[1]See, for example, N. F. Mott and H. W. Massey, "The Theory of Atomic Collisions" (Oxford University Press, New York, 1952) pp 200-201.

[2]See, for example, L. Landau and E. Lifshitz, Mechanics (Addison-Wesley Publishers, Reading, Mass., 1960), pp. 73-75.

[3]M. Gryziński, Phys. Rev. Letters 14, 1059 (1965).

[4]M. Gryziński, Institute of Nuclear Research Report No. 641/XVIII/PP, 1965.

[5]M. Gryziński, in Proceedings of the First International Conference of Atomic Physics, New York, 3-7 June 1968 (unpublished).

USE OF LIQUID-DROPLET MODEL IN CALCULATIONS OF THE CRITICAL EXPONENT δ *

C. S. Kiang

Physics Department, Clark College, Atlanta, Georgia 30314

The liquid-droplet model is used to derive a formula relating the exponent δ and the compressibility factor $P_c/k_B T_c \rho_c$ at the critical point of a fluid. For fluids (the van der Waals continuum, the Bragg-Williams lattice gas, and Ising lattice gases) where both these quantities are known, the proposed relation is in agreement with experiment and theoretical prediction. Therefore, in other cases this relation may be used to predict δ from the known P_c, T_c, and ρ_c. On this basis we predict a δ between 4.2 and 4.5 for nonpolar molecules, about 5 for hydrocarbons, and larger than 5 for polar molecules.

Three basic assumptions were used in Fisher's liquid-droplet model[1] in order to formulate the cluster theory in mathematical form: (1) It is a classical model. (2) The excluded-volume effect between droplets is neglected. (3) The most probable surface area $\bar{S}$ of a cluster of size l will vary as

$$\bar{S}(l) \simeq a_0 l^\sigma \quad (l \to \infty)$$

with, necessarily for $d \geq 2$, $0 < \sigma < 1$, where $a_0 = a_0(T)$. With these assumptions, the pressure and density of an infinite system for the liquid-droplet model can be expressed as

$$\frac{P}{k_B T} = g_0 \sum_{l=1}^{\infty} l^{-\tau} x^{l^\sigma} y^l, \tag{1}$$

$$\rho = g_0 \sum_{l=1}^{\infty} l^{1-\tau} x^{l^\sigma} y^l, \tag{2}$$

where

$$x = \exp[-a_0(w - \omega T)/k_B T], \tag{3a}$$

$$y = z \exp[E_0/k_B T + S_0/k_B], \tag{3b}$$

and k_B = Boltzmann constant, w = surface energy arising through loss of binding energy by particles near the surface of the cluster, ω = corresponding entropy per unit of cluster surface, z = fugacity, E_0 = bulk energy per particle in the cluster, S_0 = bulk entropy per particle in the cluster, and g_0 is a constant. Here τ, $2 < \tau < 2.5$,[2] is a parameter due to the "close" effect on the surface of the clusters near the critical point.[1] At

the critical point $x = 1$, and $y = 1$, and hence

$$\frac{P_c}{k_B T_c} = g_0 \sum_{l=1}^{\infty} l^{-\tau} = g_0 \zeta(\tau), \tag{4}$$

$$\rho_c = g_0 \sum_{l=1}^{\infty} l^{1-\tau} = g_0 \zeta(\tau-1), \tag{5}$$

where $\zeta(x)$ is the zeta function of x. Therefore the compressibility factor at the critical point can be written as

$$P_c/k_B T_c \rho_c = \zeta(\tau)/\zeta(\tau-1). \tag{6}$$

Also, from Fisher's analysis,[1] the critical exponent δ, which describes the behavior of the critical isotherm as $|P - P_c| \sim |\rho - \rho_c|^\delta$, at $T = T_c$, can be expressed in terms of τ as

$$\delta = 1/(\tau - 2), \tag{7}$$

From Eq. (6) it appears that the compressibility factor at the critical point is simply a function of τ only. Therefore, by the known P_c, T_c, and ρ_c, with Eqs. (6) and (7), we are able to calculate the value of τ, as well as the critical exponent δ, or for given δ, we can predict the compressibility factor at the critical point.[3] On this basis, we have investigated the δ for fluids with given compressibility factors at the critical point, and the compressibility factor at the critical point for the van der Waals continuum, Bragg-Williams lattice gases and Ising lattice gases from the known δ values.

From the experimental point of view, it is eas-

ier to determine the critical pressure P_c, critical temperature T_c, and critical density ρ_c, and hence the compressibility factor at the critical point, than the critical exponent δ. With this in mind, we have chosen the known compressibility factor at the critical point to predict the δ value for fluids. Three classes of substances, which include simple almost spherical nonpolar molecules, most ellipsoidal hydrocarbons, and polar gases are investigated.[4] For the simple almost spherical nonpolar molecules, δ varies from 4.2 to 4.5. As for the hydrocarbons, we have examined 17 different substances which are ethane, propane, isobutane, n-butane, isopentane, n-

pentane, n-hexane, n-heptane, n-octane, benzene, cyclohexane, diisopropyl, diisobutyl, ethylene, propylene, and acetylene. The value of δ for this group is approximately equal to 5.0, except for ethylene and n-butane which have the value of δ 4.48 and 5.3, respectively. There are large deviations for the class of polar gases. Among them we have examined CH_3CH, H_2O, CH_3OH, CH_3Cl, and C_2H_5Cl. The calculated value of δ ranges from 4.9 to 7.9; however, except for C_2H_5Cl, all of them are larger than 5.0 (see Table I). Compare these calculated δ values with the available results obtained by experimental analysis for some nonpolar almost spherical gases (Table II). The proposed relation is in excellent agreement with experiment. Therefore, we have predicted that the δ value is about 5.0 for hydrocarbons and larger than 5.0 for polar molecules. Both of these quantities are exactly known for the van der Waals continuum and the Bragg-Williams lattice gas. Therefore, we can use either quantity as our input data. Here we use $\delta = 3$, and the corresponding compressibility factor at the critical point calculated by the proposed relation is 0.392, which is very close to the val-

Table I. Calculated data for the critical exponent δ.

Molecule	Compressibility factor[a]	τ	δ
Simple, almost spherical, nonpolar molecules			
He^4	0.305	2.237	4.218
He^3	0.30378	2.235	4.240
H_2	0.302	2.234	4.272
Ne	0.296	2.228	4.383
Ar	0.291	2.223	4.479
Xe	0.290	2.222	4.499
N_2	0.292	2.224	4.460
O_2	0.292	2.224	4.460
CH_4	0.290	2.222	4.499
CO_2	0.287	2.219	4.558
Hydrocarbons			
Ethane	0.267	2.200	5.000
Propane	0.270	2.203	4.921
Isobutane	0.276	2.209	4.788
n-Butane	0.257	2.191	5.308
Isopentane	0.268	2.201	4.967
n-Pentane	0.266	2.199	5.013
n-Heptane	0.258	2.192	5.206
n-Octane	0.258	2.192	5.206
Benzene	0.265	2.198	5.037
Cyclohexane	0.276	2.209	4.788
Diisopropyl	0.266	2.199	5.013
Diisobutyl	0.262	2.196	5.107
Ethyl ether	0.262	2.196	5.107
Propylene	0.273	2.206	4.854
Acetylene	0.275	2.208	4.810
Polar molecules			
CH_3CH	0.181	2.126	7.926
H_2O	0.224	2.162	6.177
NH_3	0.238	2.174	5.744
CH_3OH	0.220	2.158	6.311
CH_3Cl	0.258	2.192	5.206
C_2H_5Cl	0.269	2.202	4.944

[a]Hirschfelder, Curtiss, and Band, Ref. 4.

Table II. Available experimental analysis of the critical exponent δ.

Gases	δ	Ref.
CO_2	4.6 ± 0.06	a
	4.0^f	b, c
Xe	4.6 ± 0.1	a
	4.2^f	b, d
H_2	4.2^f	b, e
He^4	4.45 ± 0.10	a

[a]M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, Phys. Rev. Letters 22, 389 (1969).

[b]B. Widom and O. K. Rice, J. Chem. Phys. 23, 1250 (1955).

[c]A. Michels, B. Blaisse, and C. Michels, Proc. Soc. (London), Ser. A 160, 358 (1937).

[d]H. W. Habgood and W. G. Schneidere, Can. J. Chem. 32, 98, 164 (1954).

[e]H. L. Johnston, K. F. Keller, and A. S. Friedman, J. Am. Chem. Soc. 76, 1482 (1954).

[f] Larson and Sengers suggested that in the critical region the P-ρ isotherms may in fact be much flatter than has been inferred from PVT work because of inherent limitations in the method. [S. Y. Larson and J. M. H. Levelt Sengers, in Symposium on Thermophysical Properties. Papers. Third, 1965, edited by S. Gratch (American Society of Mechanical Engineers, New York, 1965), p. 74.] Therefore the values of δ are expected to be larger than the values given.

Table III. Comparison of compressibility factor at the critical point predicted by the proposed relation with results obtained by other theoretical models.

	δ	$P_c/k_B T_c \rho_c$ (model)	$P_c/k_B T_c \rho_c$ (prediction)
van der Waals	3	0.375	0.392
Bragg–Williams	3	0.3863	0.392
Square lattice	15[a]	0.0986[b]	0.1018
Triangular lattice	15[a]	0.1112[b]	0.1018
Simple cubic lattice	5.20 ± 0.15[a]	0.246[b]	0.258 ± 0.006
Fcc lattice	5.20 ± 0.15[a]	0.258[b]	0.258 ± 0.006

[a]Fisher, Ref. 5.

[b]S. Y. Larson and J. M. H. Levelt Sengers, in Symposium on Thermophysical Properties. Papers. Third, 1965, edited by S. Gratch (American Society of Mechanical Engineers, New York, 1965), p. 74.]

ues obtained by the theoretical models (see Table III). For Ising lattice gases, we have checked square and triangular lattices in two dimensions, and simple cubic and fcc lattices in three dimensions. In three-dimensional Ising lattice gases, the value of δ is suggested as 5.20 ± 0.15,[5] which will give the compressibility factor at the critical point, from the proposed relation, as 0.252–0.2645. When one compares this with the results estimated for the Ising lattice gases themselves,[6] the agreement is reasonable (see Table III). In two-dimensional Ising lattice gases, it is generally believed that the δ value is exactly equal to 15 for a variety of lattices.[5] From our calculation, the corresponding compressibility factor at the critical point is 0.1018. Comparison with the data listed in Table III shows that we have less than 10 and 5% deviations for triangular lattice and square lattice, respectively.

Here, we would like to call attention to a matter which concerns the liquid-droplet model for describing critical phenomena. In order to get the value of τ of interest, for fixed compressibility factor at the critical point, large l is needed for the zeta-function sums in Eq. (6). For instance, the compressibility factor at the critical point for He[4] is 0.305; if we take the sum only to $l = 10$, the corresponding value of τ will only be 1.0678; if to $l = 100$, the corresponding τ is 1.978; and for $l = 1000$, the corresponding τ is 2.140. All these corresponding pair numbers will give the compressibility factor at the critical point 0.305; however, the value of τ, and hence δ, will not be significant unless we take l as large as possible. This in turn means the terms needed for large l are playing an important role near the critical point, which is in

agreement with the original assumption of the liquid-droplet model. However, in order to get the value of the compressibility factor at the critical point of interest, for fixed δ, the $l = 1$ term gives a significant contribution in the zeta function sums in Eq. (1), Eq. (2), and consequently also in Eq. (6). Let us take the case for $\delta = 4.92$ ($\tau = 2.203$); then the ratio in Eq. (6) turns out to be 0.108, rather than 0.27, by not including the $l = 1$ term, and is 0.195 for half-contribution of the $l = 1$ term. This means that the cluster which only contains a single molecule is also playing an important role near the critical point, which is not assumed in the original model. Therefore, the droplet model, in our calculation, has been extended far beyond the region where physical intuition provides some justification. However, with our examination both theoretically and experimentally, the model-dependent proposed relation strongly suggests that there is a connection between the critical exponent δ and the compressibility factor at the critical point. The extremely sensitive relation between these two measurable quantities, which we have examined in various ranges, also indicates that our results are not merely a numerical accident. At the same time, within the model, the structure dependence of the τ value,[7] which is generally believed as a parameter only dependent on dimensionality,[1] may also throw some light on the significance of the critical exponents.

It will be interesting to have some experimental measurements of the critical exponent δ for some substances in the class of hydrocarbons and polar gases to confirm or demonstrate the inadequacies of the proposed formula.

The author wishes to acknowledge the com-

ments from Professor M. E. Fisher and Professor H. A. Gersch. He is also indebted to Dr. G. H. Walker for his help in computer analysis.

[1]M. E. Fisher, in Lectures in Theoretical Physics, edited by Wesley E. Brittin et al. (University of Colorado Press, Boulder, Colorado, 1965), pp. 1-159, and in Proceedings of the Centennial Conference on Phase Transition, University of Kentucky, 1965 (unpublished).

[2]This bound for τ is different from Fisher's (Ref. 1). Landau has shown that $\partial P/\partial V = \partial^2 P/\partial V^2 = 0$, at $t = T_c$, and therefore it is impossible for $\delta < 2$, hence, by Eq.

(7), $2 < \tau < 2.5$ instead of $2 < \tau < 3$.

[3]A computer program has been made for Eq. (6) to calculate the value of τ with corresponding compressibility factor. We are able to get the accuracy of τ to 10^{-6}.

[4]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1964).

[5]M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967), Pt. II.

[6]M. E. Fisher, Phys. Rev. 136, A1599 (1964).

[7]From Ref. 2 we notice that the value of τ should be between 2 and 2.5 for the critical region; this means that the maximum possible change of τ is 0.5 for a substance which has a transition. In our calculations, the value of τ changes from 2.216 (CH_3CH) to 2.237 (He^4). Compared with the range of τ for the critical region, it is a significant difference.

ARE THERE THERMOELECTRIC EFFECTS IN SUPERCONDUCTORS?

Seth Putterman
Rockefeller University, New York, New York 10021

and

R. de Bruyn Ouboter
Kamerlingh Onnes Laboratorium, Leiden, The Netherlands
(Received 8 December 1969)

A comparison between He II when the normal fluid is clamped and the superconducting state of metals leads to an extension of the two-fluid equations of London. The following consequences are discussed: (a) A nonstationary thermal emf (thermal electric effect) can exist in a superconductor, (b) a stationary potential difference (not an emf) can exist.

It is commonly accepted that there can be no thermoelectric effects in superconductors. This is based on the early experiments of Casimir and Rademakers on the Seebeck effect and of Daunt and Mendelssohn on the Thomson heat which show that in the usual stationary-state arrangement these effects vanish in the superconducting state.[1] Balazs[2] has in addition tried to show that in the macroscopic theory of London there is no room for any thermoelectric currents. In this Letter we will show that an extension of the two-fluid interpretation of the London theory leads to thermoelectric effects in nonstationary situations which are perhaps observable.

The motivation for the extension of the two-fluid model for superconductors comes from the comparison of superconductors with the superfluid state of helium (He II). It is well known that they have many similar properties (e.g., persistent currents), but it is perhaps not sufficiently realized that there is the following major difference. In He II both the normal and the superfluid components are in first approximation able to flow reversibly (that is, without dissipation) but in a superconductor the normal electrons are in first approximation clamped by the lattice.[3] Any flow of normal electrons involves dissipation. It seems therefore much better to compare the behavior of a superconductor with that of He II when the normal fluid is clamped (normal fluid velocity $\vec{v}_n = 0$) such as is experimentally realized in a superleak. This suggests that one has only one dynamical equation, namely for the superfluid component. For the superconductor this becomes in first approximation

$$\frac{D_s \vec{v}_s}{Dt} = -\vec{\nabla}\mu + \frac{e}{m}\left(\vec{E} + \frac{1}{c}\vec{v}_s \times \vec{B}\right) \qquad (1)$$

which differs only by the $\vec{\nabla}\mu$ term (μ = chemical potential per gram) from the equation London proposed ($\vec{v}_s$ is the superfluid velocity).[4] This still leads for the analog of irrotational flow to