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THE COEXISTENCE CURVE OF HEPTANE NEAR THE CRITICAL POINT

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The coexistence curve of standard heptane is studied by means of optical and microfloat measurements of the density in thin layers of matter near the critical point. Reduction of the experimental data by a digital computer shows that the coexistence curve is asymmetric in density-temperature coordinates. It is pointed out that to compare the experimental data on the coexistence curve with model lattice theories, possible thermal expansion of the lattice cell should be taken into account. By suitable reduction of the experimental data it is possible to determine the critical exponent of the symmetrized coexistence curve of heptane; it is found to be $\beta^* = 0.358 \pm 0.009$.

It is necessary to determine the form of the vertex of the liquid-vapor coexistence curve in order to test the theory of critical phenomena and of second-order phase transitions[1]. In particular, the question of the asymmetry of this curve has been discussed in recent work[2]. Obtaining the pertinent experimental data involves a number of difficulties. Density measurements on coexisting phases near the critical point are complicated by the gravitational effect that arises in this region of the state parameters.[3] A number of investigators have attempted to remove the substance inhomogeneities caused by gravitation either by stirring or by using vessels of less height[4,5].

In our investigations we carried out density measurements on thin layers of material in the liquid and the vapor state. The same procedures were employed in the study of heptane as were used in studying benzene and pentane[6,7]. Simultaneous use was made of the microfloat method and Toepler's method with the addition of knife edges; this made it possible to determine the densities of liquid or gas layers at any height of the container, including right at the meniscus. In the reduction of the optical-measurement data we used for the refraction the value determined by us for states of the material near the critical point[8]. Standard heptane was used.[9]

To obtain data closer to the critical point, a double-thermostat system was devised[10]. The introduction of a secondary thermostat guaranteed that the temperature was maintained at the critical point with accuracy ±0.001°. The temperature of the material studied was determined by means of a 10-ohm platinum resistance thermometer connected to an R-348 potentiometer. The errors in the measurements of the temperature changes near the critical point did not exceed ±0.0003°.

Figure 1 shows the temperature dependence of the heptane densities measured in layers of the material located at different heights in the chamber. It is immediately apparent that a gravitational effect appears at roughly 5° before the critical temperature and leads to branching of the plots of the temperature dependence of the liquid and vapor densities. At the critical temperature, the density curves of the material, measured in layers only 1 mm away from the meniscus, do not come close together (Fig. 1, curves 4 and 5).

The critical parameters T_{cr} and ρ_{cr} were deter-

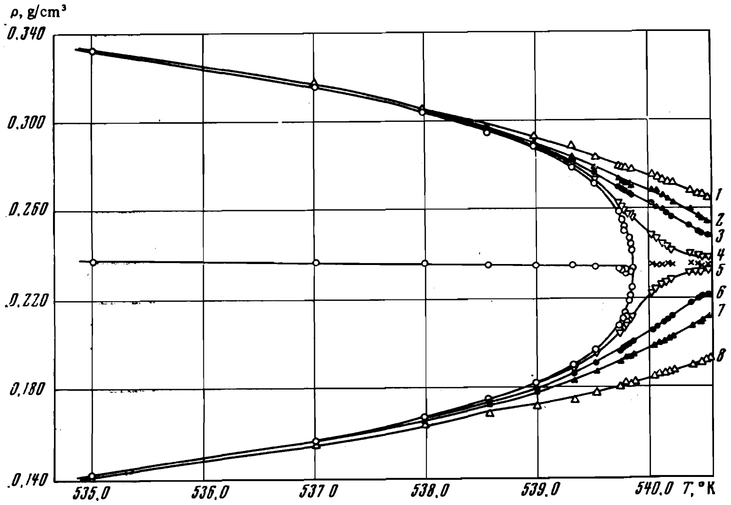

FIG. 1. Temperature dependence of the equilibrium values of the heptane density at different chamber heights $\Delta z = z - z_{cr}$: 1–Δz = −28.0, 2–Δz = −10.0, 3–Δz = −5.0, 4–Δz = −1.0, 5–Δz = +1.0, 6–Δz = +5.0, 7–Δz = +10.0, 8–Δz = 28.0 mm. ×–densities at the maxima of the density gradients, ○–heptane coexistence curve and linear diameter.

mined in the following manner from the full range of experimental points. The critical temperature was determined as the boundary between the family of gravitational curves having a density discontinuity corresponding to the meniscus and the family of curves in which the density varies smoothly with height. The accuracy of the result so determined is ± 0.005° K. Within the indicated limits of accuracy, the corresponding critical temperature, $T_{cr} = 539.860 \pm 0.005$°K, agrees with the temperature at which the meniscus disappears, which was found directly on the basis of numerous direct visual observations. The critical density $\rho_{cr} = 0.2340 \pm 0.0010$ g/cm^3 was found by several methods: as the coordinate of the coalescence point of the temperature-dependence curves of the densities of the actually coexisting liquid and gas, as the point of intersection of the straight diameter and the vertical $T = T_{cr}$ = const, and as the place where the density gradients are maximal on the gravitation curves obtained somewhat above the critical temperature.

For any given temperature the densities of the layers of the material located directly at the meniscus were determined by means of a joint reduction of the microfloat measurements and of the optical measurements. These data and the arithmetic means of the densities of the coexisting phases are listed in the table. The experimental points that are closest to the critical state are separated in temperature by only 0.006°, which in relative magnitude amounts to $\tau = |T - T_{cr}|/T_{cr} = 1 \times 10^{-5}$. The arithmetic-mean densities of the coexisting liquid and gas phases fit a somewhat inclined straight line.

The data obtained on the density of the actually coexisting layers of liquid and gas near the critical point were employed by us to test the power law discussed in the literature in the three forms[5,2]:

$$(\rho_L - \rho_G) / \rho_{cr} = B\tau^{\beta}, \tag{1}$$

$$(\rho_L - \rho_{cr}) / \rho_{cr} = B_L\tau^{\beta}{}_L, \tag{2}$$

$$(|\rho_G - \rho_{cr}|) / \rho_{cr} = B_G\tau^{\beta}{}_G. \tag{3}$$

To find the parameters of Eqs. (1) to (3), the experimental data on the coexistence curve were plotted in log-log coordinates. The disposition of the points corresponding to the test of the power law in the three forms shown above is illustrated in Fig. 2.

The absolute weights were found for the experimental points shown in Fig. 2, and the slope of the linear dependence was determined by least squares[11]. The calculations were made with a "Razdan-2" computer. In assigning weights we assumed the existence of two independent error sources: errors in the density and errors in the temperature measurements, represented by the rms values σ_ρ and σ_T. An estimate of the error in the temperature measurements for all the experimental points yielded $\sigma_T = 0.001$°. The corresponding error ranges are shown in Fig. 2. A calculation of the rms error in the density measurements at temperatures that deviate from the critical temperature by more than $\Delta T = -0.05$°K gives $\sigma_\rho = 5 \times 10^{-4}$ g/cm^3. This error does not exceed the dimensions of the points on the drawing. The experimental points closer than $\Delta T = -0.05$° K to the critical temperature are subject to greater experimental density errors, but their values can not be accurately determined because of the difficulty of recording the large deflections of optical rays in this region of measurement, so that the corresponding error ranges are not shown in Fig. 2. In calculating the parameters of Eqs. (1)—(3) we assumed the same value, $\sigma_\rho = 5 \times 10^{-4}$ g/cm^3, for all the points. This can not significantly affect the rms error of the final results, since the noted points have considerably less weight than all the rest, owing to the error in the measurement of the temperature difference $(T - T_{cr})$ near the critical point.

Densities of coexisting liquid and vapor directly at the meniscus near the critical point of heptane.

T, °K	$\tau = \frac{\lvert T - T_{cr} \rvert}{T_{cr}}$	ρ_L, g/cm³	ρ_G, g/cm³	$\rho_L + \rho_G/2$
534.987	$9{,}03 \cdot 10^{-3}$	0,3323	0.1420	0,2371
537,010	$5{,}28 \cdot 10^{-3}$	0.3155	0,1568	0.2361
537.991	$3{,}46 \cdot 10^{-3}$	0.3038	0,1673	0.2355
538.573	$2{,}38 \cdot 10^{-3}$	0.2941	0.1749	0,2345
538.987	$1.62 \cdot 10^{-3}$	0,2867	0.1818	0.2342
539.319	$1.00 \cdot 10^{-3}$	0.2785	0,1900	0.2342
539,521	$6{,}28 \cdot 10^{-4}$	0.2712	0.1968	0.2340
539.737	$2{,}28 \cdot 10^{-4}$	0,2581	0.2076	0.2328
539,772	$1{,}64 \cdot 10^{-4}$	0.2544	0.2102	0.2323
539.787	$1{,}35 \cdot 10^{-4}$	0.2526	0.2122	0.2324
539.790	$1{,}30 \cdot 10^{-4}$	0.2499	0.2129	0.2314
539,827	$6{,}11 \cdot 10^{-5}$	0,2461	0.2182	0.2321
539.844	$2{,}96 \cdot 10^{-5}$	0.2435	0.2202	0.2318
539.854	$1{,}11 \cdot 10^{-5}$	0.2409	0.2242	0.2326
539.860	—	0.2340	0,2340	0.2340

To find the slope of the linear plot of $\log|\rho_L - \rho_G|$ vs $\log \tau$, the error in $\log|\rho_L - \rho_G|$ was determined by taking into account the rms errors σ_ρ and σ_T, using the transfer formula[12]:

$$\Delta(\lg|\rho_L - \rho_G|) = \delta(\lg|\rho_L - \rho_G|) + \frac{d(\lg|\rho_L - \rho_G|)}{d(\lg\tau)}\delta(\lg\tau), \tag{4}$$

and the absolute weight w, which is proportional to $1/[\Delta(\log|\rho_L - \rho_L|)]^2$, was calculated from the formula

$$w[\Delta(\lg|\rho_L - \rho_G|)] = \left\{0.43\left[\frac{\sqrt{2\sigma_\rho^2}}{|\rho_L - \rho_G|} + 0.355\frac{\sqrt{2\sigma_T^2}}{\Delta T}\right]\right\}^{-2}.$$

Relations (2) and (3) were obtained in analogous fashion.

After computer reduction of all the experimental

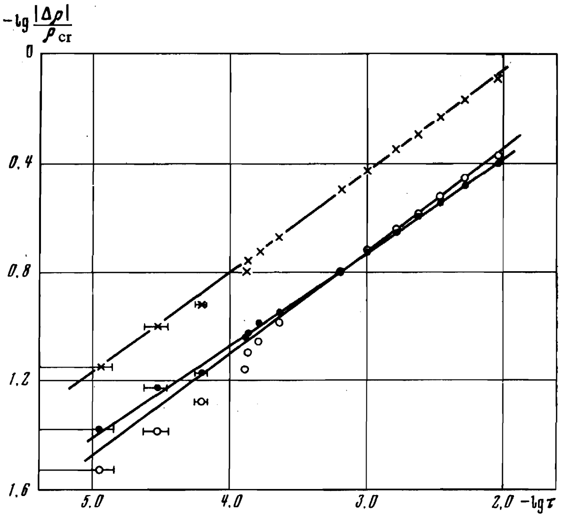

FIG. 2. Log-log plots of data on the heptane coexistence curve, used to verify the power-law in three forms (formulas (1)–(3). ×–$\Delta\rho = \rho_L = \rho_L - \rho_G$, ○–$\Delta\rho = \rho_L - \rho_{cr_1}$, ●–$\Delta\rho = |\rho_G - \rho_{cr}|$.

points on the coexistence curve we obtained, using the optimal critical parameters,

$$\beta = 0{,}361 \pm 0{,}008, \qquad B = 4{,}50 \pm 0{,}23;$$
$$\beta_L = 0{,}385 \pm 0{,}016, \qquad B_L = 2{,}61 \pm 0{,}24;$$
$$\beta_G = 0{,}340 \pm 0{,}004, \qquad B_G = 1{,}96 \pm 0{,}05.$$

The indicated errors are double the rms deviations, corresponding to a 0.95 confidence level.

The obtained coefficients and exponents of the coexistence curve plotted in the ordinary coordinates ρ and T agree with analogous data for substances with lower critical temperatures and show the curve to be asymmetric. In the opinion of some investigators, this contradicts the theoretical lattice-gas model and the Ising model[2]. In reality, however, when the experimental data on the liquid-vapor coexistence curve are compared with the lattice-gas model it is necessary to allow for possible "thermal expansion" of the lattice cell. As was shown by one of us, allowance for the increase in the dimensions of the cell with increasing temperature in the lattice-gas model leads to the appearance of asymmetry in the coexistence curve and causes the straight diameter to become inclined even in calculations based on the self-consistent field hypothesis.[13] The experimentally observed inclined straight diameter is evidence that thermal expansion of the cell actually takes place. It follows that when comparing the experimental results with cell theories one must either use formulas that take into account the change in the dimensions of the cell with temperature, or else compare with the theory that takes no account of thermal expansion not the directly measured curves of density variation with temperature, but the temperature dependences of the occupation numbers of the lattice cells (dimensionless phase densities). The first course is impractical because it is not yet theoretically possible to find the coefficients of thermal expansion of the lattice cell. The occupation numbers of the lattice cell N_i in the liquid or in the gas at any given temperature are found from the formula

$$N_i = \rho_i / 2[\rho_{cr} + \nu(T_{cr} - T)], \tag{5}$$

where ν is the slope of the straight diameter and ρ_i is the density of the liquid or the gas.

In N, T coordinates the coexistence curve proves to be symmetric and suitable for a comparison with the lattice theories that do not allow for thermal expansion. The critical exponent of the thus-symmetrized curve should be found by analyzing the temperature variations of the differences $N_L - N_{cr}$ and $N_{cr} - N_G$ (where $N_{cr} = 1/2$), which are equal at any fixed temperature. It is easily shown that each of these differences reduces to the expression $(\rho_L - \rho_G)/2(\rho_L + \rho_G)$. Since the numerical coefficient does not affect the exponent, one should expect that

$$(\rho_L - \rho_G) / (\rho_L + \rho_G) = B^* \tau^{\beta^*}. \tag{6}$$

It must be pointed out that the ratio $(\rho_L - \rho_G)/(\rho_L + \rho_G)$ was proposed previously by Buckingham as a natural variable characterizing the deviation of a two-phase system from the critical point.[14,15] However, Buckingham assumed the existence of a more complicated, nonanalytical temperature dependence of that quantity.

The analytic reduction of the symmetrized coexistence curve yields $\beta^* = 0.358 \pm 0.009$ and $B^* = 2.20 \pm 0.13$. We note that $0.361 \pm 0.008 = \beta \approx \beta^* = 0.358 \pm 0.009$. Such an agreement can always be expected when the slope of the straight diameter is small. In our case it is equal to $\nu = 0.00071$ g/cm^3-grad.

The critical exponent we obtained for the symmetrized coexistence curve is considerably lower than the classical value 0.5 and somewhat higher than the value 5/16 obtained in the three-dimensional Ising model.

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[1] M. Fisher, The Nature of the Critical State (Russ. transl.), Mir, 1968.

[2] J. M. H. Levelt-Sengers, J. Straub, and M. Vicentini-Missoni, J. Chem. Phys. **54**, 5035 (1971).

[3] M. Sh. Giterman and S. P. Malyshenko, Zh. Eksp. Teor. Fiz. **53**, 2079 (1967) [Sov. Phys.-JETP **26**, 1176 (1968)].

[4] A. V. Voronel', V. A. Smirnov and Yu. P. Chashkin, ZhETF Pis. Red. **9**, 387 (1969) [Sov. Phys.-JETP Lett. **9**, 229 (1969)].

[5] B. Wallace and H. Meyer, Phys. Rev. **A2**, 1563 (1970); L. A. Weber, Phys. Rev. **A2**, 2379 (1970).

[6] L. M. Artyukhovskaya, E. T. Shimanskaya and Yu. I. Shimanskiĭ, Ukr. Fiz. Zh. **15**, 1974 (1970).

[7] L. M. Artyukhovskaya, E. T. Shimanskaya and Yu. I. Shimanskiĭ, Zh. Eksp. Teor. Fiz. **59**, 688 (1970) [Sov. Phys.-JETP **32**, 375 (1971)].

[8] L. M. Artyukhovskaya, E. T. Shimanskaya and Yu. I. Shimanskiĭ, Optika i Spectroskopiya **34** (1973), in press.

[9] Spravochnik Pokazatelei Kachestva Khimicheskikh Reaktivov (Handbook of Quality Indices of Chemical Reagents), ed. by L. B. Brovkin and L. N. Larichevaya, I, Khimiya, 1968.

[10] L. M. Artyukhovskaya, E. T. Shimanskaya and B. V. Sharovskiĭ, Vestnik Kievskogo Gosuniversiteta. 14, seriya fiziki, 1973, in press.

[11] J. Squires, Practical Physics (Russ. transl.), Mir, 1971.

[12] D. Hudson, Statistics for Physicists (Russ. transl.), Mir, 1970.

[13] Yu. I. Shimanskiĭ, Ukr. Fiz. Zh. **13**, 252 (1968).

[14] M. J. Buckingham, Critical Phenomena, Proc. of Conf. Washington, D. C., 1965; National Bureau of Standards, Miscellaneous Publication, No. 273, 1966, p. 95.

[15] In: Physics of Simple Liquids, ed. H. N. V. Temperley, J. S. Rowlinson and G. S. Rushbrooke, North-Holland Publishing Co., Amsterdam, 1968.

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