$$O_2 + M_T^* \xrightarrow{\gamma_1} MO_2^* \quad (1)$$

and expressions of the type

$$\gamma_1 = \frac{1}{9} k_1 \sum_i \frac{k_s |S_i|^2}{k_{-1} + k_s |S_i|^2},$$

where $|S_i|^2$ is the amplitude of the singlet component of the spin function of the pair $O_2 + M_T$ in the i-th state, k_s is the frequency of the transition to the singlet product at $|S_i|^2 = 1$, k_{-1} is the frequency of the "back scattering" in the interacting particles, and k_1 is the rate constant of the collision of O_2 with M_T^*. A magnetic field that is weak in comparison with the zero field of the molecule O_2 causes the appearance of a singlet component in a larger number of spin states than in the absence of an external field, and consequently increases the γ_1. The maximum increase of γ_1, needed to explain the observed effects, reaches 20 - 40%. It is possible that the singlet product formed directly upon interaction of M_T^* with O_2 is singlet oxygen and the tetracene molecule in the ground state, the reaction between which yields MO_2^*. The photochemical reaction (1) is partly reversible. This possibly explains the weakening of the influence of the magnetic field on the rate of accumulation of MO_2 with increasing time, since the rate of constant of the inverse decay reaction

$$MO_2^* \xrightarrow{\gamma_2} O_2 + M_T^*$$

depends on the magnetic field in the same manner as γ_1.

[1] E.L. Frankevich and E.I. Balabanov, ZhETF Pis. Red. 1, No. 6, 33 (1965) [JETP Lett. 1, 169 (1965)].
[2] E.L. Frankevich and B.M. Rumyantsev, ibid. 6, 553 (1967) [6, 70 (1967)].
[3] R.C. Johnson, R.E. Merrifield, P. Avakian, and R.B. Flippen, Phys. Rev. Lett. 19, 285 (1967).
[4] J.-M. Donnini and F. Abertino, C.R. Acad. Sci., Paris, 266B, 1618 (1968).
[5] E.L. Frankevich, Zh. Eksp. Teor. Fiz. 50, 1226 (1966) [Sov. Phys.-JETP 23, 814 (1966)].
[6] R.E. Merrifield, J. Chem. Phys. 48, 4318 (1968).
[7] V. Ern and R.E. Merrifield, Phys. Rev. Lett. 21, 609 (1968).
[8] A.T. Vartanyan, Dokl. Akad. Nauk SSSR 71, 641 (1950).
[9] A. Bree and L.E. Lyons, J. Chem. Soc. 5179 (1960).
[10] S. Sakai, M. Yoshida, S. Tanaka, H. Mitsudo, and Y. Ooshika, J. Phys. Chem. Solids 28, 1913 (1967).
[11] V.V. Slobodyanik and A.N. Faidysh, Zh. fiz. khim. 39, 1041 (1965).
[12] E.L. Frankevich, Disc. Faraday Soc. 51, 37 (1971).
[13] N. Geacintov, M. Pope, and F. Vogel, Phys. Rev. Lett. 22, 593 (1969).

EXPERIMENTAL VERIFICATION OF SCALE LAW IN THE CRITICAL REGION OF CYCLOPENTANE

A.D. Alekhin and N.P. Krupskii
Kiev State University
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According to the hypothesis that the thermodynamic functions are homogeneous [1], the scale equation of state near the liquid-vapor critical point is given by [2]

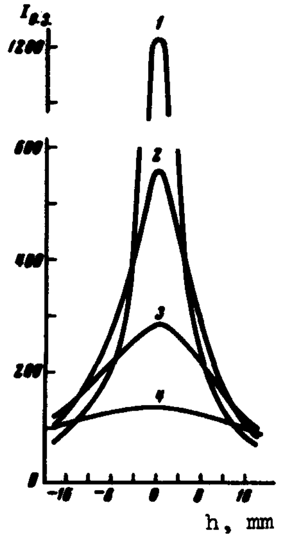

Fig. 1. Isotherms of height distribution of the intensity of scattered light in cyclopentane ($\lambda = 5461$ Å) for four transcritical temperatures $T - T^{cr}$ (1 - 0.37°, 2 - 0.84°, 3 - 1.40°, 4 - 2.89°).

$$\frac{|\Delta\mu|}{|t|^{\beta\delta}} = m(y), \tag{1}$$

where $\Delta\mu = \mu(\rho, t) - \mu(0, t)$ is the deviation of the chemical potential from the value on the critical isochore; ρ and t are the dimensionless deviations of the density and temperature from the critical values; $m(y)$ is a universal function of the argument $y = |\rho|/|t|^{\beta}$; β and δ are the critical exponents of the coexistence curve and of the critical isotherm. Differentiating (1) with respect to ρ, we obtain the scale equation of state in differential form $(\partial\mu/\partial\rho)|t|^{-\gamma} = m'(y)$, where $\gamma = \beta(\delta - 1)$.

Thus, the scale theory is based on the assumption that there exist scaled thermodynamic quantities m and y, the transition to which transforms the surface $\mu(\rho, t)$ into the line $m(y)$.

The scale theory does not give the explicit form of the function $m(y)$. All that is known is that as $y \to 0$, i.e., near the critical isochore, we have

$$m(y) = a_1 y + a_3 y^3 + a_5 y^5 + \ldots, \tag{2}$$

and near the critical isotherm, where $y \to \infty$,

$$m(y) = b_0 y^{\delta} \pm b_1 y^{\delta - \frac{1}{\beta}} + b_2 y^{\delta - \frac{2}{\beta}} \pm \ldots, \tag{3}$$

where the minus sign corresponds to the case $t < 0$.

For an experimental verification of the homogeneity hypothesis, we used data obtained in investigations of the scattering of light at $\lambda = 5461$ Å at an angle of 90° in cyclopentane at $T > T^{cr}$ [3] (see Fig. 1). The errors in the determination of the intensity of single scattering, equal to 4 - 6%, consist of the random errors due to the noise in the electronic apparatus (1 - 2%) and of the errors (2 - 4%) arising when corrections are introduced for the attenuation of the incident and scattered light fluxes and for secondary scattering, which have a systematic character within the limits of an individual intensity isotherm $I(h, t)$.

Integrating the relations $I_{RE}(h, t) = -k\partial\rho(h, t)/\partial h$ (h - height reckoned from the level with critical density), we determined, accurate to a factor $k \sim (I_0 V\pi^2/2R^2\lambda^4)(\partial\varepsilon/\partial\rho)^2 k_B T$, the isotherms of the height distribution of the density deviations $k\rho(h, t)$. The method for separating the Rayleigh-Einstein intensity I_{RE} from the experimental data is described in [4]. Numerical integration smooths out the random errors of the initial data, i.e., the errors in the determination of $k\rho(h, t)$ are smaller than the errors in the determination of the scattering intensity. The height dependences of the averaged quantities $\overline{k\rho} = 0.5(|k\rho|_{+h} + |k\rho|_{-h})$ are listed in the table.

In a gravitational field $\Delta\mu \sim h$, making it possible to interpret the height dependences of the density and of the susceptibility as the dependence of these quantities on $\Delta\mu$ and to use on this basis the "gravitational" data to verify the scale theory.

Height distributions of $\overline{k\rho} \times 10$ for eight trans-critical temperatures

$T - T^{cr}$, deg / $\|h\|$, mm	0,37	0.54	0.72	0,84	1.40	2,04	2,43	2,89
2	2,640	1,820	1,360	1,200	0.596	0.377	0.330	0.284
4	3,880	3,080	2,430	2,140	1,150	0,738	0,651	0.562
6	4.650	3,940	3,280	2,920	1,680	1,090	0.965	0,834
8	5,160	4,560	3,980	3,580	2,160	1,430	1,270	1,110
10	5,550	5,050	4,530	4,120	2,620	1,760	1,570	1,360
12	5,860	5,420	4,960	4,550	3,030	2,080	1,860	1,610
14	6,110	5.720	5,310	4,910	3,390	2,380	2,130	1,840
16	6,330	5,980	5,590	5,200	3,710	2,670	2,390	2,070
18	6,510	6,190	5,830	5,450	3,990	2,930	2,630	2,290

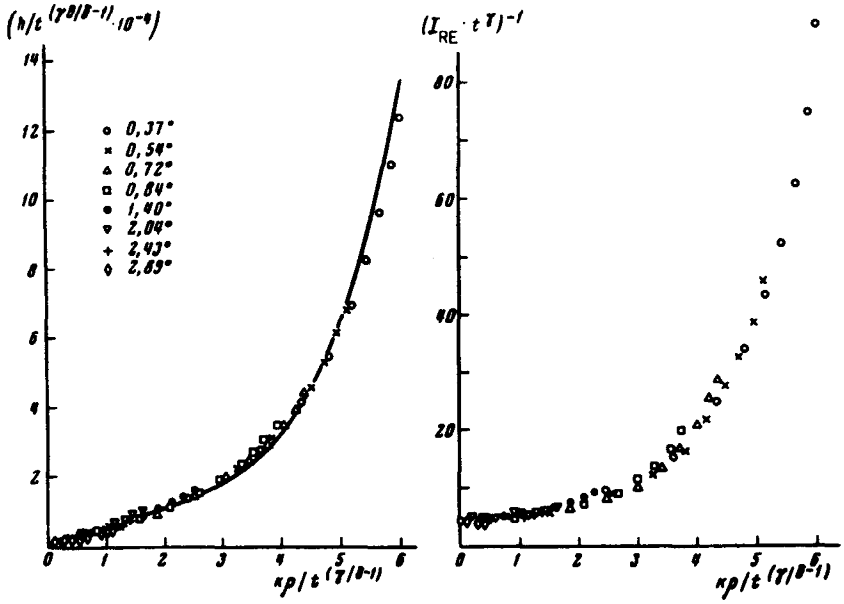

Fig. 2. a - Dependence of the scaled chemical potential on the scaled density: o - 0.37°, × - 0.64°, Δ - 0.72°, □ - 0.84°, ● - 1.40°, ∇ - 0.04°, + - 2.43°, ◊ - 2.89°; b - dependence of the reciprocal scaled susceptibility on the scale density.

Figures 2a and 2b show the dependences of the scaled quantities m and m', defined apart from constant coefficients as $|h|/|t|^{\beta\delta}$ and $(I_{RE}t^{\gamma})^{-1}$, on the scale density $\overline{k\rho}/|t|^{\beta}$, plotted for eight transcritical temperatures in a single system of coordinates. In the calculation of the scale variables we used the critical exponents $\gamma = 1.23 \pm 0.05$ and $\delta = 5.0 \pm 0.3$, which were obtained earlier [3]. The exponent β was taken to be $\gamma/(\delta - 1)$. Within the limits of experimental error, the scale isotherms coincided, forming single m(y) and m'(y) curves, thus confirming the validity of the homogeneity hypothesis [1] and indicating that the scale theory is applicable not only to "simple" liquids [2], but also to more complicated substances, particularly cyclopentane.

For small y it follows from [2] that $m'(y) - m'(0) = 3a_3y^2 + \ldots$ To verify this premise of the scale theory, we plotted $[I^{-1}(h) - I^{-1}(0)]t^{-\gamma}$ against $\overline{k\rho}/|t|^{\beta}$ in a doubly logarithmic scale (Fig. 3). The errors in Fig. 3 consist of systematic (2 - 4%) and random errors. To calculate the latter we used the error transfer formula [5]. In the region $\overline{k\rho}/|t|^{\beta} \leq 2$, where

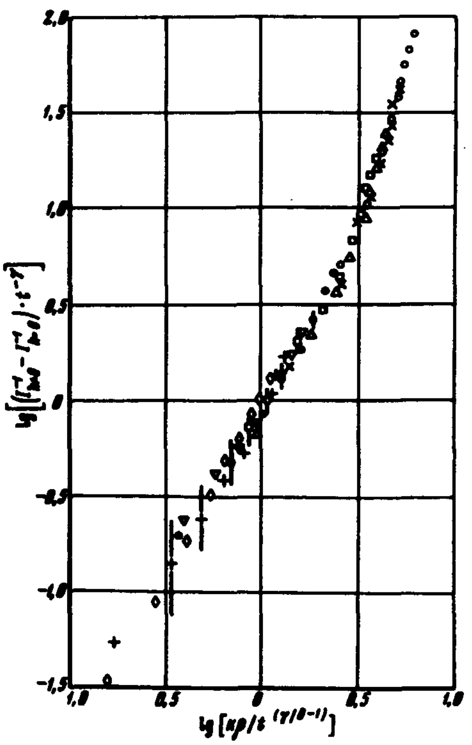

Fig. 3. Dependence of the quantity $[I^{-1}(h) - I^{-1}(0)]t^{-\gamma} \sim m'(y) - m'(0)$ on the scale density in a log-log scale.

$m(y) \simeq a_1 y$ within 15%, the plot shown in Fig. 3 is a straight line with a slope close to 2. A numerical analysis yields a value 1.9 ± 0.3. This result, which agrees with (2), means that on any transcritical isotherm there exists a section adjacent to the critical isochore, which is described by the "classical" expansion in terms of ρ, namely $\Delta\mu = A(t)\rho + B(t)\rho^3 + \ldots$ The increase of the slope with increasing y, observed in Fig. 3, is connected with the transition into the region where the expansion (3) is valid, and the transcritical isotherms approach the asymptotic form $|\Delta\mu| \sim |\rho|^\beta$ at sufficiently large $|\rho|/|t|^\delta$.

We have also compared the obtained data with the equation of state used in [4] and [6], which can be reduced to the form (1) with

$$m(y) = ay + by^\delta. \qquad (4)$$

A plot of (4), obtained by least squares [5], is shown in Fig. 2a. The deviations of the theoretical curve from the experimental one have a systematic character, but do not exceed 6 - 7%. The reason for these small deviations lies in the fact that in the limiting cases $y \to 0, \infty$, the correction terms of (4) do not coincide with the second terms of the expansions (2) and (3). Thus, near the critical isochore, the correction term in (4) is of the form by^δ, whereas our analysis, which agrees with (2), shows that the second term behaves like y^3.

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[1] R. Griffiths, Phys. Rev. 158, 176 (1967).
[2] M. Green, M. Vicentini-Missoni, and J. Levelt Sengers, Phys. Rev. Lett. 18, 1113 (1967); Phys. Rev. Lett. 22, 389 (1969).
[3] A.D. Alekhin, N.P. Krupskii, and Yu.B. Minchenko, Ukr. Fiz. Zh. 15, 509 (1970); A.D. Alekhin, Candidate's Dissertation, Kiev, 1971.
[4] A.V. Chalyi and A.D. Alekhin, Zh. Eksp. Teor. Fiz. 59, 337 (1970) [Sov. Phys.-JETP 32, 181 (1971)].
[5] D. Hudson, Statistics for Physics (Russian translation), Mir, 1970.
[6] L.M. Artyukhovskaya, E.T. Shimanskaya, and Yu.I. Shimanskii, Zh. Eksp. Teor. Fiz. 59, 688 (1970) [Sov. Phys.-JETP 32, 375 (1971)].