

a ring, and we have an ion-ring complex where the ring grows to macroscopic size. The ion-ring complex grows (and slows down) until the total drag force again balances eE . This is what Careri has termed the "giant fall." The binding of the ion to the ring has been described earlier by Donnelly and Roberts⁹; clearly if the field is further increased the ions will begin to escape from the rings and the ion velocity will, on average, be seen to increase again. This has been observed by Bruschi, Mazzoldi, and Santini.¹⁰ The entire shape of the (v_i, E) curve, then, reflects the making of complexes by the moving ion and the distinctive role played by fluctuations.

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*Permanent address: School of Mathematics, University of Newcastle upon Tyne, Newcastle upon Tyne,

England.

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⁴R. J. Donnelly, *Experimental Superfluidity* (Univ. of Chicago, Chicago, Ill., 1967).

⁵W. I. Glaberson, D. M. Strayer, and R. J. Donnelly, Phys. Rev. Lett. **21**, 1740 (1968); also W. I. Glaberson, J. Low Temp. Phys. **1**, 289 (1969).

⁶L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, Mass., 1959), Sect. 20.

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⁸The most accurate expressions for mobility come from the work of Baym, Barrera, and Pethick (Ref. 2). It is interesting to notice that the roton drag on an ion can be written down by direct analogy with Eq. (7) as $P_r^{-1} = (e/\mu_r) = f(p_0^2/3kT)N_r (kT/\mu_0)^{1/2} \sigma = (3\pi^2)^{-1} \hbar h_0^4 \sigma \times \exp(-\Delta/kT)$, the expression obtained recently by Schwarz and Stark [Eq. (5) of the second paper of Ref. 3] if $f = (2/\pi)^{1/2}$.

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Solvable Model of a Vapor-Liquid Transition with a Singular Coexistence-Curve Diameter*

N. D. Mermin†

Istituto di Fisica "G. Marconi," Università di Roma, Rome, Italy

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A lattice model with short-range interactions is proved to condense and have a singular coexistence-curve diameter at the critical point.

Widom and Rowlinson¹ have described a new model for the liquid-vapor transition with the unexpected property that if the system does condense and if it has a specific heat singularity, $c_v \sim (T_c - T)^{-\alpha'}$, then the diameter of the coexistence curve, $\rho_d(T) = \frac{1}{2}[\rho_L(T) + \rho_G(T)]$, is also singular at T_c :

$$(d/dT)\rho_d(T) \sim -(T_c - T)^{-\alpha'}. \quad (1)$$

In deducing this singularity they exploit the fact that their interacting gas is thermodynamically equivalent to an ideal gas of particles which can, however, interact with each other indirectly via their interactions with the particles of a second ideal gas occupying the same volume. This equivalent two-component system is completely symmetric in the two components, and the derivation of (1) relies on this symmetry.

In assessing the likelihood that (1) might describe the diameter of a real system, one encounters some worrisome points. For one thing, although there is nothing in our current understanding of phase transitions to cast serious doubt on the assumptions that the model system does condense and does possess a specific-heat singularity, they remain unproved assumptions, and, as Widom and Rowlinson acknowledge, the conclusion (1) must therefore "remain tentative."

Perhaps a more serious cause for concern, however, is the symmetry of the two-component model. The representation of a real one-component interacting system as an ideal gas with an effective interaction mediated by the particles of a second ideal gas is not unfamiliar. For example, a gas of mutually noninteracting pho-

tons can, for many purposes, be represented as a gas of electrons alone, with classical electromagnetic interactions. As the example suggests, however, the two components in such a representation are unlikely to be interchangeable. One would be more inclined to take (1) seriously if its derivation could be divorced from the symmetry of an underlying two-component model.

The solvable model of Hemmer and Stell,¹ with long-range interactions leading to thermodynamics of the "classical" type, sheds some light on these questions since it can rigorously be shown to possess a singular diameter, while being apparently unrelated to any two-component model. In the present note some further evidence is described, in the form of a model with short-range interactions and "nonclassical" thermodynamics, more closely related to that of Widom and Rowlinson than that of Hemmer and Stell. This model can be proved rigorously to condense, with a diameter that is logarithmically singular at the critical point,

$$d\rho_d(T)/dT \sim |\ln(T_c - T)|, \quad (2)$$

and is equivalent to an intrinsically asymmetric two-component model.

The model consists of a square lattice in which objects do not, as in the familiar lattice gas, occupy the primitive squares, but rather the line segments bounding the primitive squares. For concreteness, we imagine the objects to be bars of length slightly less than a primitive square side, one of which may or may not be present on each of the lines separating neighboring primitive squares. A state S of this gas of bars is determined when one specifies which lines have bars on them, and which do not. Thus there are 2^N states, where N is the number of sites at which a bar may be placed. In the thermodynamic limit, $N/\bar{N} \rightarrow 2$, where \bar{N} is the number of primitive squares in the lattice.

The energy of a state S is taken to be

$$U(S) = -JN_s(S), \quad (3)$$

where $N_s(S)$ is the number of primitive squares all four of whose adjacent bar sites are occupied in the state S (or, equivalently, the number of little squares of primitive size formed by the bars in the state S). This interaction can be represented as a sum of four-body interactions. The thermodynamics of the model is determined by the grand partition function

$$\Xi(z, K) = \sum_S z^{N(S)} e^{KN_s(S)}, \quad (4)$$

where $N(S)$ is the number of bars present in the state S , and $K = J/k_B T$.

This system can also be represented as a two-component model. One component consists of bars on a square lattice with properties identical to those we have just described, except that the bars are taken to be noninteracting in the two-component model. The second component consists of lattice-gas molecules, one of which may or may not be present in the interior of each primitive square. The molecules are also mutually noninteracting. However, there is a bar-molecule interaction which expresses itself in a constraint on the allowed configurations of the two-component system: Only those configurations are allowed in which the two squares separated by each unoccupied bar site are both occupied by molecules.²

The grand partition function of the two-component model is

$$\Xi^{\text{mix}}(z, \bar{z}) = \sum_S z^{N(S)} \bar{z}^{\bar{N}(\bar{S})}, \quad (5)$$

where the sum is over all states S of the bars and \bar{S} of the molecules compatible with the constraint, and where $\bar{N}(\bar{S})$ is the number of molecules present in the molecular state \bar{S} .

The equivalence of the models is established by performing the sum over \bar{S} in (5) for each fixed state S of the bars. Given a particular configuration of bars, the constraint requires a molecule to occupy every square except those with bars on all four sides. Such squares may or may not be occupied. Thus,

$$\Xi^{\text{mix}}(z, \bar{z}) = \sum_S z^{N(S)} \bar{z}^{\bar{N} - N_s(S)} (1 + \bar{z})^{N_s(S)}. \quad (6)$$

Comparing (5) and (6), we find

$$\Xi^{\text{mix}}(z, \bar{z}) = \bar{z}^{\bar{N}} \Xi[z, \ln(1 + 1/\bar{z})]. \quad (7)$$

However one can sum (5) in the opposite order. Given a particular molecular configuration \bar{S} , the constraint requires a bar to occupy every line segment, unless the two adjacent squares both contain molecules, in which case a bar may or may not be present. Thus if $\bar{N}_{nn}(\bar{S})$ is the number of nearest-neighbor pairs belonging to the set of squares occupied in the state \bar{S} , then

$$\Xi^{\text{mix}}(z, \bar{z}) = \sum_{\bar{S}} \bar{z}^{\bar{N}(\bar{S})} z^{N - \bar{N}_{nn}(\bar{S})} (1 + z)^{\bar{N}_{nn}(\bar{S})}. \quad (8)$$

Now (8) can be expressed in terms of the grand partition function for an ordinary lattice gas on a square lattice with attractive nearest-neighbor interactions:

$$\Xi(z, \bar{K}) = \sum_{\bar{S}} \bar{z}^{\bar{N}(\bar{S})} e^{\bar{K}\bar{N}_{nn}(\bar{S})}, \quad (9)$$

whence

$$\Xi^{\text{mix}}(z, \bar{z}) = z^N \bar{\Xi}(\bar{z}, \ln(1+1/z)). \quad (10)$$

By comparing (10) and (7) we can express the grand partition function of the original model in terms of that of the lattice gas:

$$\Xi(z, K) = (e^K - 1)^{\bar{N}} z^N \bar{\Xi}(\bar{z}, \bar{K}), \quad (11)$$

where

$$\bar{z} = [e^K - 1]^{-1}, \quad \bar{K} = \ln(1+1/z). \quad (12)$$

Now the equilibrium density and energy per bar in the bar model are given by

$$\rho(z, K) = \frac{z}{N} \frac{\partial}{\partial z} \ln \Xi(z, K) \quad (13)$$

and

$$u(z, K) = -J(\bar{N}/N)w(z, K), \quad (14)$$

$$w(z, K) = \frac{1}{N} \frac{\partial}{\partial k} \ln \Xi(z, K).$$

Therefore (11) tells us that

$$\rho(z, K) = 1 - (1+z)^{-1} \bar{w}(\bar{z}, \bar{K}) \quad (15)$$

and

$$w(z, K) = (1 - e^{-K})^{-1} [1 - \bar{\rho}(\bar{z}, \bar{K})], \quad (16)$$

where $\bar{\rho}$ is the equilibrium density of the lattice gas and $\bar{u} = -\bar{J}(N/\bar{N})\bar{w}$ is the equilibrium energy per molecule.

The lattice gas is known to condense at a critical temperature given by $\sinh(\frac{1}{2}K_c) = 1$. Below the critical temperature, particle-hole symmetry requires that in the two-phase region

$$\bar{z} = \bar{z}(\bar{K}) = e^{-2\bar{K}} \quad (17)$$

and, in addition,

$$\frac{1}{2}[\bar{\rho}_L(\bar{K}) + \bar{\rho}_G(\bar{K})] = \bar{\rho}_d(\bar{K}) = \frac{1}{2}, \quad (18)$$

$$\begin{aligned} \Delta \bar{\rho}(\bar{K}) &= \bar{\rho}_L(\bar{K}) - \bar{\rho}_G(\bar{K}) \\ &= \bar{w}_L(\bar{K}) - \bar{w}_G(\bar{K}) = \Delta \bar{w}(\bar{K}). \end{aligned} \quad (19)$$

From (17) and (12) it follows (i) that K is an analytic function of \bar{K} and vice versa, at all temperatures in the two-phase region including the critical point; (ii) that z is an analytic function of K in the two-phase region including the critical point; and (iii) that when \bar{z} exceeds $\bar{z}(\bar{K})$ then z is less than $z(K)$, so that below the critical temperature the homogeneous gaseous states in one model correspond to the homogeneous liquid states in the other. In particular, then,

(15) and (16) imply

$$\Delta \rho(K) = (1+z)^{-1} \Delta \bar{w}(\bar{K}), \quad (20)$$

$$\Delta w(K) = (1 - e^{-K})^{-1} \Delta \bar{\rho}(\bar{K}), \quad (21)$$

$$\rho_d(K) = 1 - \frac{1}{2}(1+z)^{-1} [\bar{w}_L(\bar{K}) + \bar{w}_G(\bar{K})], \quad (22)$$

$$\frac{1}{2}[w_L(K) + w_G(K)] = (1 - e^{-K})^{-1} [1 - \bar{\rho}_d(\bar{K})]. \quad (23)$$

Equations (18) and (19) permit (20) and (23) to be written

$$\Delta \rho(K) = (1+z)^{-1} \Delta \bar{\rho}(\bar{K}), \quad (24)$$

$$w_L(K) + w_G(K) = (1 - e^{-K})^{-1}. \quad (25)$$

Now in the two-phase region w is a linear function of density and must therefore have the form

$$\begin{aligned} w(\rho, K) &= [\rho - \rho_d(K)] \frac{\Delta w(K)}{\Delta \rho(K)} \\ &\quad + \frac{1}{2}[w_L(K) + w_G(K)]. \end{aligned} \quad (26)$$

Equations (21), (24), and (25) simplify this to

$$\begin{aligned} w(\rho, K) &= (1 - e^{-K})^{-1} \\ &\quad \times \{ [1 + z(K)] [\rho - \rho_d(K)] + \frac{1}{2} \} \end{aligned} \quad (27)$$

and therefore, since c_v is proportional to $-(\partial w / \partial K)_\rho$, $d\rho_d/dT$ will have the same critical singularity as c_v .

To establish that this singularity is in fact logarithmic, note that particle-hole symmetry in the two-phase region requires that

$$\bar{w}(\bar{\rho}_c, \bar{K}) = \frac{1}{2}[\bar{w}_L(\bar{K}) + \bar{w}_G(\bar{K})] \quad (28)$$

for the lattice gas, and therefore, from (22),

$$\rho_d(K) = 1 - [1 + z(K)]^{-1} \bar{w}(\bar{\rho}_c, \bar{K}). \quad (29)$$

Since $-(\partial \bar{w} / \partial \bar{K})_{\bar{\rho}_c}$ is known to have a logarithmic singularity at \bar{K}_c , and since $d\bar{K}/dK$ is analytic at the critical point, $d\rho_d/dK$ must also have a logarithmic singularity at the critical point.

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†Permanent address: Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, N. Y. 14850. The author gratefully acknowledges the kind support of the John Simon Guggenheim Memorial Foundation, and the hospitality of the Istituto Guglielmo Marconi.

¹B. Widom and J. S. Rowlinson, *J. Chem. Phys.* **52**, 1670 (1970). A singular diameter has been discovered in a very different model by P. C. Hemmer and G. Stell, *Phys. Rev. Lett.* **24**, 1284 (1970). The experimental status of the coexistence-curve diameter has recently been discussed by B. Wallace, Jr., and H. Meyer, *Phys. Rev. A* **2**, 1610 (1970); J. M. H. Levelt Sengers, J. Straub, and M. Vicentini-Missoni, to be published.

²The interaction is more easily pictured, and the relation to the two-component model of Widom and Rowlinson more readily grasped, by stating the interaction as a hard-core repulsion between antibars and anti-molecules: If an antibar occupies any line segment,

no antimolecule can be present in the square on either side. The antibar-antimolecule model is of some interest in itself, and has been studied by B. Widom, *J. Chem. Phys.* **46**, 3324 (1967), who also exploited its equivalence to the lattice gas.

Dynamic Shear Properties of Some Smectic Liquid Crystals

S. V. Letcher

Department of Physics, University of Rhode Island, Kingston, Rhode Island 02881

and

A. J. Barlow

Department of Electronics and Electrical Engineering, University of Glasgow, Glasgow W-2, Scotland
(Received 17 November 1970)

The real part of the shear mechanical impedance has been measured for three smectic liquid crystals using a shear-wave reflection technique. Results at 30 and 450 MHz are considerably lower than those expected for an isotropic, Newtonian fluid, suggesting the existence of viscoelastic relaxation.

A study has been made of the behavior in shear of three smectic liquid crystals, ethyl *p*-azoxybenzoate, heptyloxyazoxybenzene, and ethyl *p*-[(*p*-methoxybenzylidene) amino] cinnamate. The shear-wave properties of a liquid may be represented by the shear mechanical impedance, $Z_L = R_L + iX_L$, defined as the negative ratio of shear stress to the rate of change of shear displacement. For a Newtonian fluid, i.e., one exhibiting no viscoelastic relaxation, $R_L = X_L = (\pi\rho\eta f)^{1/2}$, where ρ is the density, η the steady-flow viscosity, and f the shear-wave frequency. For a viscoelastic fluid R_L and X_L diverge with increasing frequency. In the limit where the material behaves as an elastic solid, R_L attains a maximum value and X_L becomes zero.

The experimental technique involved determination of the reflection coefficient for shear waves at a solid-liquid interface.¹ Measurements were made at two frequencies, 30 and 450 MHz. At 30 MHz a pulse of shear waves was obtained by means of a thin *BC*-cut transducer bonded to one end of a fused quartz rod; at 450 MHz a rod of *BC*-cut crystal quartz was used and shear waves were generated directly by surface excitation. The free end of the rod was loaded by the sample, and the change in the reflection coefficient gave the real part R_L of the shear impedance. No particular efforts were made to achieve uniform orientation of the samples and the orientation in situ was not observable.

The liquid crystal samples were obtained from

Eastman Kodak Co., and were used as supplied. The results obtained did not differ significantly from those obtained using recrystallized material.

Ethyl *p*-azoxybenzoate has a single mesomorphic phase, smectic *A*, from 114 to 123°C. The viscosity has been reported by Vorländer² to be up to 9 cP for the isotropic liquid and from 30 to 160 P in the smectic phase. The variation of the shear resistance at 450 MHz is shown in Fig. 1. Although there is a large increase in steady-flow viscosity upon cooling through the isotropic liquid-to-smectic phase transition at 123°C, there is no appreciable change in R_L . At the freezing point (somewhat below the nominal transition temperature of 114°C) the shear reflection loss increases rapidly because of shear-wave transmission into the solid. The value of R_L below the freezing point indicates an elastic modulus approaching 10^{10} dyn/cm², a value typically obtained for simple organic glasses.³ Upon heating, R_L changes less abruptly, and a difference between the values for heating and cooling persists until the isotropic liquid state is reached. During the heating part of the cycle, pretransitional softening of the solid is evident. A Newtonian liquid of viscosity 100 P and unit density has a shear resistance of 0.96×10^5 dyn sec/cm³ at 30 MHz and 3.7×10^5 dyn sec/cm³ at 450 MHz. At 115°C the measured values of R_L were 3.6×10^3 and 1.3×10^4 dyn sec/cm³ at 30 and 450 MHz, respectively. Within the limits of experimental error,