agreement with the value extrapolated from heat-capacity measurements by Sample and Swenson.[13] This compares with 29°K as calculated by DeWette, Nosanow, and Werthamer.

We find no indication of any anomaly in the phonon dispersion curves which might explain the low-temperature specific-heat anomaly.[13-16] And indeed, this anomaly has recently been attributed by Varma[17] as arising from a phonon-mediated long-range spin interaction, although some criticism has been raised by Guyer.[18]

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FLUIDS WITH SEVERAL PHASE TRANSITIONS

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For a fluid in which the interaction potential has a hard core plus a negative part, softening of the hard core can produce a second transition if a first already exists. We give a general argument for the occurrence of the second transition in the lattice gas, plus explicit results for one-dimensional fluid models with two first-order transitions. One such model also provides an example of the breakdown of the law of rectilinear diameters.

For a model of a fluid in which the pair potential $\varphi(r)$ has a hard core plus a negative part, the occurrence of a first-order transition depends upon dimensionality and upon the range of the attraction.[1] In this note we further conclude that in such models already exhibiting a phase transition, one can induce a second transition by simply softening the hard core judiciously.

We begin with a general argument relevant to a lattice gas of any dimensionality and then give explicit exact results for a one-dimensional fluid.

I. The ν-dimensional lattice gas.—The lattice gas is a cell model of a fluid in which the interparticle potential depends only upon the relative location of the cells containing the particles. The hard core is provided for by exclusion of multiple occupancy of a cell; suppose in addition that the positive potential V_0 between pairs of particles in adjacent cells is also infinite. Let particles in non-neighboring cells interact via a negative potential capable of producing a first-order transition[1] with a critical point at (ρ_1, T_1). Using the cell volume as the volume unit, the maximum density of the system is clearly $\leq \frac{1}{2}$.

Now consider V_0 finite but arbitrarily large.

Since the equation of state depends on V_0 only through the Boltzmann factor $\exp(-\beta V_0)$ which is now arbitrarily small, we expect the first-order transition still to exist, shifted by an arbitrarily small amount. But by the symmetry between occupied and unoccupied cells (particle-hole symmetry[2]) there must then be a second critical point arbitrarily close to $(1-\rho_1, T_1)$ and therefore the system has two first-order transitions[3] at lower temperatures.

A simple choice for the attraction is a negative potential of the form

$$\gamma^{\nu} F(\gamma r), \tag{1}$$

where $a = -\frac{1}{2}\int F(\vec{r})d\vec{r}$ exists and is positive, and where the limit $\gamma \to 0$ is taken after the thermodynamic limit.[4] The one-dimensional system is mathematically equivalent to an Ising chain, which indeed has two transitions. This was recently demonstrated by Nagle,[5] whose work inspired this note. The heuristic argument given above, however, is independent of dimensionality and of the details of the attractive part of $\varphi(r)$.

For continuum fluids the hole-particle symmetry argument is no longer available. Nevertheless, one could expect a similar phenomenon to appear: A hard-core system showing a first-order phase transition could be capable of exhibiting two phase transitions if the hard core is softened in a reasonable way. We show next that this expectation is justified in the one-dimensional case.

II. A one-dimensional continuum fluid.—As an explicit example we consider a one-dimensional fluid with the following pair potential:

$$\begin{aligned} \varphi(r) &= \infty \quad \text{for } r < d, \\ &= V_0[1-(r-d)/d\lambda] \quad \text{for } d < r < d(1+\lambda), \\ &= -a\gamma e^{-\gamma r} \quad \text{for } d(1+\lambda) < r, \end{aligned} \tag{2}$$

where the limit $\gamma \to 0$ is to be taken at the end [see Fig. 1(a)]. For $V_0 = \infty$ the hard core extends to $r = d(1+\lambda)$, and by taking V_0 finite the outer part of the core is softened. For $\lambda \leq 1$ the positive part of the potential acts only between neighboring particles and the free energy $F_+(V, T)$ of a system with only this interaction is easily found.[6] The free energy when the weak long-ranged attraction is also taken into account is then[4]

$$F(V, T) = \mathrm{CE}\{F_+(V, T) - a/V\}. \tag{3}$$

Here CE denotes the convex envelope of the function, the maximal convex function not exceeding the function.

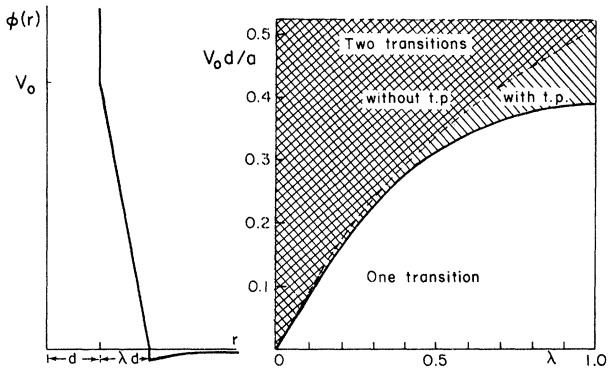

FIG. 1. The one-dimensional potential and the range of potential parameters for which two transitions exist (t.p. means triple point).

The main properties of the resulting equation of state are the following:

(i) For a given value of λ, a minimum value of $V_0 d/a$, shown in Fig. 1(b), is required for two transitions to appear. One of the striking facts revealed by this figure is that regardless of the smallness of λ, the relative range of the soft repulsion, there will be two transitions if $V_0 > a\lambda d$.

(ii) For the positions (p_1, ρ_1, T_1) and (p_2, ρ_2, T_2) of the critical points, we content ourselves with the following qualitative observations, all for $\lambda \leq 1$: One critical point always has parameters p_1, ρ_1, T_1 that lie between the values they attain for the limiting cases $V_0 = 0$ and $V_0 = \infty$, and for fixed λ they vary monotonically between these limiting values. The second critical point always has higher critical density and lower critical temperature than the former, and for fixed λ both ρ_2 and T_2 decrease slightly with increasing V_0, while p_2 increases without bounds when $V_0 \to \infty$. When $\lambda \to 0$ for a fixed V_0, p_2 and ρ_2 increase while T_2 decreases to zero. Details will be given elsewhere. Note the difference from the lattice gas where $T_2 = T_1$ and $\rho_2 = 1-\rho_1$ by particle-hole symmetry.[5]

(iii) When the potential parameters yield two transitions, a triple point where all three fluid phases are in equilibrium occurs if $V_0 d/a \leq \lambda/(1+\lambda)$ [see Fig. 1(b)]. The difference in behavior of the coexistence curves depending upon the existence of a triple point is exhibited in Fig. 2.

(iv) Both critical points have the classical critical indices

$$\delta = 3, \quad \beta = \tfrac{1}{2}, \quad \gamma = \gamma' = 1, \quad \alpha = \alpha' = 0. \tag{4}$$

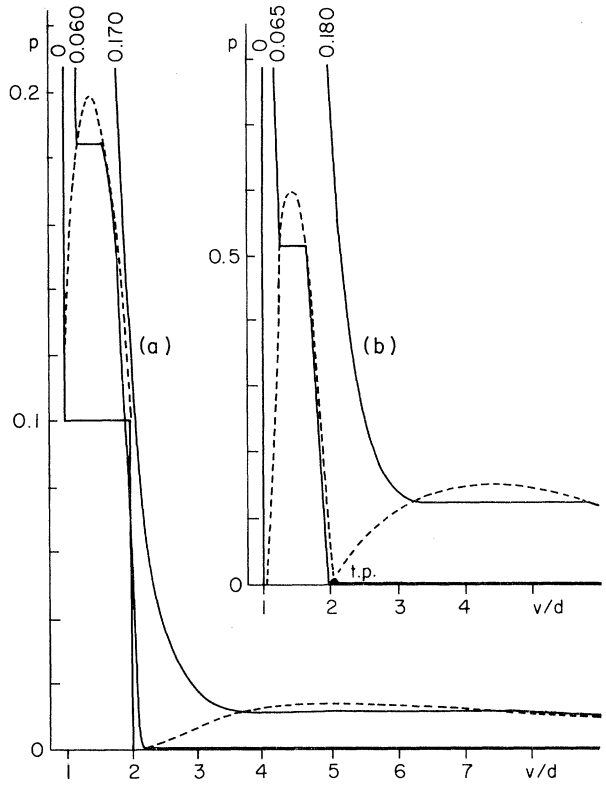

FIG. 2. The coexistence curves with isotherms for the following parameter sets: (a) $\lambda = 1$, $V_0 d = 0.06a$ (no triple point), and (b) $\lambda = 1$, $V_0 d = 0.45a$ (one triple point, marked t.p.). (The pressure units are a/d^2; the temperature units, a/kd.)

III. Confluence of critical points; breakdown of the law of rectilinear diameters.—When one decreases the value of V_0 in the one-dimensional model above, the second critical point finally disappears into the high-density side of the coexistence curve of the first transition. This is in contradistinction to the lattice-gas case where the symmetry forces the two critical points to coalesce when V_0 is decreased. A confluence of the critical points would presumably occur for a value of $\lambda > 1$, but instead of investigating that we have turned to the potential

$$\varphi(r_{12}) = \infty \text{ for } r_{12} < d,$$
$$= \epsilon V_0 \text{ for } d < r_{12} < d(1+\lambda), \tag{5}$$

with the same weak, long-ranged attraction as in (2). Here $\epsilon = 0$ if particles 1 and 2 are not adjacent, and $\epsilon = 1$ otherwise. The sole purpose of this restriction is to simplify the problem of finding the equation of state.

The results for $\lambda \leq 1$ are qualitative the same as for the potential (2). For one particular value of λ, $\lambda_c = 1.2269\cdots$, the two critical points coalesce when $V_0 d/a$ reaches the value of $0.1651\cdots$. These values of the parameters are such that the first four derivatives of the pressure with respect to the density vanish at the critical point, resulting in the critical exponents

$$\delta = 5, \quad \beta = \tfrac{1}{4}, \quad \gamma = \gamma' = 1, \quad \alpha = 0, \quad \alpha' = \tfrac{1}{2}, \tag{6}$$

instead of (5). This is a realization of the case of a free energy which is analytic in ρ and T in the one-phase region. If the first $2s$ density derivatives of the pressure vanish at the critical point, then[7] in general $\delta = 2s+1$, $\beta = \frac{1}{2}s$, $\gamma = \gamma' = 1$, $\alpha = 0$, $\alpha' = (s-1)/s$. The law of rectilinear diameters breaks down if $s > 1$. We find, namely, for $T \to T_c^-$, in usual notation,

$$\rho_l + \rho_g = 2\rho_c + \text{const}(T_c - T)^{1-\alpha'}. \tag{7}$$

This result may also hold for real fluids.[8] Note that for the lattice gas the same symmetry that forces the confluence also forces the constant in (7) to vanish; in fact $\rho_l + \rho_g = 2\rho_c$ for all $T < T_c$.

Our model satisfies thermodynamic homogeneity in the neighborhood of its critical points. Generally,[9] such homogeneity will lead to $\alpha = \alpha'$, but under certain conditions, such as when the one-phase free energy is free of singularities, it does not rule out $\alpha \neq \alpha'$. (As one of us has discussed elsewhere,[10] it does not seem to rule out $\gamma \neq \gamma'$ either.)

IV. More than two transitions.—The possibility of inducing more than one extra transition is most easily verified by considering the potential

$$\varphi(r) = \infty, \quad r < d,$$
$$= V_1, \quad d < r < d_1,$$
$$= V_2, \quad d_1 < r < d_2, \tag{8}$$

in addition to the same attraction as in (2). In one dimension and for $d_2 \leq 2d$ this is again nearest-neighbor repulsion. For any given values of d, d_1, and d_2 one can prove that if the three ratios V_1/a, V_2/a, and V_1/V_2 are large enough, there are three phase transitions for sufficiently low temperature. The result generalizes in the obvious way to a potential with n steps.

V. Discussion.—(i) If the multiple transitions we have found were to owe their existence to the discontinuities or the piecewise linearity of the model potentials we have used, the transitions would be of extremely limited significance for continuum fluids. However, analytic potentials arbitrarily close to the ones we have used can always be constructed, and by the nature of the convex envelope construction (3) and by continu-

ity, it follows that the transitions persist for such potentials.

(ii) An extra feature of real three-dimensional fluids that is absent in our one-dimensional models is the occurrence of a solid-liquid transition. Perhaps our anticipated second critical point (P_2, ρ_2, T_2) materializes within the solid region, giving rise to a solid-solid transition that involves no change of crystal symmetry.[11] This seems more likely to us than the possibility that the "extra" transition could play a fundamental role in determining the characteristics of the solid-liquid transition itself.

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[1]In three dimensions, presumably any finite-range attraction suffices to guarantee a phase transition. In one dimension the negative potential must be long ranged in some extreme sense, for instance, decaying like $-r^{-n}$ with $1<n<2$ [F. J. Dyson, Commun. Math. Phys. 12, 91, 212 (1969)]. In all dimensions a weak long-ranged attraction of the form (1) yields a first-order transition in the limit $\gamma \to 0$. [See J. Lebowitz and O. Penrose, J. Math. Phys. 7, 98 (1966). See also M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *ibid.*, 4, 216 (1963), and N. G. van Kampen, Phys. Rev. 135, A362 (1964), for closely related earlier work, and D. J. Gates and O. Penrose, Commun. Math. Phys. 15, 225 (1969), for closely related recent work.]

[2]See J. Rowlinson and B. Widom, J. Chem. Phys. 52, 1670 (1970), for a detailed discussion of this symmetry.

[3]A greater variety of transitions can be expected for $\nu > 1$. Consider, e.g., the two- or three-dimensional (cubic) lattice gas with a finite nearest-neighbor repulsion V_0 and no attraction. Then there are two second-order transitions (antiferromagnetic in spin language) below a critical temperature (the Néel temperature). By adding an attraction of the type (1), one obtains four transitions along low-temperature isotherms.

[4]Lebowitz and Penrose, Ref. 2; Kac, Uhlenbeck, and Hemmer, Ref. 2; van Kampen, Ref. 2; and Gates and Penrose, Ref. 2.

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[6]See the articles by H. Takahasi and L. Van Hove, in *Mathematical Physics in One Dimension*, edited by E. H. Lieb and D. C. Mattis (Academic, New York, 1966).

[7]J. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths, London, 1969), p. 86. H. D. Baehr, Forsch. Ingenieurw. 29, 143 (1963), and Brenstoff Wärme Kraft 15, 514 (1963). We are grateful to Dr. J. M. H. Levelt Sengers for making copies of Baehr's articles available to us.

[8]The exponent $1-\alpha'$ in Eq. (7) is just $1/s$ in our model and could equally well be expressed as 2β or $2/(\delta-1)$. It is, however, only the exponent $1-\alpha'$ that one might expect to carry over to real fluids, since fluid values of 2β or $2/(\delta-1)$ are inconsistent with the experimental indications that the exponent must be close to unity. Eq. (7) was also conjectured in Ref. 2 on the basis of a very different model.

[9]B. Widom, J. Chem. Phys. 43, 3098 (1969).

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[11]Such transitions are known to exist. See, for example, A. Jayaraman, Phys. Rev. 137A, 179 (1965).

THERMOLUMINESCENCE OF KCl:Tl BETWEEN 30 AND 400°C DETERMINED BY SIMULTANEOUS INTENSITY AND SPECTRAL DISTRIBUTION MEASUREMENTS*

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The thermoluminescence of KCl:Tl following gamma-ray irradiation was studied using a new technique. Most of the emission occurs at 3050 Å, but three weak bands also appear. The 3050-Å glow curves, after different doses, consist of one or more peaks from a set of seven peaks occuring between 312 and 537°K. The total 3050-Å emission increases and then decreases, and the most intense glow peak shifts from low to high temperature with increasing dose.

Crystals of KCl:Tl have been intensely studied both theoretically and experimentally for more than 20 years.[1,2] In fact, this particular combination of host alkali halide and intentionally introduced impurity probably has been investigated more extensively than any other similar combination. A large fraction of the experimental work, involving almost every conceivable kind of solid-state technique, has been confined to measurements at room temperature or below. In con-