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PROPERTIES OF MATTER AT SUSCEPTIBILITY EXTREMUM POINTS IN STATIONARY FIELDS IN THE VICINITY OF THE CRITICAL STATE

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A line of susceptibility extrema is established on the basis of experimental data on light scattering in the supercritical region of one- and two-component systems. It is shown by methods of scaling (similarity) theory that the scale parameter $y = \eta/t^{\beta}$ along the line is a constant. The properties of the substance along this line are described.

THE aim of this research is the study of the properties of a substance for values of the temperature t_M and ordering parameter η_M corresponding to the susceptibility extremum $\chi(t_M, \eta_M)$ for fixed external fields that are different from zero. The scaling theory of critical phenomena[1] allows us to consider this problem, without loss of generality, by means of the example of the liquid-vapor critical point. We take as our ordering parameter the deviation of the density in a one-component system, or of the composition in a solution, from the critical value. The role of the external field is played by the gravitational field, which is measured at $T > T_c$ from the upper level $H = 0$ on which the ordering parameter is equal to zero, and at $T < T_c$ from the phase separation boundary.

The analysis of the experimental data on light scattering near the critical liquid-vapor state shows that in the region $T > T_c$ at certain temperatures: the intensity of the scattering at fixed heights $H \neq 0$ passes through a maximum $I_M = (T - T_c)T_c \neq 0$ (Figs. 1 and 2). The corresponding dependences of $t_{RE} \sim \chi$ on η also have extrema at $\eta_M \neq 0$. As $H \to 0$, the coordinates of the susceptibility maximum $t_M \to 0$ and $\eta_M \to 0$. The method of calculation of the scattering intensity in the Rayleigh-Einstein approximation

$$I_{RE} = k\frac{\partial\eta}{\partial h}, \quad k \sim I_0 \frac{\pi^2 V k_B T}{2\lambda^4 R^2}\left(\frac{\partial\varepsilon}{\partial\eta}\right)^2, \quad h = \frac{\rho_c g H}{P_c},$$

has been given in a previous paper.[2]

The experimentally observed extremal behavior of the scattering properties can be established by the methods of scaling theory. For this purpose, we use the equation of state

$$\Delta\mu = t^{\beta\delta} G(y)\,\mathrm{sign}\, h, \tag{1}$$

where $G(y)$ is the scale function of the variable $y = \eta/t^{\beta}$, and is known only for $y \ll 1$ and $y \gg 1$.[3] Recognizing that the deviation of the chemical potential of the pure substance (or the difference of the chemical potentials of the components of a solution) on the value on the critical isochore $\Delta\mu$ is connected with the "field" variable h by the relation $\Delta\mu = -h$, we can obtain the following formulas for the temperature and "field" dependences of the ordering parameter:

$$\eta(t, h) = -\frac{|h|}{a_1 t^{\gamma}}\left[1 - \frac{a_2}{a_1^3}\left(\frac{h}{t^{\beta\delta}}\right)^2 + \ldots\right]\mathrm{sign}\, h, \quad y \ll 1, \tag{2}$$

$$\eta(t, h) = -\left(\frac{|h|}{b_1}\right)^{1/\delta}\left[1 - \frac{b_2}{\delta b_1^{1-1/\beta\delta}}\left(\frac{|h|}{t^{\beta\delta}}\right)^{-1/\beta\delta} + \ldots\right]\mathrm{sign}\, h, \quad y \gg 1, \tag{3}$$

where a_1, a_2, b_1, and b_2 are constants which are the parameters of the equation of state (1), and β, γ, δ are the critical indices. It follows from (2) and (3) that

$$\frac{\partial I_{RE}}{\partial t} \approx -\frac{k\gamma}{a_1 t^{\gamma+1}} < 0 \text{ for } y \ll 1,$$

$$\frac{\partial I_{RE}}{\partial t} \approx \frac{k(1-\beta)b_2}{\beta\delta^2 b_1^2}\left(\frac{|h|}{b_1}\right)^{-(\gamma+1)/\beta\delta} > 0 \text{ for } y \gg 1.$$

Since the function $I_{RE}(t, \eta)$ is differentiable in the critical region, this means that it should have an extremum inside the range ($y \ll 1$, $y \gg 1$).

Using the results of[4], we can show that, within the framework of self-consistent field theory, the value $y \approx 1$ corresponds to this extremum. In the same way, the investigation of the properties of the substance at the points (t_M, η_M) is connected with the intermediate region of the variation of y.

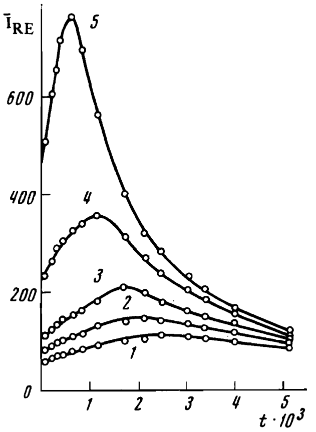

FIG. 1

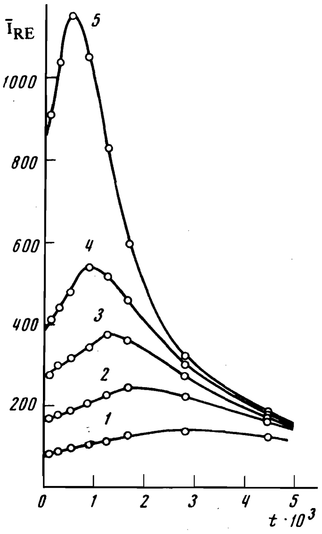

FIG. 2

FIG. 1. Temperature dependence of the symmetrized scattering intensity $I_{RE} = \frac{1}{2}[I_{RE}(H > 0) + \bar{I}_{RE}(H < 0)]$ in n-pentane at different values of H: curve 1–1.30; 2–1.00; 3–0.75; 4–0.40; 5–0.15 cm.

FIG. 2. Temperature dependence of the symmetrized scattering intensity in an n-pentane–cyclopentane solution at various values of H: curve 1–1.40; 2–0.70; 3–0.40; 4–0.25; 5–0.10 cm.

	n-pentane						n-pentane-cyclopentane solution				
$t_M \cdot 10^3$	2.61	2.25	1.81	1.21	0.87	0.68	2.79	1.67	1.24	0.89	0.52
y_M	19.4	19.6	19.6	20.2	20.0	19.2	20.3	21.3	21.0	21.6	20.5
$G(y_M)$	0.134	0.131	0.138	0.140	0.147	0.138	9,5	10.3	9.6	10.0	9.3
$G'(y_M)$	10.2	9.8	9.5	9.5	8.9	9,0	9.7	10.7	10.1	10.5	9.9

Using the scale equation of state (1), we represent the extremal condition of the intensity for different fixed h in the form

$$\left(\frac{\partial I_{RE}}{\partial t}\right)_h = -I_{RE}\frac{\beta\delta G(y)}{tG'(y)}\left[\frac{d}{dy}\left(\ln\frac{G^{\gamma/\beta\delta}}{G'}\right)\right]=0. \tag{4}$$

We can show that (4), as also the second condition of the extremum $(\partial I_{RE}/\partial\eta)_h = 0$, is satisfied in the range $0 < y < \infty$ for some constant value $y = y_M$, which has the derivative

$$\frac{d}{dy}\left\{\ln\frac{[G(y)]^{\gamma/\beta\delta}}{G'(y)}\right\}$$

at zero.

In the space of the thermodynamic variables t, η, and μ the experimentally observed line of extremum susceptibility points corresponds to the value $y = y_M$; at these points the substance possesses the following important properties:

1. The temperature dependence of the ordering parameter behaves in the same fashion as on the coexistence curve, i.e., $\eta_M \sim t_M^{\beta}$.

2. The condition y_M = const denotes the simultaneous constancy of the scale functions $G(y_M)$, $G'(y_M)$, etc., which is equivalent to the temperature dependence of the susceptibility $I_{RE} \sim t_M^{-\gamma}$, of the heat capacity $C_\eta \sim t_M^{-\alpha}$ (as on the critical isochore) and the "field" dependences of the ordering parameter $\eta_M \sim h^{1/\delta}$, the susceptibility $I_{RE} \sim h^{-(\delta-1)/\delta}$, heat capacity $C_\eta \sim h^{-\alpha/\beta\delta}$ (as on the critical isotherm).

From the experimental data on the light scattering in n-pentane and in an n-pentane—cyclopentane solution, we calculated the values of the ordering scale parameter $y = k\eta/t^{\beta}$ and the function $G'(y) = k/t^{\gamma}I_{RE}$ at points of maxima on the scattering intensity. The absolute values of $G(y) = \rho_c gH/P_c t^{\beta\delta}$ were calculated for n-pentane. The values of G(y) in the solution were found with accuracy to within a constant coefficient, as $(H/t^{\beta\delta}) \times 10^{-3}$. The value of $k\eta$ was determined by integration of the expression $I_{RE} = k\,\partial\eta/\partial h$.[2,4] In the calculation of y, G(y), and G′(y), we used the critical indices of n-pentane $\gamma = 1.2$ and $\delta = 4.9$[2] and the values $\gamma = 1.23$ and $\delta = 5.0$, which we found from data on light scattering for a solution of 0.386 mole fraction cyclopentane in n-pentane. The index β was determined as $\gamma/(\delta - 1)$.

The results of the calculation, given in the table, show that the scale quantities y_M, $G(y_M)$, and $G'(y_M)$, which correspond to the maximum susceptibility points at the various heights, agree within the limits of experimental error. The scatter relative to the average values, which did not exceed 5—7%, has a random character and is due to errors of measurement of the scattering intensity and the inaccuracy in the determination of the coordinates of the maxima.

The constancy of the scale quantities y, G(y) and G′(y) that has been found confirms the validity of the conclusions reached above and means that the study of the various singular properties of the substance as the critical point is approached can be carried out along a single experimental observed line $y = y_M$.

In the case of n-pentane, $G(y_M) = 0.137 \pm 0.08$. It can be shown from our data[5] that the absolute value of $G(y_M)$ in cyclopentane is equal to 0.135 ± 0.06. This means that the known asymptotic expansions of G(y) as $y \to 0$ and $y \to \infty$ describe regions where $G(y) \ll 0.14$ and $G(y) \gg 0.14$.

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