

# RAREFACTION WAVES IN LIQUID AND GAS-LIQUID MEDIA

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## *Introduction*

In recent years the thermodynamics of a substance having parameters close to critical values has attracted considerable attention from physicists, physicochemists, and thermal physicists. One can single out two basic reasons stimulating the increased interest in this problem:

1. Since the mid-1950s, the findings of experimental studies have gone beyond the scope of the existing concepts based on the van der Waals equation for real gas.
2. The processes occurring in the apparatuses of interior ballistics, nuclear power, and chemical technology lie in wide ranges of temperature and pressure, including the critical state of a working body.

The thermodynamics of a substance in the critical state has been extensively studied, and a strong dependence of the thermodynamic parameters on the temperature and pressure near the critical point has been revealed. However, processes such as heat exchange and finite-amplitude waves (shock waves) have not been as thoroughly investigated in the region of the critical point. In fact, the question of the dynamics of finite-amplitude perturbations of pressure, density, and temperature in the critical region has not been considered at all. One should mention just one study devoted to shock waves near the critical point, namely that by Zel'dovich (1946), who analyzed the entropy condition for shock-wave stability and theoretically the possible existence of rarefaction shock waves. The effect of the sign of  $(\partial^2 P / \partial V^2)_S$  on the structure of compression and rarefaction waves was discussed by Thompson & Lambrakis (1973).

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In practice, there are no theoretical or experimental works dealing with the propagation of finite-amplitude waves near the critical point. This situation may be explained by the difficulties involved in solving the thermodynamic equations when the singular behavior of the thermodynamic parameters (heat capacity, compressibility, etc.) at the critical point is taken into account. Possibly, experimental work on the propagation of finite-amplitude waves near the critical point has been complicated by the difficulties encountered by the experimentalist in obtaining the critical state in a measurement cell having a considerable length (several meters).

The peculiarity of the critical point lies in the fact that even small perturbations of the parameters of a medium lead to a qualitative change in the character of the anomalies of the thermodynamic parameters because of the infinite "susceptibility" near the critical point. The anomalies observed in that vicinity—opalescence, complete light absorption, dramatic growth of sound absorption, infinite increase of heat capacity—are of great interest for a researcher. The nonanalytic character of the change in the physical properties near the critical point, and the universality in the behavior of both the equilibrium and kinetic quantities of substances different in nature, make the critical point an object of great concern for those fields of physics where cooperative effects determine the character of a phenomenon (nuclear physics, elementary-particle physics, biophysics).

Before we discuss the propagation processes of finite-amplitude waves in the critical region, we first consider briefly the properties of a substance in this region, since it is clear that the final solution will depend on the parameters of the unperturbed state, critical or near-critical in our case.

### *Thermodynamic Properties of a Substance Near the Critical Point*

In the 1960s, Widom (1965), Kadanoff (1966), and Patashinsky & Pokrovsky (1966) suggested the thermodynamic law of corresponding states near the critical point. According to the statistical hypothesis of similarity, the nonanalytic (singular) part of the free energy is assumed to be a generalized homogeneous function of its argument. It may, therefore, be represented as a function of one variable that is a combination of temperature and density. In this case, the asymptotic behavior is described by simple power laws. The hypothesis of similarity results in functional relationships between the power indices.

L. Kadanoff, A. Z. Patashinsky, and V. L. Pokrovsky have advanced the hypothesis of similarity of critical fluctuations, linking the law of corresponding states in thermodynamics and between the critical indices to the behavior of correlation functions in the critical region. They have

assumed the correlation functions to be homogeneous in their arguments near the critical point. The similarity hypothesis states that the singular dependence of the physical quantities on the temperature and density is a consequence of the divergence of the correlation radius, since this radius is the only significant scale for a nonanalytic change. The physics of critical phenomena is explained by large regions having the same density rather than by details in the behavior of the density on large scales. The similarity hypothesis was discovered and generalized by Migdal (1968) and Polyakov (1968) using the methods of quantum field theory. Wilson (1971) succeeded in obtaining the formalism allowing an explicit calculation of the critical indices, which was referred to as the renormalization-group method. One consequence of the equations of the renormalization group, in addition to the similarity laws, is the universality principle.

For kinetic coefficients, the divergence was accounted for by Kawasaki (1966) by means of the dynamic hypothesis of similarity and the theory of interacting modes. Indeed, near the critical point the density fluctuations are very intensive, and the velocity gradient created by viscous shear forces at the fluid boundary leads easily to the homogeneity in density. When the fluid returns to a homogeneous condition, energy is dissipated. This may be interpreted as a consequence of interaction between the viscous and acoustic modes, and an abnormally large viscosity occurs as a result.

Near the critical point the isochoric heat capacity  $C_V/T \sim \partial^2 P / \partial T^2$  is temperature dependent as  $|T - T_c|^{-\alpha}$ . The compressibility is given by  $\partial \rho / \partial \mu = \rho \partial \rho / \partial P = |T - T_c|^{-\gamma}$ , where the most probable values for the exponents are  $\alpha = 0.12$  and  $\gamma = 1.23$ , according to Anisimov (1974).

**VELOCITY AND ABSORPTION OF SOUND WAVES** In what follows we discuss the propagation of finite-amplitude compression waves of arbitrary duration. In accordance with its Fourier expansion, such a wave may be represented as a set of harmonics of different small-amplitude frequencies, i.e. as a set of sound waves. The regularities of the propagation of these waves near the critical point are therefore of interest.

The experiments performed by Schneider (1951) are likely to be among the fundamental studies on the measurement of ultrasound at the critical point. Schneider investigated the velocity and absorption of ultrasonic waves in overheated and saturated vapors of  $\text{SF}_6$  and discovered the minimum ultrasonic velocity at this point. In this work he also measured the damping per wavelength at a frequency of 0.6 MHz and found an abnormally high value in the vicinity of the critical point.

As Botch & Fixman (1965) assumed, the observed damping is due to the dynamic heat capacity connected with large-scale density fluctuations. For numerical calculations they used Ornstein-Zernike's equation for the

correlation function and the Debye form of a dependence of correlation length on temperature. The damping per wavelength  $\alpha_i = \alpha\lambda = \alpha c/f$ , found from the imaginary part of the complex sound velocity, has the form  $\alpha_i \sim \omega^{-0.25} \cdot I_2(t, \omega)$ , where the obtained integral  $I_2$  is a rapidly varying function of the temperature  $t$  and is very weakly dependent on the frequency  $\omega$ .

The expression for the classical damping, complemented by the bulk viscosity  $\xi$ , is of the form

$$\alpha = \alpha_{\text{clas}} + \frac{2\pi^2 f^2 \xi}{\rho c^3} = 2\pi^2 f^2 [4\eta/3 + \xi + \kappa(c_v^{-1} - c_p^{-1})]/\rho c^3.$$

The main contribution to sound absorption is determined by the term  $\frac{4}{3}\eta + \xi$ , since in the frequency band we are concerned with the role of the term  $\kappa(c_v^{-1} - c_p^{-1})$  seems to be insignificant. Kadanoff & Martin (1963) have derived an expression for the low-frequency and long-wave limits of this quantity:

$$\lim_{\omega \rightarrow 0} \lim_{q \rightarrow 0} \omega^2 q^{-4} \text{Im} [c(q, \omega)] = \frac{4}{3} \eta + \xi.$$

Here  $\text{Im} [c(q, \omega)]$  is the imaginary part of the double Fourier transform of the dynamic correlation function for the density fluctuation

$$\langle [\rho(r, t) - \langle \rho(r, t) \rangle] [\rho(0, 0) - \langle \rho(0, 0) \rangle] \rangle.$$

Kadanoff & Swift (1968) and Kawasaki (1966) have calculated the functional form of  $\frac{4}{3}\eta + \xi$  using the schemes of interaction between modes, including the thermal and sound modes as intermediate states.

The situation is complicated by the fact that there are at least three isolated frequency regions. In region I (the lowest frequencies  $\omega \leq \omega_1 = \kappa/\rho c_p \xi^2$ ) the sound wave splits into two thermal modes, and as a result, damping is characterized by a very strong divergence (approximately as  $t^{-2}$ ) and a quadratic dependence on the frequency. In regions II and III ( $\omega_1 \ll \omega \ll c/\xi$ ) Kadanoff & Swift (1968) predict that  $\alpha \sim \omega^2 t^{-\nu-\alpha} \sim \omega^2 t^{-2/3}$ . Kawasaki (1966), however, indicates a different behavior in these two regions: In region II ( $\omega_1 \ll \omega \ll \omega_2$ ), damping of the sound wave is still connected with the contribution of thermal modes to the bulk viscosity, but  $\alpha \sim t^2$  and thus is not dependent on the frequency  $\omega$ ; in region III ( $\omega_2 \ll \omega \ll c/\xi$ ), sound waves are a dominant intermediate state and  $\alpha \sim \omega^2 t^{-2/3}$ , just as in Kadanoff's study. The characteristic frequencies  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  are temperature dependent, and, according to Kawasaki's approximate estimation, they change, respectively, as  $a_1 t^2$ ,  $a_2 t^{4/3}$ , and  $a_3 t^{2/3}$ , where  $a_1$ ,  $a_2$ , and  $a_3$  are roughly equal to 10 MHz. Hence,

region I usually lies below the ultrasonic frequencies, and the upper limit of  $c/\xi$  is obviously above these frequencies for all the interesting and accessible values of  $\omega$ . Summing up the above, we obtain

$$\text{Region I } \omega < \omega_1: \quad \alpha \sim \omega^2 t^{-2},$$

$$\text{Region II } \omega_1 \ll \omega \ll \omega_2: \quad \alpha \sim \omega^0 t^2,$$

$$\text{Region III } \omega_2 \ll \omega \leq c/\xi: \quad \alpha \sim \omega^2 t^{-2/3}.$$

We should note that as the critical point is approached,  $\omega_2$  rapidly decreases and the experimental frequency can shift from region II to region III. This means that when both terms have comparable magnitudes, one can expect a complex dependence of the form  $\alpha \sim A\omega^2 t^{-2/3} + Bt^2$ . We should also mention that the expression for absorption holds only when  $\omega\tau_{\text{therm}} \gg 1$ , where  $\tau_{\text{therm}} = \rho c_V / \kappa q^2$  is the characteristic time of heat transfer,  $\kappa$  is the coefficient of heat conduction, and  $q$  is the wave number. The condition  $\omega\tau_{\text{therm}} \gg 1$  is closely connected with the condition of the adiabatic nature of a sound wave.

**FINITE-AMPLITUDE WAVES NEAR THE CRITICAL POINT** Fisher (1957) and Kamensky & Pokrovsky (1969) have treated theoretically questions dealing with the peculiarity of the propagation of finite-amplitude perturbations of pressure in a substance near the thermodynamic critical point. We are not aware of any experimental studies on this subject in the literature. Considering the behavior of the speed of sound in the critical region, Fisher (1957) analyzed the critical point and the critical adiabat. The shock waves in a supercritical state were qualitatively shown to have no peculiarities in their propagation. In a rarefaction wave the system will split into two phases, followed by a change in the state along the coexistence curve, and the behavior of the wave must depend considerably on the amplitude. A rarefaction wave of very small amplitude (sound) cannot propagate at the critical point, since  $(\partial P / \partial \rho)_s = 0$ . If, therefore, one attempts to excite sound using a harmonic source, the system in a critical state will serve as an "acoustic diode": All the compression half-waves will be transmitted, whereas all the rarefaction waves will be "cut." With sound of small but finite amplitude, the propagation of rarefaction waves seems to be possible, but their velocity will be very low and will be considerably different from that of compression waves. The signals from the harmonic source will, therefore, be generated as a very complex nonlinear wave, with breaks in it from the very beginning. Kamensky & Pokrovsky (1969) have shown that if a phase transition from a one-phase to a two-phase state occurs in the sound wave, then the problem becomes nonlinear, even for small amplitudes, owing to a jump in the speed of

sound on the phase coexistence curve. As a result, the “acoustic-diode” effect has been calculated quantitatively.

In Jouguet’s formula the subscripts 1 and 2 designate the parameters of a substance prior to and after the wave, respectively. The conjectural closeness of the Poisson adiabat to the Hugoniot shock adiabat for a weak wave permits the following two conditions to be regarded as satisfied: (a) the thermodynamic shock-wave possibility condition  $S_2 > S_1$ , and (b) the mechanical shock-wave stability condition  $c_1 + u_1 < D < c_2 + u_2$ , where  $c$ ,  $u$ , and  $D$  are the speed of sound, the wave velocity, and the medium velocity, respectively. The minimum value of heat capacity at which the existence of rarefaction shock waves is possible is equal to  $80 \text{ J mol}^{-1} \text{ K}^{-1}$ . In Figure 1 the regions are shown in coordinates  $P, V$ , where  $(\partial^2 P / \partial V^2)_S < 0$ . According to Borisov & Khabakhpashev (1982), increasing the molar heat capacity increases the rarefaction shock wave existence region.

Novikov (1948) analyzed one more possibility for the existence of rarefaction shock waves, which is referred to the region of two-phase states of a substance, namely to the flow of wet steam. During the heat-insulated reversible flow of wet steam, its state changes according to the adiabat

$$dP/dV = -\gamma P/V.$$

In this equation,  $\gamma$  and  $V$  are the adiabatic exponent and the specific volume for wet steam, respectively. Differentiating with respect to  $P$  at

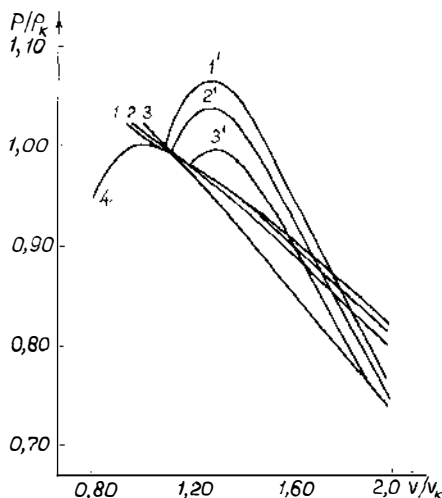


Figure 1 Regions of abnormal thermodynamic properties. 1':  $-c_v = 40$ , 2':  $-c_v = 32$ , 3':  $-c_v = 24$ ; curves 1, 2, and 3 are the adiabats of van der Waals gas that correspond to these heat capacities; curve 4 denotes the boundary of the two-phase region.

$S = \text{constant}$ , we get

$$(\partial^2 P / \partial V^2)_S = V[(\gamma + 1)/P + (\partial\gamma / \partial P)_S] / \gamma^2 P.$$

An analysis of the experimental data for water vapor shows that for pressures from  $P_c = 22.5$  MPa to  $P = 21.5 \pm 0.21$  MPa, we have  $\partial\gamma / \partial P < -(\gamma + 1)/P$  and thus  $(\partial^2 P / \partial V^2)_S < 0$ ; thus the rarefaction shock wave can exist.

Fortov & Krasnikov (1970) calculated the shock adiabats of cesium at the parameters typical for shock tubes with heating. In the range of experimentally accessible parameters, an adiabat has an inflection caused by the cesium excitation and ionization processes.

Kahl & Mylin (1969) considered the question of the possible existence of rarefaction shock waves in a van der Waals–Maxwell fluid and concluded that their existence in any phase or in a two-phase state is impossible. However, they pointed out that a rarefaction shock wave can exist in the range of parameters very close to the critical ones at  $c_p^* \geq 16.65$  and at  $c_p^* \geq 86$  in the two-phase medium. Existence of a rarefaction shock wave depends on the equation of state and on the specific heat at constant volume  $c_v$ . The form of the specific heat used here takes into account the translational, rotational, and vibrational energy of the molecules. The disadvantage of this work is that the abnormal increase of  $c_v$  in the vicinity of the critical point is neglected.

One should also mention Thompson's (1971) studies. He has analyzed the structure of the steady isentropic gas flow in a nozzle and of Prandtl–Meyer flow with  $(\partial^2 P / \partial V^2)_S < 0$ . Based on calculations using tabular data, Lambrakis & Thompson (1972) identified a number of high-molecular substances (hydrocarbons and fluorocarbonic compounds) whose range of abnormal thermodynamic properties includes the critical isotherm. Using the first integral of the Navier–Stokes one-dimensional equation, Thompson & Lambrakis (1973) found the structure of a plane stationary rarefaction wave in general form.

For media with arbitrary equations of state, Galin (1958, 1959) showed that if  $(\partial^2 P / \partial V^2)_S$  changes sign, it is impossible to answer unambiguously the question of the possible existence of compression and rarefaction shock waves for the whole region. Shock transitions were shown to be possible only when the shock adiabat does not lie in the  $(V, P)$  plane to the right of a vector drawn from the initial to the final state. For the general case, the wave adiabat was constructed by Sidorenko (1968). He showed that if the wave adiabat has two points of inflection, then there exist two shock waves linked by a continuous wave or two continuous waves separated by a shock wave. This conclusion was based on theorems that he proved later (Sidorenko 1982).

Thus, an analysis of the experimental and theoretical studies devoted to the behavior of a substance in the region of the thermodynamic critical point enables the following conclusions to be drawn:

1. In the range of temperatures and densities of a substance close to the critical values ( $T \lesssim T_c, \rho \lesssim \rho_c$ ), the behavior of the substance is well described by the van der Waals equation of state, and by the scaling equation of state in the immediate vicinity of the critical point ( $T \approx T_c, \rho = \rho_c$ ). The anomalies of the thermodynamic quantities in the asymptotic region ( $T \rightarrow T_c, \rho \rightarrow \rho_c$ ) are described by simple power laws. The critical exponents are universal for different substances.
2. Experiments on sound speed and absorption in the critical region indicate the availability of a minimum of the speed of sound at  $T = T_c$ . In the vicinity of the critical point the speed of sound slows down as the pressure decreases, while the absorption of sound waves depends on both the frequency and the temperature difference.

A theoretical and experimental investigation of the dynamics of finite-amplitude waves near the critical liquid-vapor point would be of extreme interest. The evolution of the initial signal should be strongly dependent on the values of the thermophysical parameters, which show unusual behavior near the critical point.

### *Experimental Study of Finite-Amplitude Waves Near the Critical Point*

Compression waves in media near the critical point can be of considerable length (up to a few tens of centimeters). Thus for an experimental study of the dynamics of compression and rarefaction waves, the length of a test section—the shock tube—must constitute a few meters.

The maximum sizes of the cells that have been used so far for the measurement of the thermodynamic properties of substances close to the critical point have been no more than a few centimeters, and hence the mass of the substances studied has been no more than a few tens of grams.

In the experiments under discussion, it was important to ensure highly accurate temperature control of the test section. For this purpose, the shock tube was contained in a closed hydrodynamic system. The experimental set-up was described in detail by Borisov et al. (1983).

The experiments demonstrated for the first time the existence of non-broadening rarefaction waves in a substance at near-critical conditions. Figure 2 illustrates the structure of rarefaction waves in Freon-13. The oscilloscope traces in Figure 2*A* were triggered simultaneously. In Figure

2B the triggering of trace 4 with respect to trace 3 was done with a time delay of  $3.8 \times 10^{-2}$  s. From the oscillograms in Figure 2, the velocity of the rarefaction shock wave is calculated to be  $50 \text{ m s}^{-1}$  under the given initial conditions. The width of the rarefaction shock wave is  $33.7 \times 10^{-3} \text{ m}$ . This value of the width is in agreement with the theoretical estimates given below. The initial parameters of the substance in front of the rarefaction wave were chosen near the thermodynamic critical point of Freon-13. From the Figure 2 oscillograms it can be seen that the rarefaction wave propagates as a surface of sudden, very sharp change in the state of the substance (pressure) followed by a gradual change.

In the theory of nonlinear waves (Whitham 1974), the steady state of a

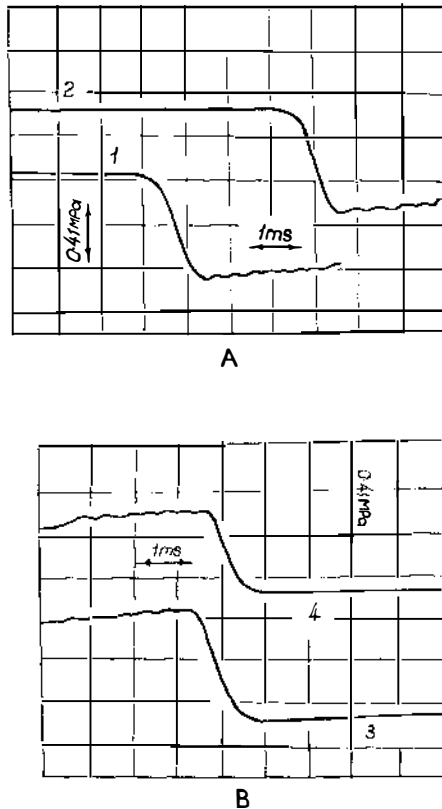


Figure 2 The evolution of a rarefaction shock wave in Freon-13 near the critical point. Curves 1, 2, 3, and 4 correspond to the transducers placed at a distance of 0.15, 0.30, 0.45, and 2.35 m from the diaphragm, respectively.

shock wave is characterized by the time  $\tau = \Delta P / (dP/dt)_{\max}$ , where  $\Delta P$  is the amplitude difference and  $(dP/dt)_{\max}$  is the maximum steepness of the wave profile. This time must be short compared with the characteristic propagation time  $t_p$  of a wave in a shock tube. In our case the ratio  $\tau/t_p$  is quite small ( $1.35 \times 10^{-2}$ ). The values of  $\Delta P$  and  $(dP/dt)_{\max}$  for the wave profiles shown in Figure 2 were determined by numerical differentiation of the curves  $P(t)$ .

In the wave-propagation process, the time  $\tau$  remained unchanged and was  $6.75 \times 10^{-4}$  s. In addition, during the experiments it was also established that the steepness of the rarefaction wave had not changed after traveling through the high-pressure chamber. In these experiments both the initial state of the substance and the state of the substance in the wave itself were always in a one-phase region near the critical point. Thus our experiments clearly demonstrated that the observed phenomenon is the rarefaction shock wave, defined by Ya. B. Zel'dovich as a surface of sudden, very sharp change in the state of a substance that propagates relative to the unperturbed substance.

To confirm that negative shock waves exist only in the critical region, experiments were performed on the evolution of rarefaction waves far from the critical point in Freon-13 and in nitrogen. We present here some of the results. The initial parameters ahead of the wave were chosen far from the critical point, as  $T/T_c = 0.98$ ,  $P/P_c = 0.83$ ,  $\rho/\rho_c = 0.465$  for Freon-13 (Figure 3). As expected, in none of the experiments did rarefaction shock waves develop. During its evolution, the rarefaction wave



Figure 3 The structure of a rarefaction wave in Freon-13 outside the abnormal region. Here  $P_0 = 3.30$  MPa,  $\rho_0 = 270$  kg m $^{-3}$ ,  $T_0 = 295.15$  K. Curves 1, 2, and 3 correspond to transducers at distances of 0.15, 0.45, and 2.35 m from the diaphragm, respectively.

spreads in such a way that over the same distances as in Figure 2, its steepness is reduced by a factor of five or more.

Experiments performed at different times gave good agreement for all oscillograms.

### *Theory of the Evolution of Finite Perturbations Close to the Critical Liquid-Vapor Point*

It is known that near the thermodynamic critical point, compressibility, heat capacity, and kinetic coefficients become abnormally high, and they tend to infinity when the thermodynamic variables are exactly at the critical point. Under conditions near the critical state, the medium becomes very sensitive to external thermal or dynamic perturbations, and the anomalies in turn have a strong effect on the structure of these perturbations.

Consider the propagation of finite perturbations of pressure, density, or particle velocity in a medium whose initial state is close to the critical point. The perturbations are assumed to be long wave, i.e. the correlation radius is much smaller than the characteristic length of the perturbations. In this case, the contribution from relaxation processes is significantly smaller than that of dissipation.

The complete set of equations describing the motion of the medium near the critical point has, in the hydrodynamic approximation, the form

$$\rho[v_t + (v \nabla)v] = -\nabla P + \eta \Delta v + \left( \xi + \frac{\eta}{3} \right) \text{grad div } v,$$

$$\rho T[S_t + (v \nabla)S] = \kappa \Delta T + \xi (\text{div } v)^2 + \frac{\eta}{2} \left( \frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} - \frac{2}{3} \delta_{ik} \frac{\partial v_c}{\partial x_c} \right)^2,$$

$$P = P(\rho, S),$$

$$\rho_t + \text{div } \rho v = 0,$$

where  $S$  is the entropy,  $P$  the pressure,  $\rho$  the density, and  $v$  the velocity of the medium in laboratory coordinates  $(x, t)$ . Here and in what follows, suffixes  $t$  and  $x$  indicate partial derivatives.

**DERIVATION OF AN EQUATION FOR PERTURBATIONS PROPAGATING IN ONE DIRECTION** We assume that the relative deviations  $(P - P_0)/P_0$ ,  $(\rho - \rho_0)/\rho_0$ , and  $(v - v_0)/c_0$  from the equilibrium values  $P_0$ ,  $\rho_0$ , and  $v_0$ , which are caused by the wave, are quantities of the first order of smallness  $\mu$ . In addition, we assume the dissipative effects to also be small, i.e.  $\xi$ ,  $\eta$ ,  $\kappa \sim \mu$ . Neglecting in the original set of equations the terms exceeding the

second order of smallness, we reduce this system to the form

$$(\rho' + \rho_0) \frac{\partial v'}{\partial t} = -\nabla P' + \left( \xi + \frac{\eta}{3} \right) \nabla(\nabla v'),$$

$$\rho_0 T_0 \frac{\partial S'}{\partial t} = \kappa \nabla^2 T',$$

$$\frac{\partial \rho'}{\partial t} + \rho_0 \nabla v' = 0,$$

$$P' - \left( \frac{\partial P}{\partial \rho} \right)_s \rho' + \frac{1}{2} \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s \rho'^2 + \left( \frac{\partial P}{\partial S} \right)_p S'.$$

Expressing  $T'$  via pressure

$$T' = P' \left( \frac{\partial T}{\partial P} \right)_s$$

and substituting it into the Laplacian of the equation of heat conduction, we obtain

$$\rho_0 T_0 \frac{\partial S'}{\partial t} = \kappa \left( \frac{\partial T}{\partial P} \right)_s \nabla^2 P'.$$

From the equation of motion, we have

$$\rho_0 \frac{\partial}{\partial t} \nabla v' = -\nabla(\nabla P') + \frac{\partial}{\partial t} O(\mu^2).$$

Taking into account that  $\nabla(\nabla P') = \nabla^2 P'$ , we obtain

$$\rho_0 T_0 \frac{\partial S'}{\partial t} = -\kappa \left( \frac{\partial T}{\partial P} \right)_s \rho_0 \left[ \frac{\partial}{\partial t} \nabla v' + \frac{\partial}{\partial t} O(\mu^2) \right].$$

Since  $\kappa O(\mu^2) = O(\mu^3)$ , the latter equation may be integrated as follows:

$$S' = -\frac{\kappa}{T_0} \left( \frac{\partial T}{\partial P} \right)_s \nabla v'.$$

Then the equation of state takes the form

$$P' = c_0^2 \rho' - \frac{\kappa}{T_0} \left( \frac{\partial P}{\partial S} \right)_p \left( \frac{\partial T}{\partial P} \right)_s \nabla v' + \frac{1}{2} \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s \rho'^2, \quad (1)$$

where

$$c_0^2 = \left( \frac{\partial P}{\partial \rho} \right)_s; \quad P' = P - P_0, \quad \rho' = \rho - \rho_0,$$

$$v' = v - v_0, \quad v_0 = 0.$$

Further we consider only the propagation of plane waves, since in the shock-tube experiment this case has the most applicability. However, we note that the assumptions will be valid for cylindrically and spherically symmetrical waves. In these cases also, a single equation may be obtained for the perturbed values.

Thus, retaining terms of the second order of smallness in the equation of motion and continuity and replacing the pressure using the equation of state, we obtain the following set of equations for plane waves:

$$(\rho_0 + \rho')v'_t + \rho_0 v' v'_x = -c_0^2 \rho'_x - \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s \rho' \rho'_x + b v'_{xx}, \quad (2)$$

$$\rho'_t + (\rho_0 + \rho')v'_x + v \rho'_x = 0, \quad (3)$$

where

$$b = \xi + \frac{4}{3} \eta + \frac{\kappa}{T_0} \left( \frac{\partial P}{\partial S} \right)_\rho \cdot \left( \frac{\partial T}{\partial P} \right)_S.$$

By differentiating (2) with respect to  $x$  and (3) with respect to  $t$ , then eliminating  $v'_{xt}$  from the resulting equation using the substitutions  $v' = c_0 \rho' / \rho_0$ ,  $\rho'_t = -\rho_0 v'_x$  in the terms of second order of smallness, we obtain a hyperbolic wave equation for  $\rho'$ :

$$c_0^2 \rho'_{xx} + \frac{2c_0^2}{\rho_0} \left[ 1 + \frac{\rho_0}{2c_0^2} \cdot \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s \right] (\rho' \rho'_x)_x = \rho'_{tt} + \frac{b c_0}{\rho_0} \rho'_{xxx}.$$

This equation describes the propagation of nonlinear waves in both directions and enables us to solve problems dealing with wave interactions. However, in what follows we analyze only waves that propagate in one direction. In the experiment, this corresponds to a rarefaction wave forming after the bursting of the diaphragm separating the low- and high-pressure chambers.

Considering perturbations that propagate in one direction  $x > 0$ , we search for the solution to the last set of equations, again to second order, using the method of Khokhlov (1961). Because of the weak nonlinearity of the processes under consideration, the perturbations of velocity and

density,  $v'$

coordinates, so that  $v'$  and  $\rho' = F(\mu x, t - x/c_0)$ . This means that the perturbations change their shape only slowly as they evolve in the  $x$ -direction.

In this case, Equations (2) and (3) in the variables  $z = \mu x$ , take the form

$$\mu c_0^2 \frac{\partial \rho'}{\partial x} - c_0 \frac{\partial \rho'}{\partial \tau} + (\rho_0 + \rho') \frac{\partial v'}{\partial \tau} - \frac{\rho_0}{c_0} v' \frac{\partial v'}{\partial \tau} - \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s \frac{\rho'}{c_0^2} \frac{\partial \rho'}{\partial \tau} = - \frac{b}{c_0^2} \frac{\partial^2 v'}{\partial \tau^2},$$

$$\mu \frac{\partial v'}{\partial x} - \frac{\partial \rho'}{\partial \tau} \left( \frac{v'}{c_0} \right) = \frac{1}{c_0} \frac{\partial v'}{\partial \tau}$$

The equations describing the evolution of  $v'$  and  $\rho'$  must be of similar form, since they are characteristic of the same wave process. In this case, the nonlinear relations of the type  $v' = \rho' c_0 / \rho_0$  must be complemented by terms of the second order of smallness and by some derivatives with unknown coefficients  $a$  and  $d$  such that  $a \sim 1$ ,  $d \sim O(\mu)$ , i.e.

$$\rho' = \frac{\rho_0}{c_0} v' + \frac{a \rho_0}{c_0} v'^2 + \frac{d \rho_0}{c_0} \frac{\partial v'}{\partial \tau},$$

$$v' = \frac{c_0}{\rho_0} \rho' - \frac{a c_0}{\rho_0^2} \rho'^2 - \frac{d c_0}{\rho_0} \frac{\partial \rho'}{\partial \tau}.$$

By substituting now the perturbation of the velocity  $v'$  density, i.e.  $v = f_1(\rho')$

equation of continuity, we get

$$\mu \frac{c_0}{\rho_0} \frac{\partial \rho'}{\partial x} - 2 \frac{\rho'}{\rho_0^2} \frac{\partial \rho'}{\partial \tau} \left[ a c_0 + \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s \frac{\rho_0}{2 c_0^2} \right] = \left[ \frac{b}{c_0^2 \rho_0} + d \right] \frac{1}{\rho_0} \frac{d^2 \rho'}{d \tau^2},$$

$$\mu \frac{\partial v'}{\partial x} - \frac{v'}{c_0^2} \frac{\partial v'}{\partial \tau} = \frac{d}{c_0} \frac{\partial^2 v'}{\partial \tau^2}$$

From a comparison of coefficients of the nonlinear and dissipative terms, we find

$$a = \frac{1}{2 c_0} - \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s \frac{\rho_0}{4 c_0^3}; \quad d = - \frac{b}{2 \rho_0 c_0^2}.$$

Substituting  $a$  and  $d$  into the equation for the velocity perturbation, we obtain

$$\mu v'_x - \left[ 1 + \frac{\rho_0}{2 c_0^2} \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s \right] \frac{v'}{c_0^2} v'_\tau = \frac{b}{2 \rho_0 c_0^3} v'_\tau \tau. \quad (4)$$

We have now obtained the Burgers equation, written in a coordinate system moving with velocity  $c_0$ . The equations for the perturbations  $P'$  and  $\rho'$  are obtained from (4) by replacing  $v'$  by  $(P'/\rho_0 c_0)v'$  and  $c_0 \rho'/\rho_0$ , respectively. For ideal gases the expression in square brackets is simply  $(\gamma + 1)/2$ . For real gases, however, the second derivative near the critical point has the abnormal form  $(\partial^2 P/\partial \rho^2)_s < 0$ , and the overall expression in the brackets may become negative. In this case, Equation (4) describes the evolution of a rarefaction shock wave. In fact, in the laboratory system of coordinates, Equation (4) for the pressure can be rewritten as

$$P_t + c_0 P_s + \frac{1}{2\rho_0^3 c_0^2} \left( \frac{\partial^2 P}{\partial V^2} \right)_s P P_s / \rho_0 c_0 = \frac{P_{xx}}{2\rho_0} \left[ \frac{4}{3} \eta + \xi + \kappa (c_v^{-1} - c_p^{-1}) \right], \quad (5)$$

where  $V$  is the specific volume.

**ANALYSIS OF THE EQUATION DERIVED** The factor in front of the nonlinear term in (5) can be written as

$$\alpha = (\partial^2 P/\partial V^2)_s / 2\rho_0^3 c_0^2 = 1 + \frac{\rho_0}{2c_0^2} \left( \frac{\partial^2 P}{\partial \rho^2} \right)_s = 1 + \rho_0 c_0 \left( \frac{\partial c_0}{\partial P} \right)_s,$$

from which it follows that a change in sign of  $\alpha$  is associated with an abnormal decrease in the speed of sound when the pressure increases near the critical point (Figure 4). From (5), the velocity of a pressure jump with amplitude  $P'$  is as follows:

$$D(P') = c_0 + \frac{P'}{2} \left[ \left( \frac{\partial c_0}{\partial P} \right)_s + \frac{1}{\rho_0 c_0} \right]. \quad (6)$$

It can be seen from Figure 4 that in a rarefaction wave, the derivative  $(\partial c_0/\partial P)_s$  is negative near the critical point and quickly attains that value at which the expression in the square brackets in (6) also becomes negative. Hence we have  $P'[(\partial c_0/\partial P)_s + 1/\rho_0 c_0] > 0$ , and therefore the velocity at each point of the wave profile increases when the modulus of the pressure amplitude increases. This leads to the formation of a discontinuity in the rarefaction wave, i.e. to the formation of a rarefaction shock wave. A similar effect for the temperature jumps in superconducting fluids was reported by Khalatnikov (1971). Furthermore, the jump velocity satisfies the condition for mechanical stability ( $c_0 < D < c_1 - v$ ). In fact, if we substitute the values of the jump velocity from (6) for the speed of sound in the perturbed state  $c_1$  and the particle velocity  $v$ , we get

$$c_0 < D < c_0 + P'[(\partial c_0/\partial P)_s + 1/\rho_0 c_0].$$

In this case the entropy condition

$$S_1 - S_0 = (\partial^2 P / \partial V^2)_S (V_0 - V_1)^3 / 12 T_0$$

is satisfied automatically, since  $(\partial^2 P / \partial V^2)_S < 0$  for the same range of parameters as the coefficient  $(\partial c_0 / \partial P)_S + 1 / \rho_0 c_0$  in the condition for mechanical stability.

The factor in the square brackets in (5) takes abnormally high values close to the critical point, and it may be evaluated by one of Kawasaki's (1966) models. Let us estimate the width of the transition zone, i.e. the "thickness"  $\delta$  of a rarefaction shock wave. Its value is determined by

$$\delta = \frac{bc_0}{P'(\partial^2 P / \partial V^2)_S / 2\rho_0^3 c_0^2}. \quad (7)$$

By means of the theory of interacting modes, Kadanoff & Swift (1968) determined the damping factor  $\beta$  via the unknown  $b$ :

$$\beta = b\pi\omega / c_0^2 \rho,$$

which near the critical point behaves as  $\beta = \omega\varepsilon^{-2}$ , where  $\varepsilon = |T - T_c| / T_c$ .

Such a formula for  $\beta$  holds for values  $\omega\varepsilon^{-2} < 5 \times 10^{-3}$ . In our case this inequality is fulfilled. We now estimate the nonlinearity coefficient using Bethe's formula (Lambrakis & Thompson 1972):

$$\begin{aligned} \left( \frac{\partial^2 P}{\partial V^2} \right)_S &= \left( \frac{\partial^2 P}{\partial V^2} \right)_T + \frac{3T}{c_V} \left( \frac{\partial P}{\partial T} \right)_V \frac{\partial^2 P}{\partial V \partial T} + \frac{3T}{c_V^2} \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial^2 P}{\partial T^2} \right)_V \\ &+ \frac{T}{c_V^2} \left( \frac{\partial P}{\partial T} \right)_V^3 [1 - T(\partial c_V / \partial T)_V / c_V]. \end{aligned}$$

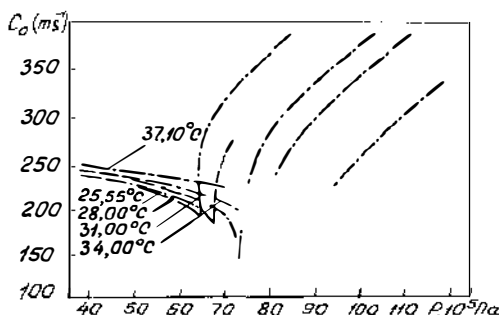


Figure 4 The dependence on pressure of the speed of sound in carbonic acid near the critical point.

It can be shown that when the critical point is approached, the first term on the right-hand side goes to zero according to the definition, the second term also goes to zero, and the third term tends to zero as  $\varepsilon^{2\alpha_1}$ , where  $\alpha_1 \simeq 0.1$  is the critical exponent of the heat capacity  $c_V \sim |T - T_c|^{-\alpha_1}$  ( $T_c$  is the critical temperature). The last term increases as  $\varepsilon^{-1+2\alpha_1}$  when  $T \rightarrow T_c$ . Thus we have

$$\alpha = V^3(\partial^2 P / \partial V^2)_S / 2c_0^2 = \varepsilon^{-1+2\alpha_1} \varepsilon^{-\alpha_1} = \varepsilon^{-1+\alpha_1}$$

and hence

$$\delta = \delta_0 \{|T - T_c| / T_c\}^{-1-\alpha_1/2}.$$

Here  $\delta_0$  is a value independent of the temperature difference  $T - T_c$  and is therefore the transition-zone width of a compression shock wave far from the critical point. The value of  $\delta_0$  is  $0.88 \times 10^{-7}$  m, i.e. of the order of several mean free paths. For the case in our experiment, where  $T - T_c = 10^{-3}$ , we obtained  $|T - T_c| / T_c = 3 \times 10^{-6}$ ,  $\delta / \delta_0 = 629,540$ , from which it follows that  $\delta = 0.88 \times 10^{-5} \times 629,540 = 5.6$  cm. Thus the transition-zone width of the rarefaction shock wave near the critical point is determined not by the mean free path of molecules but by the other scale, which is nearly one million times greater than the mean free path. Close to the critical point, indeed, a new scale appears, a correlation radius, which also increases infinitely as  $T \rightarrow T_c$ . The correlation radius here seems to be a determining scale for the width of the rarefaction shock wave.

According to Rudenko & Soluyan (1974), Equation (5) has a solution describing a stationary shock wave:

$$P = P_0 + \Delta P / [1 + \exp(\varepsilon \alpha \Delta P / bc)],$$

where

$$\Delta P = P_{\xi=-\infty} - P_{\xi=+\infty}, \quad \xi = x - Dt, \quad \partial P / \partial \xi|_{\xi=\pm\infty} = 0.$$

It is seen from the solution that if  $\alpha < 0$ , there exists a steady solution in the form of a rarefaction shock wave. In the case  $\alpha > 0$ , no steady solutions exist in the form of a rarefaction shock wave; rarefaction shock waves decay away in the process of evolution.

**THE STRUCTURE OF ARBITRARY-AMPLITUDE COMPRESSION AND SHOCK WAVES IN VAN DER WAALS GAS WITH CONSTANT HEAT CAPACITY** In the previous sections we have considered the behavior of finite-amplitude waves near the critical point. In what follows we do not impose restrictions on the wave amplitude and instead consider the solutions for arbitrary amplitudes. For this purpose, we take advantage of the following. In a recent paper, Zel'dovich (1981) points out that thermodynamic equilibrium in the critical

region is established slowly because of strong fluctuations. Thus, immediately after a rapid change in the state, equilibrium will occur only in first order (neighbor molecules). Therefore, the assumption has been made that such a change may be described by classical theories that do not take into account the fluctuations and that "just in this sense a retoration of the van der Waals critical point occurs in rapid processes." Owing to this situation, in what follows we use the van der Waals equation of state, and the heat capacity is assumed to be large but constant. The van der Waals equation of state is usually written as follows:  $(P + a/V^2)(V - b) = R_G T$ , where  $a$  and  $b$  are van der Waals constants,  $R_G = R/\mu$ ,  $R$  is the universal gas constant, and  $\mu$  is the molecular mass.

Let the specific isochoric heat  $c_V$  be constant. This assumption is valid for the same range of parameters where the van der Waals equation is applicable. Then for the specific internal energy, we have  $E = c_V T - a/V$ .

In addition, consider the equations for the isentropic and shock adiabats. The dimensionless equation of the isentropic adiabat for a van der Waals gas with constant heat capacity can be written in a fairly simple form:

$$P^* = (P_0 + 3/v_0^2) [(v_0 - 1/3)/(v - 1/3)]^\gamma - 3/v^2, \quad (8)$$

where  $P^* = P/P_c$ ,  $v = V/V_c$ ,  $\gamma = 1 + 1/c_V$ , and  $c_v = c_V/R_G$ ; the subscripts "c" and "0" indicate the critical thermodynamic values and the initial values, respectively.

We also write down the dimensionless expression for  $(\partial^2 P / \partial V^2)_S$ :

$$(\partial^2 P^* / \partial v^2)_S - \gamma(\gamma + 1) (P^* + 3/v^2) / (v - 1/3)^2 - 18/v^4.$$

The dimensionless equation of the shock adiabat for a van der Waals gas with constant heat capacity can be written as

$$P^* = [2P_0 c_V (v_0 - 1/3) - P_0 (v - v_0) - 6c_V (v - 1/3)/v^2 + 6c_V (v_0 - 1/3)v_0^2 + 6(1/v - 1/v_0)] / [2c_V (v - 1/3) + (v - v_0)]. \quad (9)$$

It can be seen from a comparison of formulas (8) and (9) that the equation of the shock adiabat is of a more complicated form than the equation of the isentropic adiabat. However, in the ranges of pressure, volume, and heat capacity under consideration, these adiabats essentially coincide. This fact is further used below to substantiate the difference scheme.

**ALGORITHM OF NUMERICAL SOLUTION** When solving numerically the problem of the decay of an arbitrary breakup it is convenient to write the mass, momentum, and energy conservation laws for an arbitrary mobile element of the medium with a boundary through which there is no flux of substance.

In the one-dimensional case, we have

$$\oint \rho \, dx = 0, \quad \oint \rho u \, dx - p \, dt = 0,$$

$$\oint \rho(E + u^2/2) \, dx - pu \, dt = 0,$$

where  $\rho$  is the density of the medium and  $u$  is its velocity. The dissipative terms are neglected in the equations, since with the grid steps  $\Delta x$  and  $\Delta t$  appropriately chosen, the “viscosity” and “heat conduction” inherent in the difference scheme itself are of the same order as the real viscosity and heat conduction.

Consider an ideal model of the shock tube: a cylindrical tube with closed ends that consists of two sections, the high- and low-pressure chambers, separated by a partition. At a certain moment of time the partition is removed and the compression wave travels to the low-pressure chamber, while the rarefaction wave propagates toward the high-pressure chamber. To consider this process, we use the method suggested by Godunov (1959).

The difference analogues of the equations for the  $i$ th cell can be written as follows:

$$\rho'_i \Delta x'_i = \rho_i \Delta x_i, \quad (\Delta x_i = x_{i+1} - x_i, x'_i = x_i + \bar{u}_i \Delta t),$$

$$\rho_i \Delta x_i (u'_i - u_i) = (\bar{P}_i - \bar{P}_{i+1}) \Delta t,$$

$$\rho_i \Delta x_i (E'_i - E_i) = P_i (\bar{u}_i - \bar{u}_{i+1}) \Delta t,$$

where  $x_i$  and  $x_{i+1}$  are the coordinates of the cell boundaries (contact discontinuities),  $\bar{u}_i$  and  $\bar{u}_{i+1}$  the velocities of the cell boundaries, and  $\bar{P}_i$  and  $\bar{P}_{i+1}$  the pressures at the boundaries of the cell; all primed symbols indicate the quantities relating to the moment of time  $t' = t + \Delta t$ . For weak shock and simple waves, good calculational accuracy of  $\bar{u}_i$  and  $\bar{P}_i$  can be achieved using a “sound approximation”:

$$u_i = (p_{i-1} - p_i + a_{i-1}u_{i-1} + a_i u_i) / (a_{i-1} + a_i),$$

$$P_i = [a_{i-1}a_i(u_{i-1} - u_i) + a_{i-1}P_i + a_iP_{i-1}] / (a_{i-1} + a_i),$$

where  $a_i = \rho_i c_i$  and  $c$  is the adiabatic speed of sound. The application here of the two last equations is justified, in addition, by the coincidence mentioned above of the shock and isentropic adiabats.

Thus the set of equations is mathematically closed and well founded from a physical point of view. In a numerical solution, the time step  $\Delta t$

has been chosen so as to ensure that the difference scheme is stable and has good convergence. The approximation and stability of a similar difference scheme were considered in detail by Godunov (1976).

The calculations are presented in Figures 5–8. The dimensionless coordinate is  $\xi = x/\Delta x_0$ , where  $\Delta x_0$  is the initial size of the calculational cell. The dimensionless time is given by  $\tau = t/t_*$ , where  $t_*$  is the characteristic time of the process (the time for which the stationary profile of a shock wave is established). The dimensionless perturbation of pressure is  $\Delta P_L^* = P^* - P_L^*$  in the compression wave and  $\Delta P_H^* = P_H^* - P^*$  in the rarefaction wave. ( $P_L$  and  $P_H$  are the initial pressures in the low- and high-pressure chambers, respectively.)

Figure 5 demonstrates the evolution of a compression wave at  $c_V = 30$ . Curves 1–4 correspond to the moments of time  $\tau = 1, 10, 20$ , and 30. In this case, the perturbed and unperturbed states were in the range of abnormal thermodynamic properties. (The initial parameters on the discontinuity were the following:  $P_L^* = 0.912$ ,  $v_L = 1.54$ ,  $P_H^* = 1.040$ , and  $v_H = 1.11$ .) In Figure 6, the unperturbed state was outside this range ( $P_L^* = 0.846$ ,  $v_L = 1.85$ ,  $P_H^* = 1.160$ , and  $v_H = 1.00$ ). It can be seen from Figure 5 that the width of the compression wave front increases with time, just as is the case with the rarefaction wave in an ideal gas. Figure 6 shows that the forepart of the wave front, corresponding to the range of normal thermodynamic properties, remains steep, and the back part of the wave front, corresponding to the range of abnormal thermodynamic properties, spreads. So far rarefaction shock waves with the spreaded back part of the front have been observed only in media with relaxation (so-called partially dispersed waves) (Becker 1974). However, in those experiments the width of the spread part was constant and was determined by the relaxation time, whereas in the case under discussion, the width of this part of the front is proportional to the path passed by the wave.

The evolution of a rarefaction wave at  $c_V = 20$  is illustrated in Figures 7 and 8. Curves 1–4 correspond to the same moments of time as in Figure

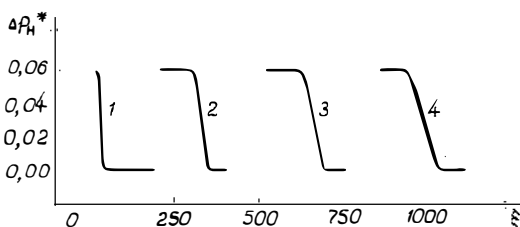


Figure 5 The evolution of a compression wave whose parameters are inside the abnormal region.

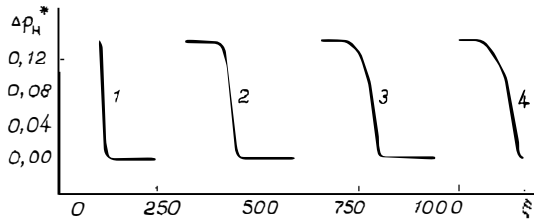


Figure 6 The evolution of a compression wave whose parameters are outside the abnormal region.

5, and curve 5 corresponds to  $\tau = 40$ . In Figure 7, the perturbed and unperturbed states were in the region of abnormal thermodynamic properties (the initial parameters at the discontinuity were  $P_L^* = 0.834$ ,  $v_L = 2.00$ ,  $P_H^* = 0.960$ ,  $v_H = 1.25$ ), and in the case of Figure 8 the perturbed state was outside this region ( $P_L^* = 0.610$ ,  $v_L = 3.33$ ,  $P_H^* = 0.960$ ,  $v_H = 1.25$ ). It can be seen from Figure 7 that the width of the rarefaction wave front does not increase with time, i.e. the rarefaction shock wave does occur. Figure 8 shows also that the forefront of the wave front, which corresponds to the range of abnormal thermodynamical properties, remains steep, and the back part of the front, which corresponds to the range of normal thermodynamic properties, spreads. Both of these forms of the structure of rarefaction waves have been predicted theoretically and observed experimentally.

If we take into account the abnormal behavior of heat capacity near the liquid-vapor critical point, then a considerable extension of the class of substances in which rarefaction shock waves can propagate should result. Since the behavior of a substance near the critical point is universal for all simple fluids, the phenomenon of rarefaction shock waves will be observed also for all substances that are close to their liquid-vapor critical points. In addition, the results should not vary qualitatively if the scaling equation of state is used instead of the van der Waals equation of state.



Figure 7 The dynamics of a rarefaction wave with the parameters in the abnormal region.

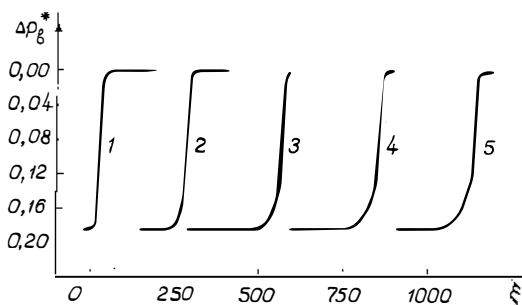


Figure 8 The dynamics of a rarefaction wave whose final state is outside the abnormal region.

### Conclusions

The experimental and theoretical results presented above enable one to conclude that the existence of a rarefaction shock wave near the liquid-vapor critical point is due to the abnormal decrease in the speed of sound when the pressure increases. We have made here no quantitative comparison between the experimental and calculated results because to do this, it is necessary to know accurate power dependencies of the heat capacity and compressibility, as well as the coefficients of viscosity and heat conduction of Freon-13, on the temperature and density. Unfortunately, no similar studies have been made so far, neither for Freon-13 nor for any other substance. Most commonly, the temperature dependencies of the thermodynamic and kinetic properties are measured.

Many results are, nevertheless, in good qualitative agreement. One can therefore argue that the theoretical models considered above are capable not only of accounting for the phenomena observed in the experiments but also of predicting new, interesting effects.

Compare the results obtained with the data on wave propagation in solids after their polymorphic transformations. In the works performed by Erkman (1961) and Ivanov & Novikov (1961), after explosive loading of iron and steel samples, spalls with smooth surfaces were observed. This phenomenon has been attributed to an interaction of rarefaction shock waves. The existence of a rarefaction jump in solids subjected to polymorphic transformations is associated with the fact that the phase transition leads to the appearance of a convex-upward section on the adiabat, i.e. the section on which the average value of the second-order pressure derivative with respect to the volume is less than zero (at constant entropy).

As for compression waves, they always propagate as shock waves (one or two) in solids that have undergone polymorphic transformations. The

compression waves, which consist of the jump and the spreading back part of the front and which are possible near the liquid-vapor critical point, cannot be observed in solids. This is because  $(\partial^2 P / \partial V^2)_S > 0$  at any point in a solid where the adiabat has no singularities.

Thus the similarity between the processes occurring in solids, subjected to polymorphic transformations, and those near the liquid-vapor critical point is associated with the abnormal behavior of the adiabat, whereas their difference is due to the physical nature of this anomaly. If in solids this anomaly is the phase transition, then close to the critical point there is a strong change in the thermodynamic properties (compressibility, etc.) of a single-phase substance.

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