[12] R. Freud, C. Sulkowski, and B. Makiej, Phys. Lett. A 27, 187 (1968).
[13] I. L. Landau, Zh. Eksp. Teor. Fiz. 64, 557 (1973) [Sov. Phys. JETP 37, 285 (1973)].
[14] H. L. Watson and R. P. Huebener, Phys. Rev. B 10, 4577 (1974).
[15] K. Hejnowicz and B. Makiej, Acta Phys. Pol. A 46, 91 (1974).
[16] A. I. Shal'nikov, Zh. Eksp. Teor. Fiz. 33, 1071 (1957) [Sov. Phys. JETP 6, 827 (1958)].
[17] Yu. V. Sharvin, Proc. Tenth Intern. Conf. on Low-Temperature Physics, Moscow 1966, Vol. 2B, Publ. by VINITI, Moscow, 1967, p. 323.
[18] Yu. V. Sharvin and I. L. Landau, Zh. Eksp. Teor. Fiz. 58, 1943 (1970) [Sov. Phys. JETP 31, 1047 (1970)].
[19] I. L. Landau, Pis'ma Zh. Eksp. Teor. Fiz. 23, 516 (1976) [JETP Lett. 23, 471 (1976)].

Translated by A. Tybulewicz

Optothermodynamic method of diagnostics of the critical point and of the investigation of the equation of state of absorbing liquids

F. V. Bunkin, V. M. Podgaetskiĭ, and M. I. Tribel'skiĭ

P.N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted 3 July 1978)
Zh. Eksp. Teor. Fiz. 75, 2309–2311 (December 1978)

A new method for the diagnostics of the critical point and for the investigation of the equation of state of an absorbing dielectric liquid is indicated.

PACS numbers: 07.20. – n, 64.30. + t

A method of optothermodynamic action of a laser pulse with a programmed waveform on an absorbing liquid, to bring a liquid is close to the critical point in the focal volume was indicated in Ref. 1. The main shortcomings of this method are the following:

1) the stringent requirements imposed on the waveform of the laser pulse;

2) the short ($\sim r_0/c$, where r_0 is the radius of the focal spot and c is the speed of sound in the liquid) lifetime of the near-critical state;

3) the inapplicability of the method when working with liquids whose critical parameters are unknown.

In the present paper we propose for the investigation of liquids an optothermodynamic method free of these shortcomings. It permits diagnostics of the critical point and investigation of the equation of state of the liquid.

The main difference from Ref. 1 is that now the investigated liquid is placed in a hermetically sealed cell, on the end face of which is incident a homogeneous light beam of intensity $I(t)$ ($I=0$ at $t\leq 0$), so that the problem of the reaction of the liquid to the action of the radiation is one-dimensional (see Fig. 1).[1)] If the laser-pulse duration τ satisfies the condition $c\tau \gg \delta$ (δ is the length of the cell), then the pressure profile established in the liquid on account of the absorption of the laser radiation turns out to be independent of x (the x axis coincides with the propagation direction of the radiation), i.e., it depends only on the time: $p=p(t)$. On the other hand, if $\chi\tau K^2 \ll 1$, where K is the absorption coefficient of the radiation and χ is the thermal diffusivity of the liquid, then the profiles of the temperature T, of the density ρ, of the specific enthalpy w, etc. will depend significantly on x. Thus, on the (p, x) planes, where $X=\rho, T, w\ldots$, the state of the liquid at each instant of time is described by a segment corresponding to a fixed value of $p(t)$ and to a continuum of values of X from a certain interval $X_m(p)\leq X\leq X_M(p)$. During the entire time of action of the radiation pulse the aggregate of the state in which the liquid is situated will occupy on the (p, X) plane a certain two-dimensional region (phase space) bounded by the phase curves $X=X_m(p), X=X_M(p)$ and by the segment $p=p_M$ corresponding to the maximum pressure produced in the liquid at the end of the flash.

In the case $K\delta \gg 1$ the problem has an analytic solution

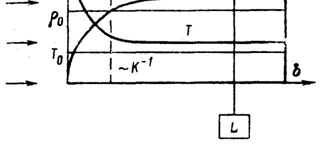

FIG. 1. Schematic profile of the density and temperature of the liquid at a fixed instant of time: L—probing laser, D—detector; the thick line represents the cell.

0038-5646/78/1201165-02$02.40

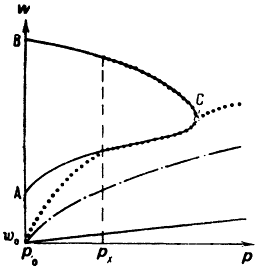

FIG. 2. Line ACB—binodal; C—critical point. The solid, dash-dot, and dashed lines show the enthalpy $w_m(p)$ and the enthalpy $w_M(p)$ at $\Lambda < \Lambda_c$ and $\Lambda > \Lambda_c$, respectively; at $p=p_x$ the system becomes stratified into two phases.

for an arbitrary equation of state and for an arbitrary dependence of K on the thermodynamic variables of the liquid.[3] In the case of mass absorption of the radiation ($K=\mu\rho$, $\mu=\text{const}$) this solution takes the form

$$p=p_0+\frac{\rho_0 c^2}{\Lambda}\int_{w_0}^{w_M}[\rho_0-\rho(w)]\left[\int_{w_0}^{w}\rho(w')dw'\right]^{-1}dw, \tag{1}$$

where

$$w_M=w_0+\mu\int_0^t I(t')dt', \tag{2}$$

$\Lambda=\mu\rho_0\delta$ is the optical thickness of the unperturbed liquid, $\rho(w)$ is the equation of the isobar that passes through the critical point, and p_0, ρ_0, and w_0 are the initial values of the thermodynamic variables. For the sake of brevity we leave out the expressions that describe the functions $w(t,x)$, $\rho(t,x)$. The phase plots of the system are shown schematically in Fig. 2. The quantity $w_m(p)=w_0+(p-p_0)/\rho_0$ does not depend on Λ. On the other hand, the $w_M(p)$ curve is determined by Eqs. (1) and (2). We see there that a change of Λ is equivalent to a change of the scale of p, i.e., the $w_M(p)$ curve remains similar to itself when Λ changes.[2)]

At $\Lambda<\Lambda_c$ the phase space of the system lies entirely in the single-phase region. At $\Lambda>\Lambda_c$ the $w_M(p)$ curve crosses the liquid-vapor phase-equilibrium curve (binodal). The liquid begins to boil, and with further heating by the radiation the system, moving along the binodal, inevitably lands in the critical point (see Fig. 2). The value of Λ_c depends on the type of liquid and on the initial conditions. For water under normal initial conditions, $\Lambda_c=37$. The instant when the critical point is reached can be determined from the onset of the critical opalescence. We emphasize that in the considered formulation the vicinity of the critical point can be reached only in a small region near the forward wall of the cell (i.e., near $x=0$), where the enthalpy of the liquid is maximal and is determined by relation (2). With further increase of the energy input into the liquid, the critical value of the enthalpy w_c will be reached in regions of the liquid farther and farther from the plane $x=0$, but this will occur already at pressures exceeding the critical pressure p_c of the liquid.

Thus, by measuring the energy that has been delivered to the liquid by the instant of the onset of the critical opalescence, and by measuring the change of the density in the region[3)] $Kx \gg 1$ (which is connected with the change of the pressure by the relation[3] $\Delta p=c^2\Delta\rho$), measurements that can be made with high accuracy by optical means, we can determine directly two critical parameters of the investigated liquid, p_c and w_c. The missing third parameter can be determined either by means of more complicated measurements or from the principle of corresponding states. Similarly, by measuring all three thermodynamic variables, or else the pressure and the density of the absorbed energy, and by inverting relation (1), we can study the equation of state of the liquid.

We emphasize that in this case no substantial limitations are imposed on the waveform or on other parameters of the laser pulse, and since everything is based on optical measurements, no direct contact occurs in the course of the measurement with the investigated liquid, so that toxic and agressive liquids can be investigated when necessary.

By way of a rough estimate we note that the pressure produced in the liquid is of the order of the volume density of the energy input, so that at $\delta\sim 1$ cm and $p_c\sim 100$ bar the corresponding energy input is of the order of 10 J/cm². The lifetime of the investigated state is $t_0 \sim(\chi K^2)^{-1}$. At $\chi\sim 10^{-3}$ cm²/sec (a typical value for dielectric liquids) and $K\sim 10$ cm⁻¹ we have $t_0\sim 10$ sec.

[1)] We note that a hermetically sealed cell was used for laser heating of mercury in Ref. 3, where the first attempt was made of observing directly in experiment the bleaching of metals under the influence of high-power radiation. The experimental conditions in that reference, however, do not satisfy the quantitative requirements given below and therefore our present conclusions cannot be extended to experiments under the conditions of Ref. 2.

[2)] Variation of Λ is possible by variation of either δ or μ, by dissolving in the liquid special dyes which, owing to their low concentration, hardly change the thermodynamic properties of the solvent.

[3)] Measurements of the density in the region $Kx \lesssim 1$ entail considerable difficulties because of the large density gradient.

---

[1] F. V. Bunkin, Pis'ma Zh. Eksp. Teor. Fiz. **19**, 302 (1974) [JETP Lett. **19**, 175 (1974)].

[2] A. M. Bonch-Bruevich and S. E. Potapov, Pis'ma Zh. Tekh. Fiz. **1**, 353 (1975) [Sov. Tech. Phys. Lett. **1**, 167 (1975)].

[3] G. A. Matyushin, L. S. Mel'nikov, V. M. Podgaetskiĭ, and M. I. Tribel'skiĭ, Kvantovaya Elektron. (Moscow) **4**, 1076 (1977) [Sov. J. Quantum Electron. **7**, 603 (1977)].

Translated by J. G. Adashko