

Specific Heat of a Gas Near the Critical Point

MICHAEL E. FISHER*

The Rockefeller Institute, New York, New York

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Recent measurements of the constant-volume specific heat of argon (and of oxygen) at critical density and close to the critical point are compared with calculations based on the three-dimensional nearest-neighbor lattice gas models. It is argued that the configurational specific-heat density $C^*(T) = \rho C_{\text{config}}(T)/\rho_{\text{max}}$ should be compared with the theoretical configurational specific heat per lattice site. On this basis the calculations above T_c agree to within 10% with the observations for argon and are consistent with a divergence like $(T - T_c)^{-1/2}$ over the range $(T - T_c)/T_c = 10^{-1}$ to 10^{-4} . Below T_c the strength of the apparently logarithmic divergence of the specific heat for the fcc lattice agrees to within 10% with the experimental data but the theoretical magnitude of $C^*(T)$ is too small for $T > 0.9 T_c$ by an almost constant amount of $1.05k$ per site.

1. INTRODUCTION

IT has been known experimentally for some time that the specific heat at constant volume $C_V(T)$ of a simple fluid displays an "anomaly" near the gas-liquid critical point.¹⁻³ In particular $C_V(T)$ has a maximum above T_c at or near the critical density ρ_c and the height of this maximum rises sharply as T approaches T_c . Similarly in the two-phase region below T_c the specific heat rises as the critical point is approached along the critical isochore ($\rho = \rho_c$). Further details of the critical behavior, however, have been revealed only in recent experiments by Voronel' and co-workers on argon⁴ (and, more recently, on oxygen⁵).

The over-all results of their measurements are shown in Fig. 1 where the reduced configurational specific heat per atom⁶

$$C(T)/k = [C_V(T) - \frac{3}{2}Nk]/Nk \quad (1)$$

is plotted versus T/T_c from the triple point to some 30% above the critical point. The curve has a sharp peak characteristic of a "second-order" transition and is strongly reminiscent of the λ anomaly observed in liquid helium.⁷ (The latter, however, presumably finds its origin in quite a different physical mechanism.) The specific heat apparently becomes "infinite" at the critical point.

It is known that the two-dimensional nearest-neighbor lattice gas model (which is isomorphic to the

simple Ising model^{8,9}) has a logarithmically infinite specific heat,¹⁰ and numerical calculations suggest that the specific heat of the three-dimensional model also becomes infinite at T_c .^{8,9,11-15} Accordingly, it seems worthwhile to undertake a more detailed comparison of the lattice gas with experiment: this is the object of the present paper.

The experiments are reviewed in the next section and the comparison with theory is discussed in Secs. 3, 4, and 5. The conclusions are summarized in Sec. 6.

2. EXPERIMENTAL RESULTS

Voronel's experiments on argon cover a range of from about 15% below to 5% above the critical temperature. (See solid part of the curve in Fig. 1. T_c is close to 150.5°K.) Measurements were taken at temperature intervals of from 0.05 to 0.1°K (i.e., about 0.05% of T_c) and the values of C_V show a scatter of the order of 5%. The measurements on oxygen (with $T_c \approx 154.6^\circ\text{K}$) are broadly similar but have a somewhat larger scatter and reveal a small but unexplained anomaly some 5% below T_c . For these reasons and because oxygen, being diatomic, is presumably less suitable for a first theoretical comparison we will mainly discuss the argon measurements. However the results for oxygen are generally rather similar, following a law of corresponding states reasonably closely.

Figure 2 shows in detail the observations in the immediate critical neighborhood. It is clear that the critical temperature T_c might reasonably be located in a range of about 0.02°K, say from 150.48 to 150.50°K (see dashed lines in Fig. 2), the higher value being that

* On leave of absence for 1963-64 from Wheatstone Physics Laboratory, King's College, London, England.

¹ J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths Scientific Publications, Ltd., London, 1959), Chap. 2.

² A. Michels and J. Strijland, *Physica* **18**, 613 (1952).

³ H. W. Habgood and W. G. Schneider, *Can. J. Chem.* **32**, 164 (1954).

⁴ M. I. Bagatskii, A. V. Voronel', and B. G. Gusak, *Zh. Eksperim. i Teor. Fiz.* **43**, 728 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 517 (1963)].

⁵ A. V. Voronel', Yu. R. Chashkin, V. A. Popov, and V. G. Simkin, *Zh. Eksperim. i Teor. Fiz.* **45**, 828 (1963) [English transl.: *Soviet Phys.—JETP* **18**, 568 (1964)].

⁶ In Eq. (1) k is Boltzmann's constant, N is Avogadro's number, $C_V(T)$ is the molar specific heat at constant volume. The term $\frac{3}{2}Nk$ represents the kinetic contribution to the specific heat (ignoring quantal effects).

⁷ M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics III*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Chap. 3.

⁸ A comprehensive review of the theory of the Ising model is C. Domb, *Advan. Phys.* **9**, Nos. 34 and 35 (1960). The relation to the lattice gas is described by T. D. Lee and C. N. Yang, *Phys. Rev.* **87**, 410 (1952).

⁹ A summary of recent results on the Ising model is given by M. E. Fisher, *J. Math. Phys.* **4**, 278 (1963) (but see the correction in footnote 32).

¹⁰ L. Onsager, *Phys. Rev.* **65**, 117 (1944).

¹¹ A. J. Wakefield, *Proc. Cambridge Phil. Soc.* **47**, 799 (1951).

¹² C. Domb and M. F. Sykes, *Phys. Rev.* **108**, 1415 (1957).

¹³ M. E. Fisher and M. F. Sykes, *Physica* **28**, 939 (1962).

¹⁴ G. A. Baker, Jr., *Phys. Rev.* **129**, 99 (1963).

¹⁵ J. W. Essam and M. F. Sykes, *Physica* **29**, 378 (1963).

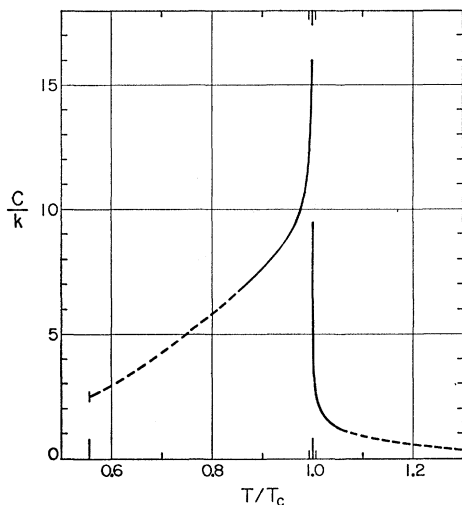


FIG. 1. Configurational specific heat of argon at constant critical density from the triple point to beyond the critical point. (The range of temperature marked on the axis close to $T/T_c=1$ is shown in detail in Fig. 2.)

quoted by Voronel'.¹⁶ Greater precision would evidently require more closely spaced measurements in this region. (The separation between the experimental points just bracketing T_c is about 0.08°K.) Uncertainties in the relative value of T_c will clearly affect the apparent asymptotic behavior of $C_V(T)$ as T_c is approached from either side (see below).

The value $T_c=150.50^\circ\text{K}$ lies some 0.20 to 0.34°K below the values quoted by other workers on the basis of PVT measurements.^{17,18} (A similar discrepancy of 0.2°K exists for oxygen.⁵) This difference may reflect a small systematic error in determining T_c from PVT data or may merely represent calibration errors. It does not otherwise seem to be significant.

The density, $\rho=0.521\text{ g/cm}^3$, used by Voronel' and co-workers is some 1½ to 3% lower than the critical density $\rho_c=0.530$ to 0.535 g/cm^3 derived from other experiments.¹⁷⁻¹⁹ The coexistence curve is known to be so flat that a deviation of 3% from ρ_c should result in a transition to the two-phase region taking place at most a few millidegrees lower than the true value of T_c ,^{17a,b,18,20} so this is unlikely to be the reason for apparently lower observed T_c . For a similar reason any

¹⁶ The quoted value of $T_c=150.50^\circ\text{K}$ was used in preparing Fig. 2 from Voronel's logarithmic plot. A change of the value would merely shift the temperature scale slightly.

¹⁷ Values for the critical and triple points and other parameters of the noble gases and other simple gases have been conveniently tabulated by (a) J. S. Rowlinson, (Ref. 1) Chap. 1; (b) E. A. Guggenheim, *Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1950), Secs. 4.53 and 4.54; (c) R. J. Lunbeck, thesis, Amsterdam, 1948 (unpublished).

¹⁸ A. Michels, J. M. Levelt, and W. De Graaff, *Physica* 24, 659 (1958).

¹⁹ But note that earlier measurements by C. A. Crommelin, *Comm. Leiden* 118a and 118b (1910) yielded the lower value $\rho_c=0.51\text{ g/cm}^3$.

²⁰ M. A. Weinberger and W. G. Schneider, *Can. J. Chem.* 30, 422 (1952).

errors in the specific-heat curve from this source should not be very significant.²¹

A short list of values of the configurational specific heat per atom [see Eq. (1)] derived from the smoothed data for argon is presented in Table I, second column.²²

TABLE I. Configurational specific heats.

T/T_c	Argon		Lattice gas	
	C/k	C^*/k	$C^*/k=\rho C/k\rho_{\text{max}}$	
1.05	1.3	0.39	0.382	0.382
1.01	2.2	0.67	0.69	0.76
1.001	5.2	1.57	1.16	1.57
0.999	15.3	4.62	3.5	3.9
0.99	11.45	3.46	2.40	2.65
0.95	8.85	2.67	1.60	1.70
0.85	6.75	2.04	1.05	1.05

These values are probably accurate to within $\pm 0.1k$ except within 0.3% of T_c where the uncertainties are three or four times larger.

Following the analysis of the λ anomaly in helium⁷ Voronel' and co-workers plotted the specific heat versus $\log|T-T_c|$.²³ A similar plot of the experimental points versus $\log_{10}|1-(T/T_c)|$ is shown in Fig. 3. [A reduced scale has been used for $C(T)$ as explained below.] The lower set of points refer to $T>T_c$ and the upper set to $T<T_c$; the data points for $T<0.99T_c$ (i.e., for

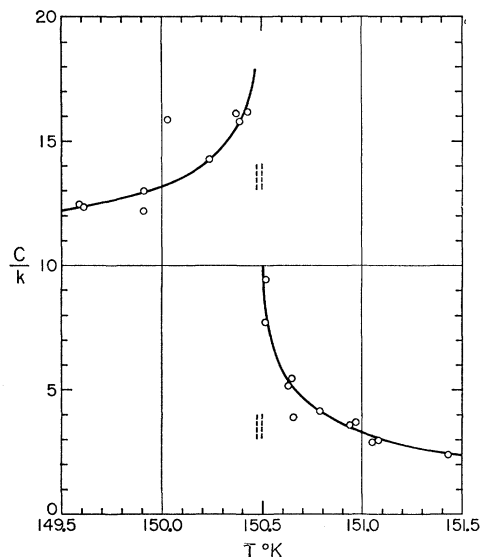


FIG. 2. Specific heat of argon close to the critical point showing the uncertainty in the determination of T_c .

²¹ The specific-heat anomaly above T_c is quite broad in density extending to more than 10% on either side of ρ_c .

²² The corresponding values for oxygen (derived from Ref. 2 by subtracting $\frac{5}{2}Nk$ from $C_{V,\text{obs}}$ to allow for the rotational degrees of freedom) lie 8 to 10% above those for argon except close to T_c where the difference increases more rapidly to 20% and more.

²³ Note that in Refs. 4 and 5, although it is not stated explicitly, $C_V(T)$ is plotted versus the logarithm to the base ten of $|T-T_c|$ in degrees Kelvin.

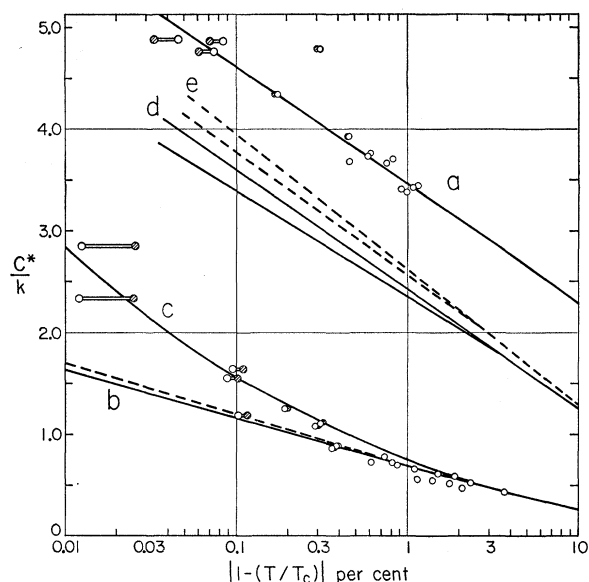


FIG. 3. Logarithmic plot of the specific-heat density $C^*(T)$ for argon [experimental points and curve (a)], and for lattice gas models; (b) above T_c assuming a logarithmic singularity (solid line fcc, dashed line s.c.); (c) above T_c assuming $\alpha=0.20$ (fcc); (d) below T_c for the fcc lattice; (e) below T_c for the s.c. lattice.

$\Delta T/T_c$ exceeding 1%) cluster rather closely to the curve (a) and are not shown. The open and shaded linked circles correspond to the assumptions $T_c=150.50$ and 150.48°K , respectively, as discussed.

The data below T_c are fitted rather well over the two decades from 0.06 to 6% by a straight line of the form²⁴

$$C(T)/k \approx A |\log_{10}[1 - (T/T_c)]| + B \quad (2)$$

with slope $kA_- = 3.8 k$ per atom per decade (or 7.6 cal/mole $^\circ\text{K}$ decade) and constant $B_- = 3.8$. Any significant upward curvature on the logarithmic plot would indicate that a better fit could be obtained with a sharper singularity of the form

$$C(T)/k \approx (A/\alpha) |1 - (T/T_c)|^{-\alpha} + B_\alpha, \quad (3)$$

with $\alpha > 0$. In fact the data suggest that α is appreciably less than 0.1. [In the limit $\alpha \rightarrow 0$ Eq. (3) becomes equivalent to Eq. (2).]

Above the critical temperature the data cannot be fitted by a single straight line. (The various curves in Fig. 3 are calculated theoretically: see next section.) In the range 0.5 to 5% a line of slope $kA_+ \approx 1.6 k$ per atom per decade gives a reasonable fit within the experimental scatter but at smaller deviations from T_c the apparent slope increases. Voronel' and co-workers suggested that the limiting slope close to T_c , becomes equal to that below T_c (as happens for helium²⁴). If this is so one may define a specific-heat discontinuity superimposed on a symmetric logarithmic singularity of magnitude about $\Delta C = (B_+ - B_-)k \approx 10k$ per atom (or

²⁴ For helium (Ref. 7) accurate linear fits with the same slope above and below T_c were found over the four decades 0.0001 to 1%.

20 cal/mole $^\circ\text{K}$).²⁵ However, this inference places undue weight on the relatively few experimental points closest to T_c . The evident upward curvature of the plot might equally well be interpreted as indicating a sharper singularity of the form (3) with a positive value for α as will be seen more clearly in the next section.

3. COMPARISON WITH LATTICE GASES

In comparing real gases with the simple nearest-neighbor lattice gas models three points must be borne in mind:

(a) Because the repulsive core of the interaction potential is represented merely by exclusion of a single lattice site the models display an artificially strong symmetry between liquid and gas⁸ which may be expressed by the law of the "constant diameter" of the coexistence curve, namely

$$\frac{1}{2}(\rho_L + \rho_G) = \rho_c = \frac{1}{2}\rho_{\max}. \quad (4)$$

(b) In the absence of rigorous analytical solutions, the specific heats of three-dimensional lattice gases must be computed from the (exact) series expansions. These series fail to converge at the critical point and although reliable extrapolation procedures have been developed the theoretical values become less certain close to T_c (as in the experimental situation!).

(c) Although the behavior of the various three-dimensional lattices is very similar when properly reduced, there is a residual numerical dependence on lattice structure which typically for the fcc and s.c. lattices amounts to some 5 or 10%.

We will discuss these points further in the following.

Critical Density

Experimentally simple fluids display a somewhat weaker symmetry between liquid and gas than do the simple lattice gases, in that real coexistence curves obey only a law of the "rectilinear diameter." For argon the relation is¹⁸

$$\frac{1}{2}(\rho_L + \rho_G) = \rho_c \{1 + 0.653[1 - (T/T_c)]\}, \quad (5)$$

which holds with an accuracy of better than $\pm 1\%$ from T_c down to $T=0.8 T_c$ or lower. By extrapolating back to zero temperature, where $\rho_G=0$, we may estimate an effective maximum density for argon

$$\rho_{\max} \approx 3.31\rho_c, \quad (6)$$

which contrasts sharply with the lattice result $\rho_{\max} = 2\rho_c$. [The estimate (6) may be compared with the experimentally observed¹⁷ zero-point density $\rho_0 = 3.26\rho_c$ and the triple point solid and liquid densities $\rho_{s,t} = 3.12\rho_c$, $\rho_{L,t} = 2.72\rho_c$.²⁶]

That this discrepancy is mainly due to the artificial

²⁵ For oxygen (Ref. 5) the apparent discontinuity is about 12k per atom.

²⁶ Taking $\rho_c = 0.521 \text{ g/cm}^3$ for argon. For oxygen we have $\rho_{L,t} = 3.05\rho_c$ and $\rho_0 = 3.84\rho_c$.

nature of the representation of the hard core by a single lattice site may be seen by considering a one-dimensional gas with hard cores of diameter b and weak long-range exponential forces. In the limit that the force becomes infinitely long-ranged [holding $\int_b^\infty \varphi(r)dr$ constant] the equation of state of the continuum model rigorously becomes the van der Waals' equation.²⁷ One then has $\rho_{\max} = 3\rho_c$. On the other hand, for the corresponding lattice model²⁸ with a single-site hard core we still have $\rho_{\max} = 2\rho_c$. By decreasing the lattice spacing h relative to the hard-core diameter b , however, one increases the ratio ρ_{\max}/ρ_c . Thus for a two-site hard core one finds $\rho_{\max}/\rho_c = \frac{1}{3}(3 + \sqrt{3}) \approx 2.366$ and generally, if $\delta = h/b = 1, \frac{1}{2}, \frac{1}{3}, \dots, 0$, one has

$$\rho_{\max}/\rho_c = 2 - \delta + (1 - \delta + \delta^2)^{1/2} = 3 - \frac{3}{2}\delta + \frac{3}{8}\delta^2 - \dots \quad (7)$$

This result follows from the appropriate limiting equation of state for the one-dimensional lattice gas, namely,

$$p/kT = k^{-1} \ln[1 + hp/(1 - b\rho)] - a\rho^2/kT. \quad (8)$$

It seems certain that if the two- and three-dimensional lattice gases with short-range forces could be solved for a finer lattice spacing (smaller δ) a similar increase in the theoretical value of the ratio ρ_{\max}/ρ_c would be discovered.

Basis of Comparison

Now the specific heat of a gas is normally quoted "per mole," i.e., per *atom* (as we have done), and for the kinetic contribution to $C_V(T)$ this is the natural convention. The configurational part of the specific heat, however, might equally well be expressed as a specific-heat *density*. Indeed the specific heat of the Ising model is usually quoted "per site"⁸⁻¹⁰ which corresponds to considering the specific heat "per *particle volume*," i.e., the quantity

$$C^*(T) = \rho C(T) / \rho_{\max}, \quad (9)$$

rather than $C(T)$. One must now ask: Which of these quantities is the more "fundamental" and should be used for a comparison of theory and experiment in the critical region? Of course if the ratio ρ_{\max}/ρ_c for the theoretical model matched that for the real gas this would be a purely academic question: but while calculations are restricted to the simplest lattice gases the problem must be faced.

Intuitively the specific-heat density $C^*(T)$, seems the more basic quantity. (One might cite the greater "naturalness" of the grand canonical ensemble, for first-order transitions, and the feeling that the cooperative transition is mainly governed by *spatial* relations through cluster integrals which become cluster sums on a lattice.) Fortunately, however, this viewpoint may be tested directly by comparing the specific heats

²⁷ M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.* **4**, 216 (1963).

²⁸ G. A. Baker, Jr., *Phys. Rev.* **122**, 1477 (1961).

of lattice and continuum gases with long-range forces (van der Waals-like fluids). As argued above, the relation between these two models should be similar to that between the lattice and continuum models with more realistic short-range forces.

The specific heat at $\rho = \rho_c$ of a continuum van der Waals gas has a simple jump discontinuity at the critical point of magnitude

$$\Delta C = 4\frac{1}{2}k \text{ per particle}, \quad (10a)$$

or

$$\Delta C^* = \frac{3}{2}k \text{ per particle volume}. \quad (10b)$$

The corresponding one-dimensional lattice gas (with a one-site hard core) has a discontinuity^{28,29}

$$\Delta C = 3k \text{ per particle}, \quad (10c)$$

or

$$\Delta C^* = \frac{3}{2}k \text{ per site}. \quad (10d)$$

Evidently the specific-heat *densities* $C^*(T)$, agree exactly while the values for the molar specific heats $C^*(T)$ differ by the factor $\frac{2}{3}$ just corresponding to the difference in critical densities. These considerations suggest that $C^*(T)$ for argon should be compared with the specific heat per site of the lattice gases and accordingly the experimental values of $C^*(T)$ are tabulated in the third column of Table I.^{30,31}

Critical Ratio

A useful index of the accuracy of a model in the critical region is provided by the value of the critical ratio which for argon is observed to be¹⁷ $p_c/\rho_c kT_c = 0.292$. For a van der Waals continuum and lattice gas the ratios are $\frac{2}{3} = 0.3750$ and $2 \ln 2 - 1 \approx 0.3863$, which exceed the experimental value by 28 and 30%, respectively. (Notice that the critical ratio seems less sensitive to the existence of a lattice structure.) For the two-dimensional lattice gases the (exact) values, given by

$$p_c/\rho_c kT_c = 2S_c^*/k - 2(U_c^* - U_0^*)/kT_c, \quad (11)$$

where S^* and U^* are the entropy and energy per site,⁸ are much smaller, e.g., 0.0968 and 0.1113 for the square and triangular lattices. In three dimensions the numerical estimates yield $p_c/\rho_c kT_c \approx 0.246$ and 0.268 for the simple cubic and face-centered cubic lattices respectively.^{9,32} The value for the fcc lattice is only 8% below

²⁹ The results for two-dimensional models with long-range forces are rather similar. Thus for a square lattice with long-range forces in the x -direction but nearest-neighbor forces in the y -direction the discontinuity is $\Delta C^* = 1.5601 k$ per *site*. [G. A. Baker, Jr., *Phys. Rev.* **130**, 1406 (1963).]

³⁰ The uncertainty (or arbitrariness) of 1 or 2% which enters in using the estimate (6) for the ratio ρ_{\max}/ρ_c is of no significance in view of the experimental uncertainties and the differences between the results for different lattices.

³¹ It is interesting that the ratio ρ_{\max}/ρ_c for oxygen appears to be about 13 to 18% larger than for argon so that the values of $C^*(T)$ for the two gases correspond more closely than do the values of $C(T)$. (Compare with footnotes 22, 25, and 26.)

³² The estimate of the entropy of the simple cubic lattice in Ref. 9 was erroneously taken from earlier work and should be replaced by $S_c \approx 0.560$ and $S_c - S_0 \approx 0.133$.

the experimental value while the s.c. result is 16% low. The closer relation of the fcc lattice to a real gas might have been anticipated in view of its larger (more "continuum-like") coordination number.

4. SPECIFIC HEAT ABOVE T_c

The specific-heat series for the three-dimensional simple cubic lattice above T_c was first examined by Wakefield¹²; longer series for this and other lattices were derived and studied later by Domb and Sykes and co-workers.^{12,13,15} The ratios of successive coefficients are found to be fairly regular,³³ and the series can be fitted quite well by a logarithmic singularity.¹³ On *assuming* a logarithmic form one finds, as $\Delta T = |T - T_c| \rightarrow 0$,

$$C^*(T)/k \approx 0.484 |\log_{10}(\Delta T/T_c)| - 0.293 + \dots \quad (12)$$

for the face-centered cubic lattice. The amplitude for the simple cubic lattice $A_+^* \approx 0.509$ is about 5% larger. The values computed from the extrapolation formula corresponding to (12) are shown in the fourth column of Table I and plotted in Fig. 3 [solid curve (b)]. The dashed curve (b) in Fig. 3 is for the s.c. lattice.

The agreement with experiment in the range of $\Delta T/T_c$ between 0.3 and 5% is seen to be very good! (The theoretical *molar* specific heats would, of course, be some 40% too small.) In particular the apparent experimental slope $A_+^* \approx 0.48$ (see Sec. 2) agrees with the strength of the logarithmic singularity in (12). Below 0.2%, however, the experimental data seem to diverge significantly from the theoretical lines.

Although the specific-heat series are not inconsistent with a logarithmic singularity it has been known for some time^{8,9,12} that a better description of the apparent asymptotic behavior of the expansion coefficients for all three-dimensional lattices is obtained with the sharper singularity corresponding to an exponent α in (3) equal to 0.20. Fitting the fcc series on this basis yields, as $T \rightarrow T_c$,

$$C^*(T)/k \approx 0.548 |1 - (T/T_c)|^{-1/5} - 0.612 + \dots \quad (13)$$

The values computed from the corresponding extrapolation formula are given in the last column of Table I and are plotted in Fig. 3 [curve (c)].

For temperatures exceeding T_c by 3% or more, the computed values of C^* are independent of which extrapolation formula is adopted (and hence are essentially exact—see Table I). Closer to the critical point, however, the curve based on (13) rises more rapidly and with marked curvature. Surprisingly, it seems to give an excellent representation of the experimental data as close to the critical point as they go, i.e., to within 1 part in 10 000 of T_c . (It will be noticed,

however, that the measured points do lie some 5 to 10% below the theoretical curve in the range 0.5 to 1.5% above T_c .)

Until appreciably more terms of the series (or an exact solution!) are available one cannot, of course, tell whether (13) would be an appropriate asymptotic form for the next two or three decades closer to T_c or whether a logarithmic singularity would take over again with a larger amplitude. Graphically the curve would continue to rise more and more steeply in the first case but straighten out at some steeper slope (perhaps parallel to the line fitting the data below T_c as suggested by Voronel') in the second case. It would be most interesting to know unambiguously the experimental behavior down to 0.001 or 0.0001% above T_c as one does at the λ point of helium.

5. SPECIFIC HEAT BELOW T_c

Except for the tetrahedral lattice,¹⁵ which has an anomalously low coordination number, the low-temperature series for the specific heat do not converge up to the critical temperature, and the coefficients for the bcc and fcc lattices are very irregular. Consequently more elaborate methods of extrapolation and analysis must be used and the results are less certain. For the simple cubic lattice there is only one intervening "non-physical singularity" [in the complex $x = \exp(-2J/kT)$ plane] and it is feasible to subtract this off numerically and examine the residual series which appears to converge up to T_c .^{11,34} More generally one may use the "metastable" method of grouping terms³⁵ or the Padé approximant procedure.¹⁴

From the numerical studies it appears reasonably certain that the specific heat diverges to infinity as T approaches T_c from below.³⁶ The rate of divergence is consistent with a logarithmic singularity but is probably not much sharper. [Certain theoretical and numerical arguments, however, do suggest a somewhat sharper singularity given perhaps by $\alpha = \frac{1}{3}$ in (3).³⁷] Assuming a logarithmic singularity, moderately accurate values for the amplitude A_- (and hence for the slope on a $\log|T - T_c|$ plot) may be estimated.

It is informative to consider the ratio A_-/A_+ of the amplitudes below and above T_c (fitting to a logarithm above T_c for this purpose^{9,13}). For all two-dimensional lattices this ratio is exactly unity and one would expect it to be reasonably constant in three dimensions also (say to within 10%). Indeed it has been evident for some time that A_-/A_+ has a value of roughly three.^{9,11,13}

³⁴ Using the longer series now available the author has re-estimated the critical behavior of $C^*(T)$ on this basis.

³⁵ See C. Domb (Ref. 8), Secs. 4.5.4 and 4.7.3; and C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) A235, 247 (1956).

³⁶ If $C^*(T_c^-)$ is finite it must certainly be quite large.

³⁷ J. W. Essam and M. E. Fisher, J. Chem. Phys. 38, 802 (1963); G. S. Rushbrooke, *ibid.* 39, 842 (1963); these arguments are reviewed by M. E. Fisher, J. Math. Phys. 5, 944 (1964).

³³ Baker (Ref. 14) also computed the Padé approximants to the high-temperature series but the method is unsatisfactory for such relatively short and weakly singular series, although the results are consistent with the previous estimates.

From Baker's Padé approximant estimates at low temperature,¹⁴ which he felt should be reliable to $\pm 10\%$, we find

$$A_-/A_+ \approx 2.58 \text{ (s.c.)}, \quad 2.27 \text{ (bcc)}, \quad 2.15 \text{ (fcc)}. \quad (14)$$

The dependence on lattice structure is a little greater than anticipated and might be an artifact due to the increased number of nonphysical singularities which intervene as the coordination number increases. From the series and metastable methods one obtains with roughly similar accuracy^{15,34,35}

$$A_-/A_+ \approx 2.6 \text{ (tet)}, \quad 2.3\text{--}2.4 \text{ (s.c.)}, \quad 2.3 \text{ (fcc)}. \quad (15)$$

These lie in the same range of 2.2 to 2.6, but are grouped together more closely.

For the face-centered cubic lattices the actual magnitudes of the amplitudes in (12) are $A_-^* \approx 1.05$ and 1.15 from (14) and (15), respectively. The latter agrees closely with the experimentally observed slope (Sec. 2) of $kA_-^* = 1.15 k$ per atomic volume per decade, the accuracy of both the experimental and theoretical results probably being no better than $\pm 5\%$.³⁸ (For the simple cubic lattice the two methods yield $A_-^* \approx 1.3$ and 1.17–1.22.)

The series estimates of $C^*(T)$ for the fcc lattice below T_c are given in the fourth column of Table I and are plotted in Fig. 3 [curves (d)]; the lower branch of the curve indicates the Padé approximant estimate (14) for the limiting slope. (The last three tabulated values should be reliable to within about ± 0.05 .) The last column in Table I below T_c is derived from the Padé approximant calculations for the simple cubic lattice. These results are represented by the dashed curves (e) in Fig. 3, the lower branch corresponding to the estimate (15) for the slope.

It is evident that although the theoretical slopes in Fig. 3 agree well with the slope of the experimental data the actual magnitude of $C^*(T)$ is *too small* by an almost constant difference of about 1.05 k (or 6.9 cal/mole °K for argon). This discrepancy is well beyond the experimental and theoretical uncertainties and represents a real deficiency of the model.

One might argue that the reason the lattice gas specific heat below T_c is too small is also associated with the one-site character of the hard core since this probably leads to an underestimate of the total possible entropy change. Studies of the Ising model for higher spin,³⁹ where the total entropy change per site is $\ln(2S+1)$, indicate that the specific heat above T_c does not change much but that most of the increased entropy is taken up below T_c leading to a larger specific heat there. However, the analogy of higher spin values with

finer lattice spacing is not very close and further theoretical calculations are really required to decide this point.

6. SUMMARY

The measurements of Voronel' and co-workers determine the specific heat of argon at constant critical volume with an accuracy of ± 5 to 10% at intervals of 0.05 to 0.1°K through the critical region (Figs. 1 and 2). The exact position of the critical point is uncertain to within about 0.02°K and this affects to some extent the apparent asymptotic behavior as $T \rightarrow T_c$.

It was argued by analogy with the Van der Waals-like continuum and lattice gas models that one should compare the configurational specific-heat density (rather than the molar configurational specific heat) of a real gas with that of a lattice gas, i.e., $C_{\text{exp}}^* = \rho C_{\text{exp}} / \rho_{\text{max}}$ should be compared with the theoretical specific heat per lattice site. (The ratio $\rho_{\text{max}} / \rho_c$ for argon is estimated from the diameter of the coexistence curve to be close to 3.31.) The critical ratio $p_c / \rho_c k T_c$ for the face-centered cubic lattice gas is only 8% below the observed value 0.292, which suggests this is the most appropriate lattice for comparison.

The best theoretical estimates of the lattice specific heats above T_c indicate a divergence like $(T - T_c)^{-1/5}$ as $T \rightarrow T_c$. The calculations of $C^*(T)$ made on this basis agree, to within the 5 or 10% uncertainties, with the experimental data over the whole range down to $(T - T_c) / T_c = 10^{-4}$ (Fig. 3). (It is not possible at present to decide, either theoretically or experimentally, whether a logarithmic form of divergence would be followed closer to T_c .)

Below the critical point the experiments indicate a logarithmic singularity in the specific heat with a rate of divergence of 7.6 (cal/mole °K) per decade change in $(T_c - T)$. [$C_V(T)$ rises to about 36 cal/mole °K at $(T_c - T) / T_c \approx 5 \times 10^{-4}$.] The theoretical calculations although less certain, also suggest a logarithmic divergence and the strength of the singularity agrees with the observations to within 5 or 10%. However, the theoretical specific heats over the whole range above $T = 0.9T_c$ are too small by an almost constant amount of 1.05 k per lattice site (equivalent to 6.9 cal/mole °K for argon). This is the principal deficiency of the standard lattice gas model and is probably associated with the oversimplified representation of the hard core by a single lattice site.

Note added in proof. Attention should be drawn to a related discussion of the specific heats of argon and oxygen and of their implications by C. N. Yang and C. P. Yang, Phys. Rev. Letters **13**, 303 (1964), which appeared after the present article had been accepted for publication. (It might be mentioned that the critical ratio quoted for the simple cubic lattice differs from our value of 0.246 due to the error noted in footnote 32.)

³⁸ For oxygen one finds approximately $A_-^* \approx 1.4 \pm 0.1$.

³⁹ C. Domb and M. F. Sykes, Phys. Rev. **128**, 168 (1962).