

FIGURE 17. Density against height for N_2O at a relative temperature $\vartheta = -0.004^\circ C$ and at different mean densities given by the small circle at each curve.

Finally figure 18 is measured with $CClF_3$ at a mean density $\rho/\rho_c = 0.989$, and the different curves correspond to temperature differences with the critical value from $\vartheta = -0.065$ until $+0.265^\circ C$.

In the CO_2 -molecule the two O-atoms are placed symmetrically on opposite sides of the C-atom, corresponding to the scheme $O=C=O$. The N_2O -molecule is asymmetric and therefore polarized following the scheme $N\equiv N=O$. The $CClF_3$ molecule has the shape of a tetraeder with the C-atom in the middle and the halogen atoms at the corners of the tetraeder. As these three molecules, differing in shape and chemical constitution show the same behavior in the neighborhood of the critical state, it is to be expected that this behavior is a general quality of all substances.

The critical data which we found are in good agreement with the results of other authors.

Measurements with H_2O are now being done. This molecule has the shape of a triangle and its behavior near the critical state seems to be the same as for the other substances. However, the measurements are much more difficult due to the higher temperature $t_c = 374.15^\circ C$ and the higher pressure $p_c = 221.3$ bar. Windows of glass and even of quartz are impossible because these substances are corroded and lose their optical quality.

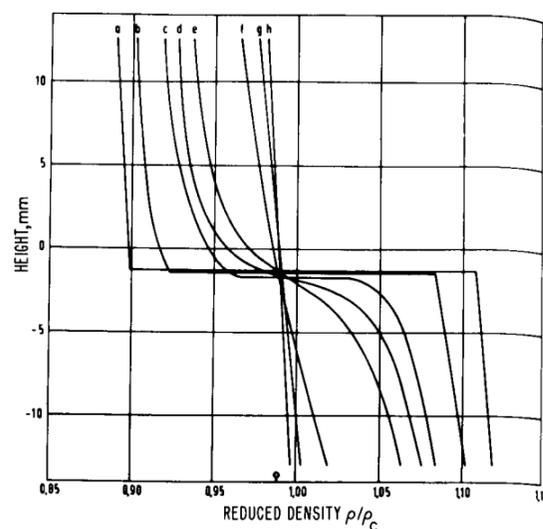


FIGURE 18. Density against height for $CClF_3$ with the mean density $0.989 \rho_c$ and the following temperatures relative to the critical temperature $t_c = 28.715^\circ C$: a. $-0.065^\circ C$; b. $-0.025^\circ C$; c. $0.000^\circ C$; d. $0.021^\circ C$; e. $0.040^\circ C$; f. $0.093^\circ C$; g. $0.183^\circ C$; h. $0.265^\circ C$.

Finally we found that sapphire windows withstand corrosion and these are used now.

6. Summary

The above experiments show undoubtedly that near the critical state of substances considerable gradients of density are produced by gravity. For the three substances encountered, the density at the critical pressure and near the critical temperature changes by about 10 percent over a height of about 10 mm. These distributions of density are stable and reproducible. After any changes of state of the fluid, they are restored by diffusion and some kind of sedimentation within times of about 2 hr for heights of some centimeters.

7. References

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Notes, Definitions, and Formulas for Critical Point Singularities

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1. Introduction

For the convenience of participants a set of definitions and notes concerning the various critical point singularities and a table of formulas relating the lattice gas and Ising ferromagnet models were distributed at the Conference. These are reproduced here with a few corrections and extensions.

Most of the results quoted are described and discussed in detail in references 1, 2, and 3 where further references to the literature are given. A few more recent results are contained in references 4 to 8 and, of course, in the work reported at this Conference particularly in connection with critical scattering by Chu, Passel, Nathans, Dietrich, and Als-Nielsen.

2. Critical Point Exponents

For theoretical discussions and in the analysis of experimental data it is useful to have a precise definition of a critical point exponent. This may be given as follows:

$$\text{if } \lim_{x \rightarrow 0^+} \log f(x) / \log x = \lambda,$$

$$\text{we say } f(x) \sim x^\lambda \text{ as } x \rightarrow 0^+.$$

Note that with this definition the statement $f(x) \sim x^\lambda$ does not exclude the possibility of a logarithmically divergent factor, i.e., $Ax^\lambda |\log x| \sim x^\lambda$. In particular if $\lambda = 0$ the function $f(x)$ might diverge as $|\log x|$ for example, or $f(0)$ might be finite, the function $f(x)$

then being either continuous or discontinuous as x passes through zero.

The definitions of the most important critical point exponents for gases and ferromagnets are set out in the following table together with certain relations between them. Analogous formulas hold for binary alloys and binary fluid systems. Note that the exponent η enters directly into the scattering of waves at the critical point through the formula

$$1/I_s(\mathbf{k}) \sim k^{2-\eta},$$

where $I(\mathbf{k})$ is the intensity of scattering at wave vector \mathbf{k} with $k = (4\pi/\lambda) \sin \frac{1}{2} \theta$ (for $d=3$).

The meanings of the symbols used in table 1 and below are

C_V, C_p, C_H, C_M	Specific heats at constant volume, pressure, field, and magnetization, respectively.
T, T_c	Temperature, critical temperature.
$\rho, \rho_c; \rho_l, \rho_g$	Density, critical density; densities of coexisting liquid and gaseous phases.
M, M_0	Magnetization, spontaneous magnetization.
K_T, K_S	Isothermal and adiabatic compressibilities.
χ_T, χ_S	Isothermal and adiabatic susceptibilities.
p, p_c, p_r	Pressure, at the critical point and at coexistence (vapor pressure), respectively.
H	Magnetic field.
$g_2(\mathbf{r})$	Pair correlation function (in a fluid).

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TABLE 1. Critical point exponents

Exponent	Fluid	Magnet
Below T_c	At coexistence as $T \rightarrow T_c$	At $H=0$ as $T \rightarrow T_c-$
α'	$C_V \sim (T_c - T)^{-\alpha'}$	$C_H \sim (T_c - T)^{-\alpha'}$
β	$(\rho_l - \rho_g) \sim (T_c - T)^\beta$	$M_0(T) \sim (T_c - T)^\beta$
γ'	$K_T \sim (T_c - T)^{-\gamma'}$	$\chi_T \sim (T_c - T)^{-\gamma'}$
α^*	$ d^2 p_\sigma / dT^2 \sim (T_c - T)^{-\alpha^*}$	
At $T=T_c$	As $\rho \rightarrow \rho_c$	As $H \rightarrow 0$
δ	$ p - p_c \sim \rho - \rho_c ^\delta$ Note the exponents β , γ' , and δ might differ on the gas and liquid sides.	$ H \sim M ^\delta$
η	At $\rho = \rho_c$ as $r \rightarrow \infty$ $ g_2(\mathbf{r}) - 1 \sim 1/r^{d-2+\eta}$	At $H=0$ as $r \rightarrow \infty$ $\langle S_\sigma^z S_r^z \rangle \sim 1/r^{d-2+\eta}$
Above T_c	At $\rho = \rho_c$, as $T \rightarrow T_c +$	At $H=0$, as $T \rightarrow T_c +$
α	$C_V \sim (T - T_c)^{-\alpha}$	$C_H \sim (T - T_c)^{-\alpha}$
γ	$K_T \sim (T - T_c)^{-\gamma}$	$\chi_T \sim (T - T_c)^{-\gamma}$
ν	Inverse Range of Correlation	$\kappa(T) \sim (T - T_c)^\nu$
Rigorous inequalities	$\alpha' + (2\beta + \gamma')_{\min} \geq 2$ $\alpha' + \beta_{\max} + (\beta\delta)_{\min} \geq 2$ $\alpha^* \leq \alpha' + \beta_{\max}$	$\alpha' + 2\beta + \gamma' \geq 2$ $\alpha' + \beta(1 + \delta) \geq 2$
Conjectured relations	$\alpha' + 2\beta + \gamma' = 2, \quad \gamma' = \beta(\delta - 1),$	$\gamma = (2 - \eta)\nu$

d	Dimensionality of the system.
S_r^z	Spin variable at site \mathbf{r} .
\mathcal{H}	Hamiltonian.
z	Activity.
μ, μ_c	Chemical potential, at coexistence.

In table 2 the exact, estimated and observed values of the critical exponents defined above are presented for various theoretical models and for real fluids and ferromagnets [1-6]. The queries indicate significant uncertainties or total ignorance! Notice that it is not clear that the existing experimental results for α' , β , and δ satisfy the rig-

orous inequality recently derived by Griffiths [7] (see table 1).

For the standard three-dimensional ($d=3$) spherical model one may add the results: $\alpha' = \alpha = 0$ (continuous), $\beta = \frac{1}{2}$, γ' not defined, $\delta = 5$, $\eta = 0$, $\gamma = 2$, $\nu = 1$. For a spherical model with long range ferromagnetic forces decaying as $1/r^{d+\sigma}$ ($0 < \sigma < 2$) one has more generally¹: $\alpha' = \alpha = 0$, $\beta = \frac{1}{2}$ as before, but (a) for $\sigma < \frac{1}{2}d$: $\gamma' = \gamma = 1$, $\delta = 3$, $\eta = 2 - \sigma$, ν undefined; while (b) for $\sigma \geq \frac{1}{2}d$: γ' undefined, $\delta = (d + \sigma)/(d - \sigma)$, $\eta = 2 - \sigma$, $\gamma = \sigma/(d - \sigma)$, ν undefined.

¹ These results have been obtained by G. S. Joyce.

TABLE 2. Values of critical point exponents

Exponent	"Classical" theory	Ising $d=2$	$d=3$	Heisenberg $d=3$	Observation	
					Fluids	Magnets
α'	0 (discon.)	0 (log)	$\geq 0?$?	≥ 0 (log)	$\geq 0?$
β	$\frac{1}{2}$	$\frac{1}{8}$	$0.312 \approx \frac{5}{16}$ 0.303 to 0.308	?	0.33 to 0.36	0.33 ± 0.015
γ'	1	$1\frac{3}{4}$	1.23 to 1.32	?	$\geq 1.2?$?
α^*	0	0 (log)	≥ 0	—	$\geq 0?$	—
δ	3	15	5.20 ± 0.15	?	4.2 ± 0.1	4.22 ± 0.05
η	0	$\frac{1}{4}$	$0.059 \approx \frac{1}{18}$ ± 0.006	0.08 ± 0.04	$> 0?$	$> 0?$
α	0 (discon.)	0 (log)	≥ 0 ≤ 0.2	$= 0$	$\geq 0?$ ≤ 0.2	$> 0?$
γ	1	$1\frac{3}{4}$	$1\frac{1}{4}$	$= 1\frac{1}{3}$ 1.32 to 1.38	$> 1.1?$	1.35 ± 0.02
ν	$\frac{1}{2}$	1	0.644 ± 0.002	0.69 ± 0.02	$> 0.55?$	≥ 0.66

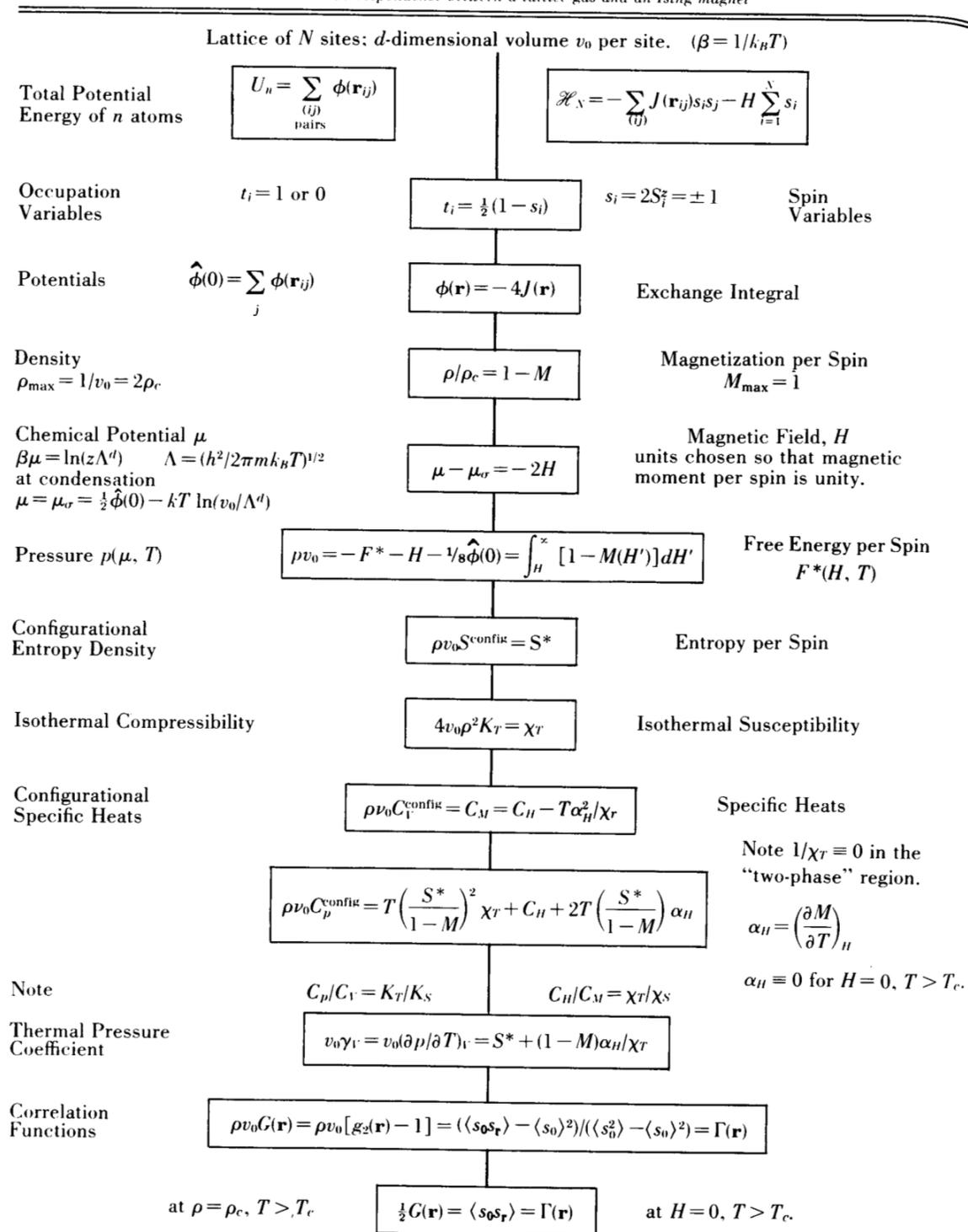
3. Relation Between a Lattice Gas and an Ising Magnet

The mathematical equivalence of the lattice gas model of a fluid and the Ising model of a magnet, stressed originally by Yang and Lee, is well known but it was felt that a more complete account of the relation between the two models than normally given would be useful. Indeed some of the experi-

mental results included in table 2 suggest that the fluid-magnet analogy might be deeper than the simplicity of the Ising model would indicate.

We consider a general d -dimensional lattice of N sites, each occupying a cell, of volume v_0 . The pair interactions are not necessarily limited to nearest neighboring sites. Positive values of the exchange integral $J(\mathbf{r})$ correspond to ferromagnetic coupling but the formulas are valid for arbitrary coupling.

TABLE 3. Correspondence between a lattice gas and an Ising magnet



From the correlation functions $G(\mathbf{r})$ and $\Gamma(\mathbf{r})$ one may derive the critical scattering intensities through the formulas

$$I(\mathbf{k}) = \hat{\chi}(\mathbf{k}) I_0(\mathbf{k})$$

where $I_0(\mathbf{k})$ is the form factor for scattering from the noninteracting system and where

$$\chi(\mathbf{k}) = 1 + \rho \sum_{\mathbf{r} \neq 0} v_0 e^{i\mathbf{k} \cdot \mathbf{r}} G(\mathbf{r}) = 1 + \sum_{\mathbf{r} \neq 0} e^{i\mathbf{k} \cdot \mathbf{r}} \Gamma(\mathbf{r}).$$

The fluctuation relation may then be written

$$K_T/K_T^0 = \hat{\chi}(\mathbf{0}) = \chi_T/\chi_T^0$$

where the superscript zero refers to an ideal non-interacting system.

4. References

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- [8] R. J. Burford, and M. E. Fisher, to be published.

Discussion

R. L. Scott: Dr. Rowlinson made some reference to our work on mixtures of CF_4 with methane. Recently Croll and I published some rather old work on mixtures of CF_4 with ethane [1]. I did not actually consider the work good enough to apply this kind of consideration, but at the request of Dr. Widom, I looked at the results again. The data give the total pressure of CF_4 with ethane at about 150.6°K, which is about 0.5° above the critical solution temperature. The curves are, in fact, nearly flat. If one ignores the fact that the only relevant data are considerably removed from the critical composition (just the point that Dr. Rowlinson made and that really vitiates the whole result), then the results are consistent with an exponent $\delta=4$, but it would not be very difficult to make the data consistent with $\delta=5$.

C. J. Pings: The one enigma in the data showed by Dr. Rowlinson for β was in the results obtained by Edwards and Woodbury for He^4 . I believe those were deduced from refractive index measurements. We have some unpublished data on the Lorentz-Lorenz function for argon and methane which suggest a possible anomaly in the Lorentz-Lorenz function in the critical region [2]. Until this is resolved, we must be dubious about any conclusions of this type deduced from refractive index measurements.

J. S. Rowlinson: I mentioned the results of Edwards and Woodbury only in passing. I did not use them in any way in the analysis. They are clearly out of line with the results on gases at high temperatures. Whether this is a particular quantum effect or not, I do not know.

S. Y. Larsen: I would like to make a remark concerning the comment of Dr. Pings. Dr. Mountain, Dr. Zwanzig, and I have made a theoretical study of the behavior of the index of refraction [3]. We find no anomaly in the behavior of the real part of the index of refraction in the supercritical region when the critical point is approached.

O. K. Rice: I may mention that some years ago Rowden and I made vapor pressure measurements on the cyclohexane-aniline system [4]. We approached the critical point to within 0.1 or 0.2°C and it looked like $\gamma=1$.

J. S. Rowlinson: Did it?

O. K. Rice: We could not say definitely whether γ was either greater or smaller than 1, but it did look very much like $\gamma=1$, as far as we could tell from the measurements.

J. S. Rowlinson: I am sorry that I omitted your results in my review. I did not try to deduce a value for γ from your results on the cyclohexane-aniline system.

M. E. Fisher: I would just like to emphasize one point, which Dr. Rowlinson made very well. There is an inconsistency with the rigorous inequalities if one takes the values of the exponents at their face value. Although one cannot be too sure that any of them are as good as they seem to be, the fact is that for δ to be consistent with the relationship (G1) a rather big change in its value is needed. It means that δ should be near 5 rather than 4.2, is not that right?

J. S. Rowlinson: It depends on what lower limit one puts on α_2^- . If one allows $\alpha_2^- = 0.06$, one can get away with $\beta = 0.36$ and $\delta = 4.4$.

M. E. Fisher: That is correct. However, since you multiply δ with 1/3 in relation (G1), the effect of a change in δ in order to satisfy the relation gets damped down. If you take the central values of β and δ , there really is quite a big discrepancy.

J. S. Rowlinson: I agree that the central values lead to a discrepancy, and if you prefer $\delta=5$, I cannot say no.

E. Helfand: In a mixture there are many new thermodynamic variables because one has one extra variable and consequently many more derivatives. One of the interesting derivatives may be $\partial\rho/\partial\rho$. This property depends on the liquid correlation functions, that is density correlation function, whereas the second derivative of the free energy with respect to the concentration depends on the concentration correlation function. One might well expect these correlation functions to have the same range and the same analytic behavior. Thus perhaps $\partial\rho/\partial\rho$ would reflect the same γ behavior.

J. S. Rowlinson: It would be very difficult to measure the $\partial\rho/\partial\rho$ in a dense fluid with the precision that is needed to get these indices.

W. W. Webb: presented measurements of the reflectivity of the interface between two phases in equilibrium just below the critical consolute temperature [5]. These measurements indicate that the effective equilibrium thickness of the transition region increases roughly as $(T_c - T)^{-0.7}$ as the critical temperature is approached, reaching $\sim 1,000 \text{ \AA}$ at $(T_c - T)/T_c \approx 10^{-3}$.

S. Y. Larsen: Dr. J. M. H. Levelt-Sengers and I have looked at the disagreement between the optical data and the isotherms derived from PVT measurements [6]. This disagreement was first noticed by Dr. Schmidt and noted in the account of his optical work given at the 1962 Symposium of the A.S.M.E. on