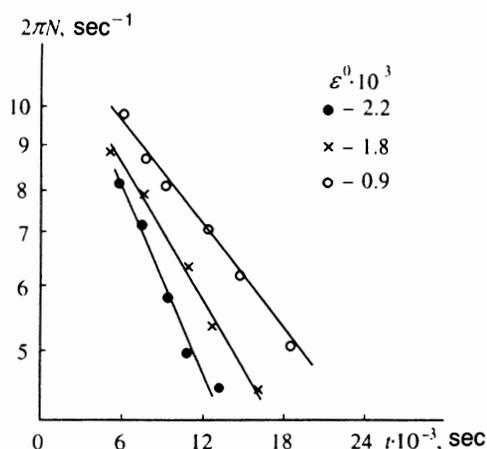


FIG. 3. Dependence of the density gradient of the vapor phase on time and temperature for small departures from equilibrium.

where  $t$  is the time measured from  $t=0$ , at which  $N=N(0)$ , and  $\tau$  is the relaxation time. In Fig. 3 we show the functions  $N(t)$  for various thermostatic control temperatures. We used the slopes of the straight lines to determine the relaxation time as a function of the degree of heating  $\varepsilon^0=(T-T_0)/T_0$ . It should be noted here that the density of the vapor that filled the working volume was below critical in these experiments, so that when the phase transition temperature  $T_0$  was reached, the boundary between the phases moved downwards until only the vapor phase remained in the entire cell. That is, the process took place in the vapor phase.

The temperature dependence of the relaxation time is shown in Fig. 4. Analysis of the results leads us to believe that these quantities are related by a power-law function,

$$\tau(T) = \tau_0 \left[ \frac{T - T_0}{T_0} \right]^{-\delta},$$

where  $\tau_0$  and  $\delta$  are constants;  $\delta$  ranges from 0.9 to 1.0.

Simultaneously with our observations of the density as it relaxed, we studied the evolution of the temperature profile with respect to height in the cell. We found the temperature relaxation time to be an order of magnitude smaller than the density relaxation time in the range of parameters we investigated.

We also investigated the density relaxation near the meniscus (when the density of vapor filling the working volume was close to critical). In Fig. 5 we show an overview of the setup. The working volume 1, which had internal dimensions  $20 \times 10 \times 10 \text{ cm}^3$ , was located in a circulating thermostat 2. System 3 provides circulation of water and maintains the temperature in the thermostat. The setup also includes a system for filling the working volume with Freon-4, a system for measuring the temperature of the water in the thermostat 5 (at different points), and a system for measuring the temperature 6 by recording the signal from 15 semiconductor microresistors positioned along the height of the working volume. The control system 7 serves to switch the electromagnets 8 alternately on and off at the specified frequency, which drives the suspended cylinder 9 into oscillation. The axis of the cylinder is perpendicular to the plane of the fig-

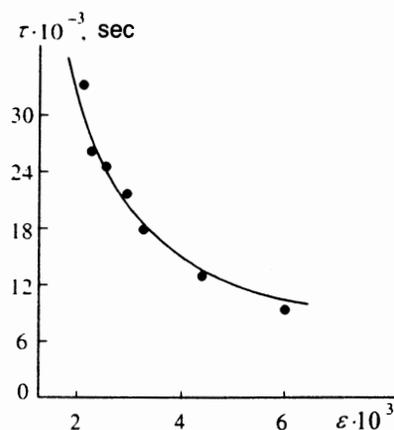


FIG. 4. Dependence of the relaxation time for the density gradient on temperature.

ure, with a length of 9.8 cm; this allows us to treat the wave processes as two-dimensional (the width of the working volume equaled 10 cm). The process was visualized using the Schlieren method through windows 10 at the front and back walls of the working volume.

The experiments were carried out as follows. First, the Freon, the working volume, and the heat-bath liquid were placed in the two-phase state below the phase transition temperature. Since the average density of the vapor filling the working volume was critical in these experiments, the phase transition temperature equaled the critical value  $T_c$ . Therefore,  $\varepsilon$  measures the degree of superheating or underheating. At the beginning of the experiment, rapid heating by the heat-bath liquid occurs. Consequently, the walls of the housing of the working volume reach a temperature  $T$  that is either higher or lower than  $T_c$ ; this wall temperature is kept constant during the entire experiment. At the same time that the heating begins, the temperature measurement system is connected to the working volume. The experiments show that once the apparatus is no longer in contact with the heat bath, convective motion rapidly evens out the temperature in

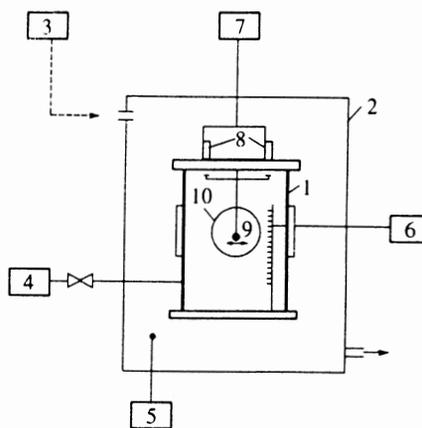


FIG. 5. Diagram of the experimental setup.

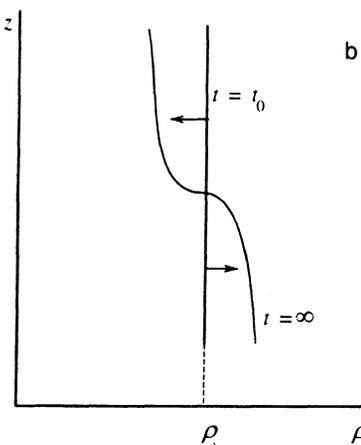
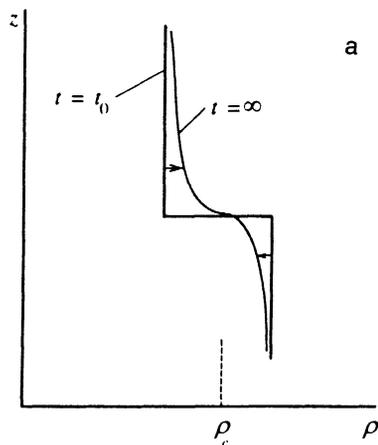


FIG. 6. Sketch of the evolution of the density profile in the presence of a meniscus.

the volume until it equals the wall temperature  $T$ . After a time  $t_0$ , the convection disappears; at this time, a uniform density profile is established in the material when it is superheated above  $T_c$  ( $\varepsilon < 0$ ), or a step-like profile when it is underheated ( $\varepsilon > 0$ ). For  $t > t_0$  there are no longer any temperature gradients in the medium, and the density relaxation proceeds to the equilibrium state. A sketch of the changes in the density are shown in Fig. 6 (a— $\varepsilon > 0$ , b— $\varepsilon < 0$ ). In this case the parameter  $N$  also reaches its equilibrium value  $N_0(\varepsilon)$ . Experiments carried out at various degrees of departure from the critical point show that during the initial period the function  $N(t)$  has the following form (the measurements were carried out between 1 and 3 cm above the level of the meniscus):

$$N(\varepsilon, t) = N_0(\varepsilon) [1 - \exp(-(t - t_0)/\tau(\varepsilon))], \quad t > t_0.$$

Figure 7 shows the experimental dependence of  $\tau$  on  $\varepsilon$ . It is clear that this dependence has no anomalies except for a small increase in the neighborhood of the critical temperature. This fact is explained as follows: in these experiments the density profile is fairly far from equilibrium, and the linear approximation for the mass flux becomes incorrect, i.e., it is necessary to include the nonlinear terms. In the experiment we observed only the initial portion of the den-

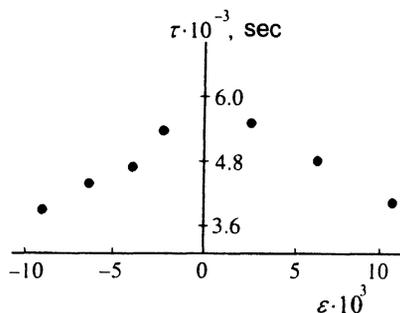


FIG. 7. Initial stage of the relaxation process of the density profile for large departures from equilibrium.

sity relaxation process, in a region where the system is far from equilibrium, i.e., the immediate vicinity of the meniscus. The large departure of the density from equilibrium in the working volume suppresses effects associated with proximity to the critical temperature; hence, the relaxation time during the initial phase does not depend strongly on  $\varepsilon$ . As for the nonlinearities, if we include the next nonzero terms of the expansion in the expression for the mass flux  $j$ , we obtain<sup>11</sup>

$$D = D_0 + D_1,$$

where

$$D_1 \sim \left( \frac{\partial^3 P}{\partial w^3} \right)_{T_c} (\Delta w)^2,$$

$w$  is the specific volume,  $\Delta w = w - w_c$ . The value of  $(\partial^3 P / \partial w^3)_T$  is given in Skripov's book,<sup>11</sup> where we find that  $D_0$  and  $D_1$  are comparable even for  $\Delta w = 0.01 w_c$ .

## 5. CONCLUSION

Thus, we have shown the effect of a gravitational field on several of the processes that take place in materials with near-critical state parameters. We have demonstrated that gravitation has a decisive influence on these processes at temperatures sufficiently close to the critical point. This influence can be so dominant that it amounts to a change in the physical state of the material.

The author is grateful to A. A. Borisov and Al. A. Borisov for their collaboration with him in Refs. 4 and 7, and for useful discussions.

<sup>1</sup>M. A. Anisimov, Usp. Fiz. Nauk **114**, 249 (1974) [Sov. Phys. Usp. **17**, 722 (1974)].

<sup>2</sup>H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Clarendon Press, Oxford (1971).

<sup>3</sup>J. V. Sengers and V. J. Van Leeuwen, Physica **116** A, 345 (1982).

<sup>4</sup>A. A. Borisov, Al. A. Borisov, and Yu. G. Leonenko, MZhG **4**, 134 (1991).

<sup>5</sup>J. Lighthill, *Waves in Fluids*, Cambridge Univ. Press, New York (1980).

<sup>6</sup>D. E. Mowbray and B. S. H. Rarity, J. Fluid Mech. **28**, 1 (1967).

<sup>7</sup>Al. A. Borisov, A. A. Borisov, and Yu. G. Leonenko, Sib. Fiz.-Tekh. Zhurnal **4**, 27 (1991).

- <sup>8</sup>M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* [in Russian], Nauka, Moscow (1987).
- <sup>9</sup>H. L. Lorentzen, *Acta Chem. Scand.* **7**, 1335 (1953).
- <sup>10</sup>J. V. Sengers and J. M. H. Sengers, in *Progress in Liquid Physics*, C. A. Croxton (ed.), New York (1978), p. 103.
- <sup>11</sup>V. P. Skripov, *Metastable Liquids* [in Russian], Nauka, Moscow, 1978.
- <sup>12</sup>R. I. Efremova and É. V. Matizen, *JETP Lett.* **35**, 281 (1982).
- <sup>13</sup>V. P. Skripov, V. S. Vitkalov, and Yu. D. Kolpakov, *Zh. Fiz. Khim.* **54**, 1754 (1980).
- <sup>14</sup>Al. A. Borisov, A. A. Borisov, and Yu. G. Leonenko, in *Experimental Heat Transfer, Fluid Mechanics, and Thermodynamics, 1991*, J. F. Keffer, R. K. Shah, and E. N. Ganic (eds.), Elsevier, Amsterdam (1991), p. 1028.

Translated by Frank J. Crowne