Evolution of rarefaction waves near the thermodynamic critical point

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(Submitted February 27, 1980)
Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 11, 619–622 (5 June 1980)

The existence of a shock rarefaction wave in a material whose unperturbed state lies near the thermodynamic critical point (CP) has been verified experimentally for the first time. An equation describing the evolution of long-wave perturbations near the CP is given.

PACS numbers: 47.40.Nm, 64.60.Ht

It was shown theoretically[1] that shock rarefaction waves can be formed near the critical point (CP). Direct measurements of the velocity of sound in the vicinity of the CP,[2] which show its anomalous increase with a decreasing pressure, make it possible to assume the existence of a shock rarefaction wave (RW). Until now, there has been no data in the literature on experimental verification of the existence of a shock RW. In order to study the evolution of compression and rarefaction waves, an experimental apparatus was built, whose unique feature is a carefully temperature-controlled shock tube (ST) with a total length of 3 m. The apparatus made it possible to obtain the unperturbed state of the material in the ST with parameters located at an arbitrary point of the P-T plane, including the critical point. The monitoring of the material in the vicinity of the CP and the displacement of the interphase boundary were done visually by means of a KM-6 cathetometer through optical windows in the ST. The measurement error of the phase boundary was 0.01 mm. The static pressure was measured with a 0.05% class piston manometer in conjunction with a membrane null indicator. The temperature gradient along the length of the ST and the absolute temperature were measured with PTS-10 resistance thermometers made at VNIIFTRI. The error of the absolute temperature measurement was 0.01 K and $\Delta T/L = 3\times 10^{-5}$ K/m, i.e., the working part of the ST was sufficiently isothermal. The error in determining the mass of the material filling the ST was less than 0.093%. The dynamic characteristics measured by using piezotransducers had an error of less than 1% in determining the wave velocity and less than 12% for the pressure amplitudes. The critical parameters were determined by using the method in Ref. 3.

One important result is the determination of the critical state of trifluorochloromethane (Freon-13) along a 3-m length. The critical parameters of F-13 are P_{cr}

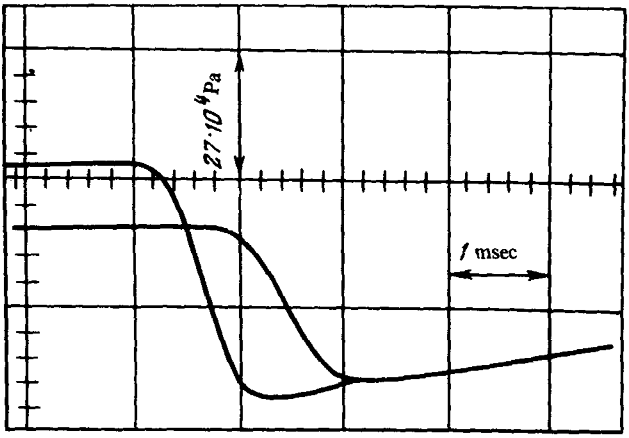

FIG. 1. Evolution of a shock rarefaction wave in Freon-13 near CP. The upper oscillogram trace corresponds to the sensor located 0.45 m from the diaphragm and the lower trace corresponds to that located 2.35 m from it.

$= 38.12 \times 10^5$ Pa, $T_{cr} = 302.02$ K, $\rho_{cr} = 0.580$ g/cm^3. The previously observed[4] behavior of small quantities of the material in the critical region was also confirmed for F-13, using our apparatus, where the mass of the material brought to the critical state is 4.311 kg. The critical state was achieved in 20 hours.

The velocity and structure of the rarefaction waves were recorded with piezoelectric pressure transducers with an independent amplitude-frequency characteristic above 50 kHz. Some results of the experiments are shown in the oscillogram (Fig. 1). The initial state in front of the rarefaction wave has the parameters $P_0 = 38.12 \times 10^5$ Pa, $T_0 = 302.02$ K, $\rho_0 = 0.576$ g/cm^3.

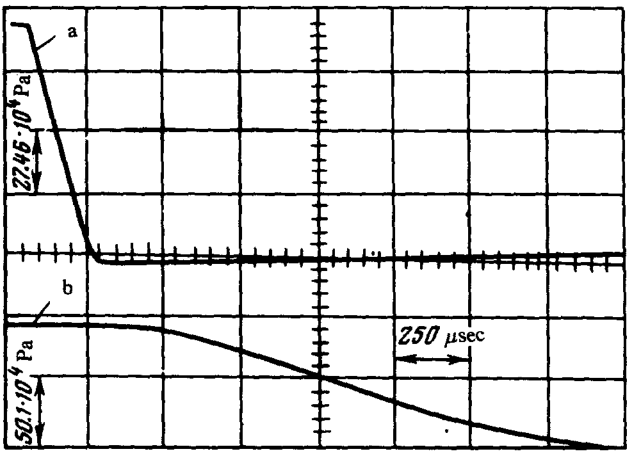

FIG. 2. Evolution of the rarefaction wave in nitrogen: a—at distance of 0.45 m from the diaphragm, b—2.35 m.

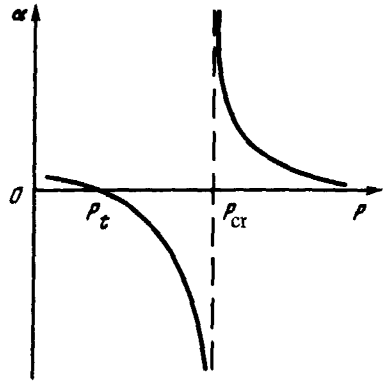

FIG. 3. Behavior of coefficient α as function of pressure near the critical point.

It can be seen in Fig. 1 that the rarefaction wave propagates as a surface of a sudden, extremely abrupt pressure change with a subsequent plateau at the vertex.

Thus, in terms of the definition[1] of a shock rarefaction wave as a surface of a sudden, extremely abrupt change in the state of a material that propagates relative to this material, our experiment graphically demonstrates that the observed effect is a shock rarefaction wave. Another important feature of shock waves is the property that the steepness of its front does not decrease in the evolution process.

It was established during the experiments that the shock rarefaction wave, after traveling several tens of units measured in lengths of its leading edge, experienced almost no change in the steepness of its leading edge, i.e., it remained constant along the length of the entire ST.

To confirm the existence of a shock rarefaction wave only in the region of critical parameters, we studied experimentally the evolution the rarefaction waves in nitrogen. The initial parameters in front of the wave were chosen to be the same as those for Freon-13, but, of course, they were not critical for nitrogen. As expected, no shock rarefaction wave was formed in any of the nitrogen experiments. In the evolution process the rarefaction waves were smeared out in such a way that the steepness of the front at the identical distances was reduced by a factor of five and more (Fig. 2). The experiments performed at different times yielded good reproducibility of all the results in the oscillograms.

Thus, the existence of a shock rarefaction wave has been proved experimentally. The velocity of the shock rarefaction wave in Fig. 1 is 58.5 m/sec. The relaxation processes can be ignored in the case of long-wave perturbations when the correlation radius is much less than the wavelength. Thus, according to the Khokhlov method,[5] for any of the perturbed quantities: $P' = P - P_0$, $\rho' = \rho - \rho_0$, $v' = v - v_0$ in the x, t coordinate system, we can obtain the Burgers equation:

$$P'_t + c_0 P'_x + \frac{1}{2\rho_0^3 c_0^2}\left(\frac{\partial^2 P}{\partial V^2}\right)_S \frac{1}{\rho_0 c_0} P' P'_x = \left[\frac{4}{3}\eta + \xi + \kappa\left(\frac{1}{c_V} - \frac{1}{c_P}\right)\right] P'_{xx}/2\rho_0. \tag{1}$$

P_0, ρ_0, v_0 are the pressure, density, and velocity of the particles of the medium in the unperturbed state, c_0 is the velocity of sound, and V is the specific volume. For real gases $\alpha = \frac{1}{2\rho_0^3 c_0^2}\left(\frac{\partial^2 P}{\partial V^2}\right)_S$ has an anomalous behavior near the CP: it changes sign and becomes negative (Fig. 3). In this case Eq. (1) gives a solution in the form of shock rarefaction waves. It can be seen in Fig. 3 that a multiple-wave rarefaction wave structure is possible, depending on the inequalities among P_0, P_{cr}, P_1, P_t . The coefficient in front of the second derivative has an anomalously high value near the CP. This fact leads to a considerable broadening of the SW front as compared with an ideal gas.

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