

CONTENTS—Continued

TRANSPORT AND RELAXATION PHENOMENA

Chairman: R. W. Zwanzig

J. V. Sengers—Behavior of Viscosity and Thermal Conductivity of Fluids Near the Critical Point.....	165
M. Bloom—Nuclear Magnetic Resonance Measurements Near the Critical Point of Ethane.....	178
D. Sette—Ultrasonic Investigation of Fluid System in the Neighborhood of Critical Points.....	183
C. E. Chase and R. C. Williamson—Ultrasonic Investigation of Helium Near Its Critical Point.....	197
C. W. Garland and R. Renard—Ultrasonic Investigation of the Order-Disorder Transition in Ammonium Chloride.....	202
Discussion.....	209

SUPPLEMENTARY SESSION

H. L. Lorentzen and B. B. Hansen—Effect of Gravity on the Equilibrium Mass Distribution of Two-Component Liquid Systems. The Observation of Reversed Diffusion Flow.....	213
S. Katsura and B. Tsujiyama—Ferro- and Antiferromagnetism of Dilute Ising Model.....	219
S. F. Edwards—The Statistical Mechanics of a Single Polymer Chain.....	225
I. M. Firth—Some Comments on Techniques of Modern Low-Temperature Calorimetry.....	233
LIST OF PARTICIPANTS.....	239

EQUILIBRIUM CRITICAL PHENOMENA IN FLUIDS

Chairman: A. M. J. F. Michels

The Classical Theories of the Critical Phenomena

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1. When the organizers of this conference on critical phenomena asked me to start the discussions with a review of the classical theories in order to provide the proper historical perspective, I had hoped that I would find the time to do this in a responsible way. However I soon found out that is not easy! The literature is large and very few (if any!) good historical studies have been made about the development of thermodynamics and statistical mechanics in the second half of the last century. I recommend it to the historian of science! There are many themes and questions which seem to me very worth while to study as for instance the penetration of the ideas of Gibbs and his methods (especially his graphical methods) into the Dutch school of thermodynamics of van der Waals, Bakhuis Roozeboom, Kamerlingh Onnes, and others; the relation of the Strassbourg school of Weiss on ferromagnetism with the ideas of van der Waals; the early controversies about the critical region versus the critical point which is now again so much in the center of attention; and so on!

I hope that you will take therefore the short historical remarks I will present with a grain of salt, and that you will consider my talk more as a kind of keynote address! I will try to mention some of the names and some of the notions which you will hear over and over again, and I will try to explain why I think the recent revival of the study of the critical phenomena is of such deep interest for the student of statistical mechanics.

2. Let me begin with some names and dates.

1869 Discovery of the critical temperature of CO₂ by Andrews. The general form of the set of isotherms for the liquid-vapor equilibrium can be

found already in Andrews' paper plus the suggestion that this was a *general* phenomenon.

1873 Dissertation of J. D. van der Waals on the continuity of the gas and liquid state. You all know that the miraculous van der Waals equation:

$$p = \frac{kT}{v-b} - \frac{a}{v^2}$$

together with the Maxwell equal area rule (added by Maxwell in 1874 in a long review of the work of van der Waals) explains the vapor-liquid equilibrium and the existence of the critical point:

$$v_c = 3b; p_c = \frac{1}{27} \frac{a}{b^2}; kT_c = \frac{8}{27} \frac{a}{b}$$

Of course this confirmed the idea that the critical point was a *general* phenomena and that there were no "permanent" gases. Made explicit by the

1880 law of corresponding states (van der Waals)

$$\frac{p}{p_c} = \pi = F(\omega, \vartheta) \quad \omega = \frac{v}{v_c} \quad \vartheta = \frac{T}{T_c}$$

with F a universal function. The role which this law played in the liquefaction of gases and especially of Helium (Kamerlingh Onnes, 1908)

was spectacular and I hope well known.

The discovery of the magnetic transition point came much later. So far as I know, it was only in:

1890 Hopkinson found that iron above a certain temperature ceased to be ferromagnetic. Confirmed and thoroughly investigated by Pierre Curie in a classical paper of 1895, and therefore now always called the Curie temperature.

1907 P. Weiss introduced the notion of the inner field and explained the existence of the Curie temperature T_c and of the spontaneous magnetization for $T < T_c$. The third critical transition phenomena is that of the order-disorder transformation in binary alloys or better substitutional solid solutions. Suspected in 1919 by Tammann, proved in 1925 by the x-ray work of Johanson and Linde, the theoretical explanation given in: 1934 by Bragg and Williams, was clearly patterned after the Weiss theory. One could still mention the discovery of the critical mixing temperature of two fluid phases for a binary mixture. Found by Alexejew around 1800. Explanation by van der Waals and a series of coworkers

1890-1905 (Kuenen, Kohnstamm, van Laar, Korteweg) 1890-1905, by generalizing the van der Waals equation for mixtures and applying for the thermodynamic discussion the graphical methods of Gibbs.

3. Leaving for a moment this sort of schoolbook history let me emphasize the great similarity of the three classical theories of van der Waals, Weiss, and Bragg-Williams although the derivations are often quite different. It is now clear and generally accepted that they are all based on the assumption that the attractive forces between the molecules which produce the cooperative effects have a very long range. As a result the type of singularity which the critical point represents is in all the theories exactly the same. To put this in evidence it is good to direct attention (following M. Fisher) to the following three theoretical predictions:

a. At the critical point the specific heat makes a finite jump and then decreases again. For a van der Waals gas at the critical density, one gets:

$$\Delta c_r \equiv c_r - \frac{3k}{2} = \begin{cases} 0 & \text{for } T > T_c \\ \frac{9}{2} k \left[1 - \frac{28}{25} \frac{T_c - T}{T_c} + \dots \right] & \end{cases}$$

For a Weiss ferromagnet:

$$\Delta c_r = \begin{cases} 0 & \text{for } T > T_c \\ \frac{5}{2} k \left[1 - \frac{13}{5} \frac{T_c - T}{T_c} + \dots \right] & \end{cases}$$

For a Bragg-Williams binary alloy:

$$\Delta c_r = \begin{cases} 0 & \text{for } T > T_c \\ \frac{3}{2} k \left[1 - \frac{8}{5} \frac{T_c - T}{T_c} + \dots \right] & \end{cases}$$

b. At the critical point the coexistence curve is parabolic. For a van der Waals gas (with reduced quantities): $\omega_g - \omega_l = 4(1 - \vartheta)^{1/2}$. For a Weiss ferromagnet:

$$I^* \equiv \frac{\mu W}{kT} M = \sqrt{15} \left(1 - \frac{T}{T_c} \right)^{1/2}$$

[also with reduced quantities: $W = \text{constant of Weiss inner field}$, $M = \text{magnetization}$; $T_c = \frac{N\mu^2 W}{3k} = \text{Curie temperature}$. Putting $H^* = \frac{\mu}{kT} H$, then

the magnetic equation of state becomes: $I^* = \frac{3}{\vartheta} L(H^* + I^*)$ where $L(x)$ is the Langevin Function].

c. At the critical point the compressibility or the susceptibility become infinite as $1/|T - T_c|$. For a van der Waals gas:

$$\left(\frac{\partial \pi}{\partial \omega} \right)_{\omega=1, T=T_c} = -6(\vartheta - 1)$$

$$\left(\frac{\partial \pi}{\partial \omega} \right)_{\text{coex}, T=T_c} = -12(1 - \vartheta).$$

For a Weiss ferromagnet: (χ is the susceptibility)

$$\chi^+ = \frac{1}{W} \frac{1}{\vartheta - 1} \quad \chi^- = \frac{1}{2W} \cdot \frac{1}{1 - \vartheta}$$

$$T > T_c \quad T < T_c$$

For a Bragg-Williams alloy, properties b and c can be defined but they have less direct observational meaning.

4. At this point one may well already raise the question, why the classical theories represent so well, at least qualitatively, the observed critical phenomena. Of course, as long as little was known about the intermolecular forces, one could think that the attractive forces had a very long range. In fact van der Waals never doubted that, and probably Weiss also had always the long range dipole-dipole forces in mind. However the later development showed more and more clearly that the cooperative forces were not of a very long range, that each atom was influenced by at best a few shells of neighboring atoms. Of course, it took a long time before this was realized. It required the elucidation, of the nature of the van der Waals attractive forces by London and of the Weiss inner field by Heisenberg which came in the late twenties as a byproduct of the quantum mechanical revolution.

Partially because of this fact, the classical theories became more and more discredited in the thirties. This was also because it turned out that the classical theories although qualitatively correct could not be fixed up so as to give a precise quantitative description of the phenomena. For the van der Waals theory this became accepted already around 1900, and as a result Kamerlingh-Onnes started then to represent the experimental data by series expansions in the density, the so-called virial expansion, for which Ursell and Mayer then gave the theoretical analysis in the thirties. For the Weiss and the Bragg-Williams theory the attempts for improvement lasted a bit longer, but also here one soon began to turn more and more to series expansions. The reason is clear. The terms in the expansions can be calculated exactly (at least in principle) and related to the intermolecular forces. And since one began to learn more and more about these forces, this was of course of the greatest interest. However, one lost the general point of view which the classical theories provided, and perhaps because of this one also lost interest in these theories. They were considered to give "convenient interpolation formula" or "semiphenomenological descriptions." Remarkable for instance is the fact that in the great international congress in 1938 to celebrate van der Waals' 100th birthday, the van der Waals equation was mentioned only once, and all attention was

centered on the so-called rigorous theories. I think one is now coming back from these theories because one has become disillusioned about the series expansions since no general point of view emerges from them.

5. The first and unfortunately till now 1944 practically the only step forward beyond the classical theories was made in the famous paper by Onsager on the two-dimensional Ising model. I will not say much about it, because you will hear much more about it later. It has dominated the subject for the last 20 years. Let me remind you only that the Ising model (proposed by Ising in 1925) can be considered as a simplified version of the ferromagnetic, and of the order-disorder and even of the vapor-liquid problem (through the lattice gas). Each atom on a lattice site can be in two states (spin up or down) and the interaction is only between neighboring pairs and is $\pm J$ depending on whether the spins are parallel or antiparallel. It is therefore a model with short range forces. The most striking result of Onsager was that there is a critical point and that the specific heat is logarithmically infinite there in contrast to the classical result.

6. So far I have only talked about the critical point and its properties for the equation of state. A deeper question is the question what happens with the correlation function near a critical point. That the density fluctuations will get large near the critical point was pointed out by Smoluchowski, but that in addition the correlation of the density fluctuation at different points will become of very long range and that this is the cause of the critical opalescence was first clearly 1914 stated by Ornstein-Zernike in 1914, and then worked out in the Groningen dissertation of 1916 Zernike of 1916.

Angular distribution of the scattered radiation is related to the Fourier transform of the correlation function:

$$g(k, v, T) = \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} \left[n_2(r; v, T) - \frac{1}{v^2} \right]$$

$$k = \frac{2\pi}{\lambda} \sin \frac{\theta}{2}$$

Ornstein and Zernike give specifically for

$$T \geq T_c \quad v = v_c$$

$$g(k; v_c, T) = \frac{kT}{a} \frac{1}{k^2 R^2 - \frac{1}{3} (\partial \pi / \partial \omega)_{\omega=1}}$$

with

$$R^2 = \frac{1}{3} \frac{\int d\vec{r} r^2 \varphi_{\text{attr}}(r)}{\int d\vec{r} \varphi_{\text{attr}}(r)}$$

$\frac{1}{g(k)}$ versus k^2 (O-Z plot) should be a straight line whose intercept with the ordinate axis would go to zero if $T \rightarrow T_c$ as $(T - T_c)$.

There are many ways of justifying the O-Z theory. I think though that always one again has to assume that the forces are of long range, so that it can be considered a natural generalization of the van der Waals theory.

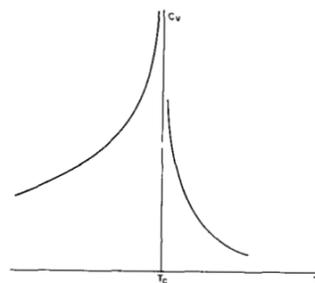
The corresponding theory for neutron scattering near the Curie point is so recent that it does not belong in a historical survey!

7. Outlook. What are the problems, and what can one hope from the present revival of interest? As always in statistical mechanics one must distinguish the equilibrium from the nonequilibrium properties.

A. I think it is wonderful that so much new experimental work is being done. For a long time experiment was too much dominated by the theory, and except in a few places (like in the van der Waals laboratory in Amsterdam) experimental work on the properties of matter near the critical point nearly ceased. I am glad that it is different now. What can one hope to find? I hope that it will turn out that again there is a deep analogy between the various critical points, that there are similarities like in the classical theories. You will hear a lot about the new experimental work, so I will only mention a few points which seem to me very suggestive.

1. Near the critical point the coexistence curve seems much better represented by the empirical Guggenheim law: $\omega_g - \omega_l = \frac{7}{2} (1 - \theta)^{1/3}$. Also the magnetization curve near T_c seems to show such a cubic behavior.

2. For Argon and O_2 , and now also for He, it seems that c_r does not show a jump but becomes logarithmically infinite. For $T \geq T_c$



$$c_r = -B^\pm \ln \left| 1 - \frac{T}{T_c} \right| + C^\pm$$

with $B^+ \cong B^-$ and $C^- - C^+ \cong 10k$.

This surprising result by the Russians, is also found for $He^{II} - He^I$ transition and I believe also for some ferromagnetic transitions. You will hear more about it tomorrow.

If there is such an universal, but nonclassical behavior, then there must be an universal explanation which means that it should be largely independent of the nature of the forces. The only corner where this can come from is I think the fact that the forces are not long range. The Onsager solution gives I think a strong hint. It may well be so that away from the critical points the classical theories give a good enough description but that they fail close to the critical point where the substance remembers so to say Onsager. I think that to show something like this is the central theoretical problem. One can call it the reconciliation of Onsager with van der Waals.

With regard to the correlation function and the Ornstein-Zernike theory I hope that the new experimental work will show that there is a *critical region*, where already deviations from the classical van der Waals-Ornstein-Zernike theories begin to show up. I think there are indications (as the specific heat anomaly) that such a region exists. Of course there is also a singularity or a critical point.

B. Finally a remark about nonequilibrium phenomena. There are very surprising experimental results found about various transport coefficients, which clearly are worth pursuing. Till now there is no theory, not even a van der Waals like theory. The development of the proper transport theory with long range forces, van der Waals-like but probably with one more constant, seems to me not impossible and very worth while.

The Coexistence Curve of He^{3*}

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In this report we wish to present the results of some recent $P-V-T$ measurements on He^3 in the critical region. A significant departure was found in the shape of the coexistence curve from the behavior expected for classical systems such as Xe and CO_2 .

The $P-V-T$ surface of liquid He^3 was investigated by Sherman and Edeskuty [1]¹ between 1.0 and 3.3 °K and for pressures from the vapor pressure to solidification. The measurements reported by these authors lacked detail in the region from 3.0 to 3.324 °K, the critical point, [2] and for pressures less than ~ 3 atm. In addition, there were no measurements reported on the fluid for $T > T_c$.

Recently 23 isochores of He^3 were measured with densities ranging from 0.015 to 0.066 g/cm³ using the apparatus of reference [1] with only slight modification. Along each isochore data were taken with temperature decreasing from 4 °K, a final observation being made along the liquid-vapor equilibrium curve (vapor pressure). Temperatures were reduced to the 1958 He^4 Scale of Temperatures [3]. Pressures were measured with a fused quartz bourdon tube gage having an accuracy of 0.05 mm Hg. While the cell has a vertical dimension of ~ 4.6 cm, measurements were not made very close to the critical point and as a result, density gradients within the cell were not of any significance.

$P-V-T$ data taken by the isochoric method have the advantage of yielding $P-T$ relations which are almost linear. Thus each isochore was extrapolated to the vapor pressure [4] to provide a $\rho-T$ point on the coexistence curve. Values of ρ_l and ρ_g were read from a smooth $\rho-T$ graph and $\rho_l - \rho_g$ was plotted as a function of $T_c - T$ using logarithmic coordinates as shown in figure 1. It is easily seen that the critical point exponent β [5, 6] in the relationship

$$\rho_l - \rho_g \propto (T_c - T)^\beta$$

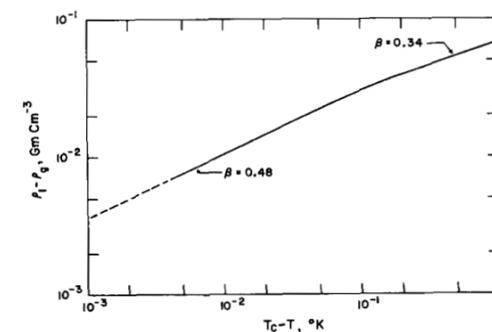


FIGURE 1. A plot of $\rho_l - \rho_g$ versus $T_c - T$ along the coexistence curve for He^3 .

deviates from the "classical" value of $\sim 1/3$, and $\beta \rightarrow 0.48 \pm 0.02$ as $T \rightarrow T_c$. This slope appears to be constant up to $T_c - T = 0.07^\circ$.

TABLE 1. Densities of He^3 along the coexistence curve.

T	ρ_g	ρ_l
°K	gm cm ⁻³	gm cm ⁻³
2.4	0.00801	0.07404
2.5	.00915	.07288
2.6	.01044	.07159
2.7	.01192	.07015
2.8	.01371	.06852
2.9	.01573	.06668
3.0	.01808	.06458
3.05	.01951	.06338
3.1	.02113	.06200
3.15	.02317	.06033
3.2	.02557	.05815
3.25	.02867	.05498
3.3	.03373	.04970
3.324	.04178	.04178

*Work performed under the auspices of the U.S. Atomic Energy Commission.

¹ Figures in brackets indicate the literature references at the end of each paper.