

theories are approximate and a discussion of their relative merits is found in the Faraday Society's "General Discussion on Dielectrics."¹³ If the molecular dipole moment were constant, Debye's theory would require that the Clausius-Mosotti function $(\epsilon-1)/d(\epsilon+2)$ be independent of density at a given temperature. Tables I and II show that there is a large decrease in the C-M ratio for CH_3F with increasing density. It is noteworthy that Keyes and Oncley² report an increase in this ratio for NH_3 . Onsager's theory would require the function $(\epsilon-n^2)(2\epsilon+n^2)/ed(n^2+2)^2$ to be similarly independent of density (here n is the refractive index). For the present case this function increases by 7 percent. These effects might arise either from the inadequacy of the theories or from changes in the dipole moment of CH_3F with density.

There is no reason to suppose that the dipole moment, μ , of a CH_3F molecule in the compressed gas is the same as that of an isolated molecule since a variation of μ with density might easily occur if the molecules were

TABLE III. Dielectric absorption in fluoromethane at 1 megacycle.^a

50°C		75°C	
Density (moles/l)	$\tan\delta$	Density (moles/l)	$\tan\delta$
≤6.6	0.00000	≤6.9	0.00000
7.03	0.00022	7.70	0.00009
7.40	0.00046	8.38	0.00030
7.94	0.00128	9.05	0.00072
8.43	0.00176	9.67	0.00164
8.93	0.00227	10.30	0.00312
9.50	0.00330	10.87	0.00504
10.06	0.00444	11.42	0.00787
10.58	0.00518	11.94	0.01022
11.03	0.00669		
11.51	0.00935		

^a Measurements to 5 megacycles showed an increase in the absorption with frequency in this range.

distorted by the intermolecular forces. In this respect the apparent dipole moments calculated from the Debye and Onsager theories and given in Table IV are of interest. The change in the Debye values is larger than would be expected from considerations of the magnitude of the intermolecular forces in the pressure range studied. Onsager's model leads to a smaller apparent change in μ and appears to be the more satisfactory in the present case.

If it were possible to calculate the distribution function for compressed CH_3F , Kirkwood's precise treatment^{13,14} of polar fluids could be applied to the experimental data to find the real change in μ . This calculation is unfortunately exceedingly difficult. In the next section the theory is used in the opposite way, assuming μ to be constant, to find the change in Kirkwood's correlation parameter, g .

¹³ "General Discussion on Dielectrics," Trans. Faraday Soc. 42A (1946).

¹⁴ J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).

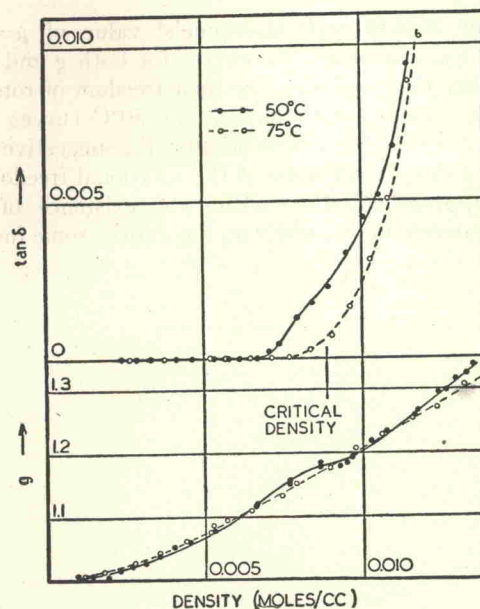


FIG. 2. Dielectric loss and correlation parameter for fluoromethane.

RESTRICTED ROTATION NEAR THE CRITICAL POINT

In an earlier note¹⁵ the sudden development of the dielectric loss near the critical density of CH_3F was taken as evidence of a fairly sharp transition between free and restricted rotation of the dipolar molecules. Some further evidence of this is found in the change of ϵ with density. Kirkwood,^{13,14} allowing for the effects of hindered rotation on the dielectric constant, obtained the expression

$$(2\epsilon+1)(\epsilon-1)/9ed = {}_D P + 4\pi N_0 g \mu^2 / 9kT,$$

where ${}_D P$ is the molar distortion polarization, N_0 is Avogadro's number, and μ is the dipole moment of an isolated molecule. The correlation parameter g can be related to the forces restricting the rotation of the molecules. Its divergence from unity is a measure of the extent of the restriction.

Figure (2) shows g as a function of density and temperature. It was calculated on the assumption that μ is

TABLE IV. Apparent dipole moment of fluoromethane.

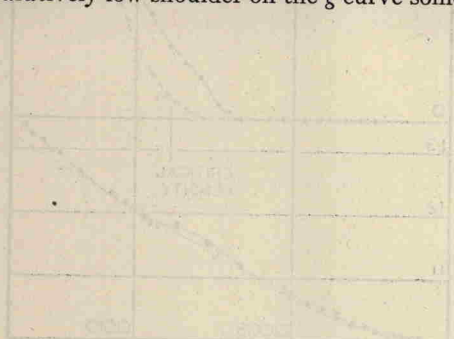
d (moles/l)	50°C		d (moles/l)	75°C	
	$\mu_{\text{App}}^{\text{Debye}}$ (esu $\times 10^{-18}$) ^a	$\mu_{\text{App}}^{\text{Onsager}}$ ^b		$\mu_{\text{App}}^{\text{Debye}}$ (esu $\times 10^{-18}$) ^a	$\mu_{\text{App}}^{\text{Onsager}}$ ^b
0.960	1.806	1.813	1.190	1.804	1.813
3.570	1.745	1.819	3.535	1.759	1.825
7.69	1.615	1.857	6.44	1.670	1.838
10.28	1.517	1.859	9.79	1.562	1.863
12.40	1.449	1.876	11.58	1.500	1.865
14.02	1.400	1.889	14.00	1.423	1.869

^a Smyth and McAlpine's figure (see reference 4) for the distortion polarization ${}_D P = 8.95$ cc/mole was used in calculating $\mu_{\text{App}}^{\text{Debye}}$.

^b An "effective" refractive index n was calculated from the relationship $(n^2-1)/d(n^2+2) = {}_D P$.

¹⁵ David, Hamann, and Pearse (to be published).

constant. Smyth and McAlpine's⁴ value of $\mu=1.81 \times 10^{-18}$ esu was used. The curves for both g and $\tan\delta$ show that the molecules lose their freedom of rotation at high densities. In addition, the 50°C curves have shoulders near the critical density, d_c , suggestive of a fairly sudden loss of some of the rotational freedom as d_c is approached. To confirm the existence of the comparatively low shoulder on the g curve some further



measurements were made several weeks after the original series. These gave results in complete agreement with the earlier ones.

The authors wish to thank Professor R. J. W. Le Fèvre for suggestions leading to this investigation and for some helpful discussions.

The advice and assistance of Dr. J. S. Dryden in the dielectric absorption measurements were of great value.

RESTRICTED ROTATION NEAR THE CRITICAL POINT

In an earlier note,⁵ the sudden development of the dielectric loss near the critical density of CCl₄ was taken as evidence of a fairly sharp transition between free and restricted rotation of the dipolar molecules. Some further evidence of this is found in the change in the dielectric loss near the critical density. It is observed that the dielectric loss near the critical density is not a smooth curve but has a shoulder near the critical density. This is shown in Figure 12, which is a plot of the dielectric loss near the critical density versus density. The curve shows a sharp peak near the critical density, and a shoulder near the critical density. This is evidence of a fairly sharp transition between free and restricted rotation of the dipolar molecules.

Figure 12 shows a plot of the dielectric loss near the critical density versus density. The curve shows a sharp peak near the critical density, and a shoulder near the critical density. This is evidence of a fairly sharp transition between free and restricted rotation of the dipolar molecules. The dielectric loss near the critical density is not a smooth curve but has a shoulder near the critical density. This is shown in Figure 12, which is a plot of the dielectric loss near the critical density versus density. The curve shows a sharp peak near the critical density, and a shoulder near the critical density. This is evidence of a fairly sharp transition between free and restricted rotation of the dipolar molecules.

Density (g/cm ³)	Dielectric Loss (tan delta)	Dielectric Constant (epsilon')
1.400	0.000	1.000
1.450	0.000	1.000
1.500	0.000	1.000
1.550	0.000	1.000
1.600	0.000	1.000
1.650	0.000	1.000
1.700	0.000	1.000
1.750	0.000	1.000
1.800	0.000	1.000
1.850	0.000	1.000
1.900	0.000	1.000
1.950	0.000	1.000
2.000	0.000	1.000
2.050	0.000	1.000
2.100	0.000	1.000
2.150	0.000	1.000
2.200	0.000	1.000
2.250	0.000	1.000
2.300	0.000	1.000
2.350	0.000	1.000
2.400	0.000	1.000
2.450	0.000	1.000
2.500	0.000	1.000
2.550	0.000	1.000
2.600	0.000	1.000
2.650	0.000	1.000
2.700	0.000	1.000
2.750	0.000	1.000
2.800	0.000	1.000
2.850	0.000	1.000
2.900	0.000	1.000
2.950	0.000	1.000
3.000	0.000	1.000

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Table II. Dielectric loss near the critical density of CCl₄ at 50°C.

Density (g/cm ³)	Dielectric Loss (tan delta)	Dielectric Constant (epsilon')
1.400	0.000	1.000
1.450	0.000	1.000
1.500	0.000	1.000
1.550	0.000	1.000
1.600	0.000	1.000
1.650	0.000	1.000
1.700	0.000	1.000
1.750	0.000	1.000
1.800	0.000	1.000
1.850	0.000	1.000
1.900	0.000	1.000
1.950	0.000	1.000
2.000	0.000	1.000
2.050	0.000	1.000
2.100	0.000	1.000
2.150	0.000	1.000
2.200	0.000	1.000
2.250	0.000	1.000
2.300	0.000	1.000
2.350	0.000	1.000
2.400	0.000	1.000
2.450	0.000	1.000
2.500	0.000	1.000
2.550	0.000	1.000
2.600	0.000	1.000
2.650	0.000	1.000
2.700	0.000	1.000
2.750	0.000	1.000
2.800	0.000	1.000
2.850	0.000	1.000
2.900	0.000	1.000
2.950	0.000	1.000
3.000	0.000	1.000

It is now possible to calculate the dielectric loss near the critical density of CCl₄ at 50°C. The dielectric loss near the critical density is not a smooth curve but has a shoulder near the critical density. This is shown in Figure 12, which is a plot of the dielectric loss near the critical density versus density. The curve shows a sharp peak near the critical density, and a shoulder near the critical density. This is evidence of a fairly sharp transition between free and restricted rotation of the dipolar molecules.

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