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A Small-Angle X-Ray Scattering Study of Critical Opalescence in Nitrogen^{1a}

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Measurements have been made of the X-ray scattering from nitrogen at a series of temperatures above and below the critical temperature at the critical pressure of 33.5 atm. and also at pressures of 31.9 and 35.0 atm. The temperature regulation equipment permitted data to be obtained at temperatures within about 0.05°K. of the critical temperature. For the conditions of temperature and pressure which were studied, the angular distribution of the scattered intensity was in good agreement with the predictions of the Ornstein-Zernike theory. The X-ray data were used to compute values of the isothermal compressibility, with the compressibilities being calibrated on an absolute scale by using compressibility and density values for argon and employing the principle of corresponding states. Short-range correlation lengths were also computed.

A large increase in the light and X-ray scattering from a system is observed when the system is near its critical point. This effect is known as critical opalescence. The authors have recently investigated the X-ray scattering from argon near its critical point.² In order to compare critical opalescence in two different one-component systems, the X-ray scattering from nitrogen near its critical point has also been studied.

The X-ray collimation system, cryostat assembly, and temperature control employed for argon were also used for nitrogen. However, for nitrogen, copper K α radiation was substituted for molybdenum, and for all scattering curves the sample chamber had a thickness of 0.437 cm. Linde "High Purity Dry" nitrogen, rated as 99.995% pure, was used.

Background scattering from the beryllium windows of the sample cell was a greater problem with nitrogen than with argon since the beryllium scattering increases more rapidly with decreasing scattering angle than does the scattering from the sample. Thus, the longer X-ray wave length, corresponding to measurements nearer the center of the scattering pattern, increased the relative magnitude of the background. To lower the background scattering, different lots of beryllium were tested to select the pieces giving the lowest scattering, and the window thickness was reduced to 0.0095 in. Under the most unfavorable conditions, the background was about 20% of the total intensity.

The electronic temperature control³ maintained the sample temperature constant within at least $\pm 0.05^\circ\text{K}$. Temperatures were measured with respect to the critical temperature with a copper-constantan thermocouple, for which calibration showed that in this temperature region the thermoelectric power was 22 $\mu\text{v.}/^\circ\text{K}$. Temperature measurements can be considered reliable within $\pm 0.05^\circ\text{K}$. Scattering curves 1L and 1V, which were taken as close to the critical temperature as possible, can be considered to represent the scattering at a temperature within 0.05°K. of the critical temperature.

Scattering curves were recorded for the values of absolute temperature T and pressure P corresponding to the values of T/T_c and P/P_c shown in Table I. For nitrogen⁴ the critical temperature T_c is 126.26°K., and the critical pressure equals 33.54 atm. Figures

TABLE I^a

Scattering pattern	T/T_c^b	P/P_c^b	D , g./cm. ³	$I_{\text{rel}}(0)$	β , atm. ⁻¹	l , Å.
7V	1.0360	1.000	0.152	3.50	0.070	11
6V	1.0180	1.000	.172	5.80	.105	13
5V	1.0090	1.000	1.96	9.10	.146	13
4V	1.0036	1.000	.216	16.0	.23	11
3V	1.0018	1.000	.230	32.	.44	12
2V	1.0005	1.000	.28	100	1.13	12
1V	1.0000	1.000	.31	600	6	12
1L	1.0000	1.000	.31	1500	15	12
2L	0.9996	1.000	.38	56.0	0.47	12
3L	.9982	1.000	.400	18.0	.143	13
4L	.9964	1.000	.413	9.00	.069	15
5L	.9910	1.000	.448	4.10	.029	17
6L	.9820	1.000	.478	2.20	.0148	23
7L	.9640	1.000	.528	1.28	.0080	42
17V	1.0281	0.953	.142	3.64	0.079	13
16V	1.0101	.953	.159	5.38	.106	14
15V	1.0011	.953	.175	7.85	.14	13
14V	0.9957	.953	.191	10.8	.18	11
13V	.9939	.953	.201	14.8	.23	12
12V	.9926	.953	.206	23.2	.36	12
11V	.9921	.953	.211	27.7	.42	12
11L	.9917	.953	.420	23.6	.18	13
12L	.9892	.953	.448	8.33	.060	15
13L	.9831	.953	.474	3.54	.024	19
14L	.9741	.953	.497	2.06	.0135	17
15L	.9560	.953	.533	1.27	.0079	29
27V	1.0435	1.045	.157	3.73	.072	12
26V	1.0254	1.045	.182	6.10	.104	12
25V	1.0164	1.045	.206	10.1	.15	12
24V	1.0110	1.045	.233	19.3	.26	11
23V	1.0092	1.045	.249	32.0	.40	12
22V	1.0081	1.045	.274	55.3	.63	12
21V	1.0074	1.045	.302	85.5	.89	11
21L	1.0072	1.045	.318	103	1.02	12
22L	1.0058	1.045	.365	39.2	0.34	13
23L	1.0041	1.045	.391	15.3	.124	13
24L	0.9987	1.045	.439	5.85	.042	17
25L	.9897	1.045	.475	2.67	.018	20
26L	.9714	1.045	.510	1.39	.0089	36

^a Values of P/P_c , T/T_c , density D , relative scattered intensity $I_{\text{rel}}(0)$ at zero scattering angle, compressibility β determined from the scattering data, and short-range correlation length l .
^b The critical temperature T_c is 126.26°K.; the critical pressure P_c equals 33.54 atm.; T is the absolute temperature; and P is the pressure.

1 and 2 give the scattering curves for the critical pressure. Similar curves were obtained at other pressures.

In order to interpret the data, the density D of nitrogen must be known for the conditions of temperature

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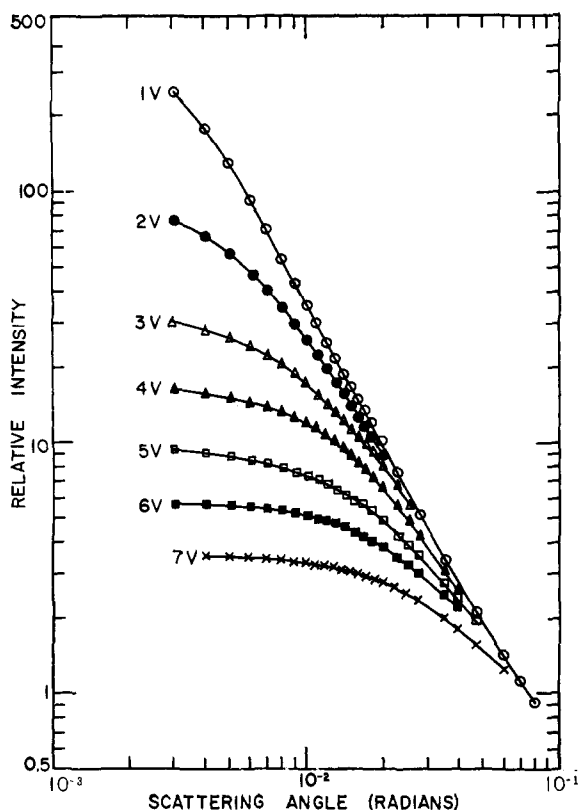


Fig. 1.—Small angle X-ray scattering patterns for nitrogen vapor at the critical pressure $P_c = 33.5$ atm., for the following values of T/T_c : 7V, 1.0360; 6V, 1.0180; 5V, 1.0090; 4V, 1.0036; 3V, 1.0018; 2V, 1.0005; 1V, 1.000. (The critical temperature T_c equals 126.26°K.)

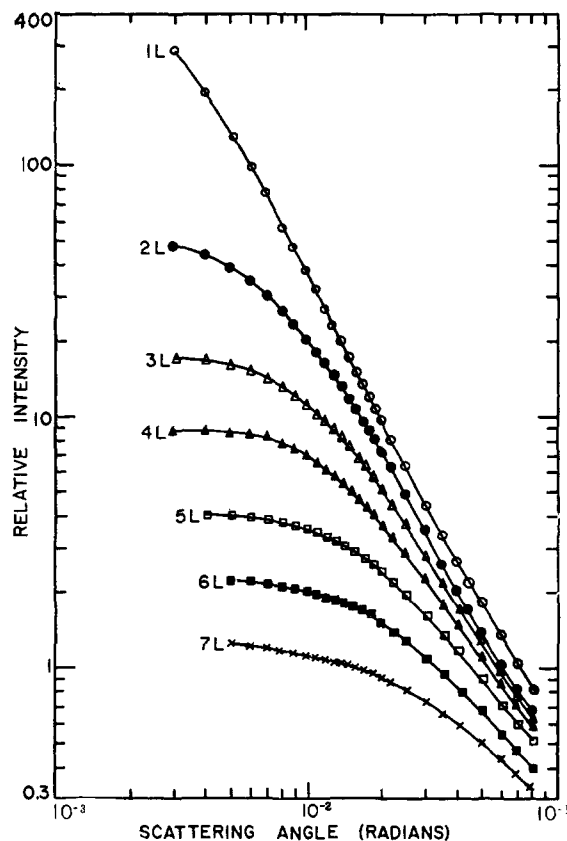


Fig. 2.—Small angle X-ray scattering patterns for nitrogen liquid at the critical pressure $P_c = 33.5$ atm., for the following values of T/T_c : 7L, 0.9640; 6L, 0.9820; 5L, 0.9910; 4L, 0.9964; 3L, 0.9982; 2L, 0.9996; 1L, 1.000. (The critical temperature T_c equals 126.26°K.)

and pressure at which the measurements are made. Since density data could not be obtained from the literature, densities were computed by the method of Pitzer, *et al.*,⁴ and also from measurements of the X-ray absorption. Densities obtained by the two methods at the critical pressure agreed within a few per cent, except for two values, for which deviation was about 10%. Similar agreement was obtained at pressures of 31.9 and 35.0 atm. Because of the possible errors involved in measurements of X-ray absorption, the values computed by the technique of ref. 4 ordinarily were used in analysis of the data.

The angular distribution of the scattered intensity for nitrogen was found to be of the same form that was observed for argon. Since the angular distribution thus is in agreement with the predictions of the Ornstein-Zernike theory, eq. 1, 2, and 3 of ref. 2 were used to analyze the scattering data. According to eq. 3, the experimental extrapolated intensity $I_{rel}(0)$ at zero scattering angle is given by

$$I_{rel}(0) = AkT\rho\beta$$

where k is Boltzmann's constant, T is the absolute temperature, ρ is the number of molecules per unit volume, β is the isothermal compressibility, and A is a proportionality constant depending on the experimental apparatus. If this constant can be evaluated, and if density values are available, the scattering data can provide values of the isothermal compressibility β .

In the authors' study of argon, by numerical differentiation of the data of Michels, Levelt, and De

Graaff,⁵ the compressibility was determined at several points somewhat removed from the critical point. For argon, these values of β , which are shown in the second column from the right in Table I of ref. 2, permitted evaluation of the constant A , which was then used to find the compressibility from the X-ray data, including values of β at temperatures so close to T_c that reliable numerical differentiation was not possible.

This procedure could not be used to evaluate A for nitrogen, because the pressure dependence of the density was not known to sufficient accuracy for the critical region. According to the principle of corresponding states, however, the quantity $P_c\beta$ should be the same for all systems at given values of T/T_c and P/P_c . This assumption was used to compute β for nitrogen at $P = P_c$ from the corresponding β -values for argon. After the compressibilities from the argon data were plotted as shown by the circles in Fig. 3, the relative compressibilities from the zero-angle X-ray scattering for nitrogen were multiplied by the constant which gave the best fit with the compressibilities computed from the principle of corresponding states. The resulting value of A for the scattering data of Table I was found to be 0.852. After this constant was evaluated from the scattering data at the critical pressure, the same constant was used to compute β from the zero-angle scattering from nitrogen at other pressures. Within experimental error, the relative compressibilities found from the scattering data

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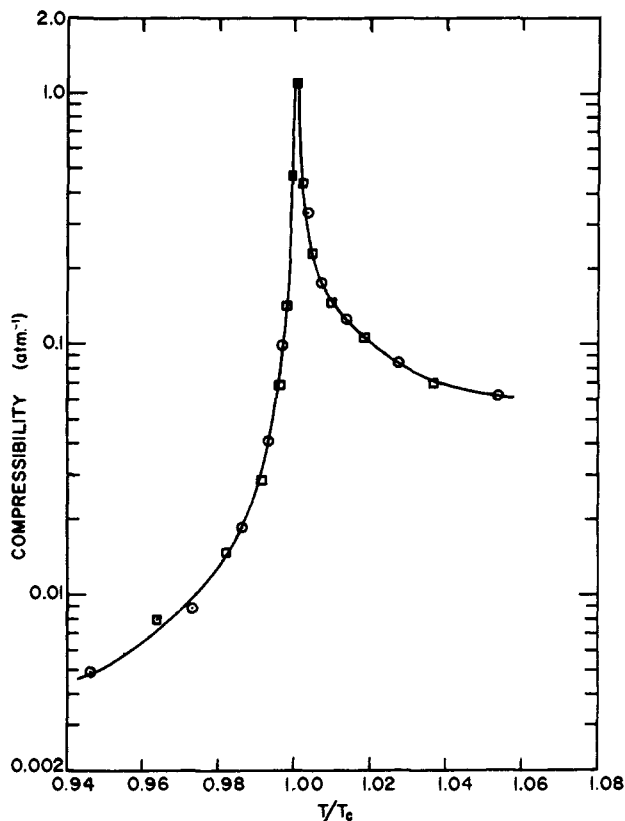


Fig. 3.—Isothermal compressibility of nitrogen at the critical pressure $P_c = 33.5$ atm., as a function of T/T_c , where T is the absolute temperature and T_c is the critical temperature. Points obtained by the principle of corresponding states are denoted by circles, while values from the X-ray scattering data for nitrogen are shown by squares.

for nitrogen fell on the same curve as the compressibilities obtained from the argon data by use of the principle of corresponding states. For $P/P_c = 1.000$ and $P/P_c = 0.953$, the argon compressibilities were taken from the second column from the right in Table I of ref. 2, while for $P/P_c = 1.045$, they were computed by numerical differentiation of the isotherms of Michels, Levelt, and De Graaff.

The X-ray values of β , except those from curves 1L and 1V, can be considered reliable within about $\pm 10\%$. Because of the difficulty of extrapolating

curves 1L and 1V to zero angle, the compressibilities for these conditions could have errors as high as $\pm 100\%$.

The short-range correlation lengths l , as defined by Fixman,⁶ were computed from eq. 2 and 3 of ref. 2 and are given in Table I. In the critical region, where $kT\rho\beta \gg 1$, the length l_D introduced by Debye⁷ is related⁸ to l by the equation $l = (15/4)^{1/2}l_D$.

Not only are the scattering curves for nitrogen in agreement with the angular dependence given by the Ornstein-Zernike theory, as was found for argon, but the values of l for nitrogen near its critical point are very near the figure of 10–11 Å. obtained for l near the critical point of argon.

In the study of critical opalescence in argon, an estimate of l_D was made by assuming that in the expression for l_D given by eq. 30 of ref. 6, the interaction potential energy was spherically symmetric and proportional to r^{-6} for an intermolecular separation r . The molecules were considered to be rigid spheres with diameter σ . Under these conditions, $l_D = \sqrt{3}\sigma$. If these results are applied to the X-ray scattering data for nitrogen,⁹ the approximate average l value of 12 Å. gives $l_D = 6.2$ Å. and $\sigma = 3.6$ Å. This value of σ is quite near the molecular diameter of 3.15 Å. obtained for nitrogen from the van der Waals equation.¹⁰

The agreement of the data with the angular distribution of the Ornstein-Zernike theory in the range of temperatures studied does not exclude the possibility that, as Fisher has suggested,¹¹ deviations from the Ornstein-Zernike angular distribution may occur at smaller scattering angles or at temperatures closer to the critical temperature.

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(9) The authors are grateful to P. Debye for suggesting this calculation.

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