Origin of the Singular Diameter in the Coexistence Curve of a Metal

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It is suggested that the large amplitudes of the singularities in the coexistence-curve diameters of cesium and rubidium, as measured by Jüngst, Knuth, and Hensel arise from the correspondingly strong thermodynamic-state dependence of the screened ion-ion interactions in these systems, especially as the metal-insulator transition is traversed. This state dependence, which is normally negligible for typical insulating fluids, corresponds to the *mixing of thermodynamic fields* present in certain lattice models and scaling theories.

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Ninety-nine years ago, Cailletet and Mathias[1] observed that the diameters of liquid-vapor coexistence curves appear to be linear functions of temperature. This empirical "law of the rectilinear diameter" has since been the subject of intense study because of predictions that the locus of tie-line midpoints actually has the same singular temperature dependence as the internal energy near a critical point. Such a result appears in a variety of models[2-4] and renormalization-group studies,[5] although there has been no microscopic explanation of the origin of the anomaly. Furthermore, the experimental evidence for its very existence is weak at best.[6] The fundamental issues being addressed are the appropriate choice of scaling variables at a liquid-vapor critical point and the correspondence between critical phenomena in magnets and fluids.

Recently, Jüngst, Knuth, and Hensel[7,8] (JKH) determined the liquid-vapor coexistence curves of cesium and rubidium, and both are remarkably different from those of typical nonmetallic fluids in their extreme *asymmetry* with respect to the critical density. Indeed, JKH find strong evidence that Cs and Rb violate the law of the rectilinear diameter in precisely the manner predicted by the above theories.

In this Letter, we suggest that the contrast between the data of JKH and the apparent experimental linearity of the diameters of essentially all[9] nonmetallic one-component systems which have been studied previously arises from many-body effects whose magnitudes fundamentally distinguish the particle interactions in metals from those in nonmetals. In particular, the characteristic screening of the bare ion-ion interactions by the electron gas in a metal is argued to lead to a *mixing of thermodynamic fields,* in that the scaling variables at the critical point are not simply the reduced temperature and the chemical-potential shift from that on the critical isochore, but rather some (asymptotically linear) combination of them.

To motivate our analysis, we begin by recalling previous theoretical work[2-5,10] which has dealt with this concept. Rehr and Mermin[10] showed that Widom's[11] original scaling equation of state can be modified to describe a singular diameter by writing the pressure $P(\mu,t)$, as a function of μ (the chemical-potential shift from that along the critical isochore) and reduced temperature $t=(T-T_c)/T_c$, in the form

$$P(\mu,t)=P_0(\zeta,\tau)+|\tau|^{2-\alpha}f_{\pm}(\zeta/|\tau|^{\beta\delta}). \qquad (1)$$

Here, the background term P_0, the effective one-body field $\zeta=\zeta(\mu,T)$, and the effective temperature $\tau=\tau(\mu,T)$ are analytic in their arguments, $f_{\pm}$ are the scaling functions of a symmetric system (i.e., one with a rectilinear diameter), and α, β, and δ are its associated critical exponents. The density $\rho=(\partial P/\partial\mu)_T$ has a diameter $\rho_d=\frac{1}{2}(\rho_l+\rho_v)$ whose leading temperature dependence is

$$\rho_d=\rho_c+(2-\alpha)f_-(0)(\partial|\tau|/\partial\mu)|\tau|^{1-\alpha}+\dots,$$

where ρ_c is the critical density. In contrast, when scaling holds in the original variables μ and t, $\rho_d-\rho_c$ is asymptotically linear in t. The important point for what follows is that a singular diameter can arise through the dependence of the effective temperature τ on the bare chemical potential μ.

This conclusion also holds when we consider a general transformation which takes an Ising spin system possessing additional degrees of freedom onto the ordinary spin-$\frac{1}{2}$ model. Let $F(\{K\},H)=(1/N)\ln Z$ be the reduced free energy per spin of such a model, with $\{K\}$ and H, respectively, the set of bare interaction parameters and the magnetic field, also reduced by the factor $-1/k_BT$. With a subscript I denoting those quantities which refer to the Ising model, the map is

$$F(\{K\},H)=F_I(K_I(\{K\},H),H_I(\{K\},H))+G(\{K\},H), \qquad (2)$$

where G, K_I, and H_I are usually analytic in their arguments. This form of the free energy is the basis for all decorated-lattice calculations[4] used to study the singular diameter. The spontaneous magnetization $M_{\pm}$

$=(\partial F/\partial H)_{\pm}$ in the two branches of the coexistence curve is

$$M_{\pm}=(\partial G/\partial H)_{\rm coex}+E_{\rm I}(\partial K_{\rm I}/\partial H)_{\rm coex}\pm M_{\rm I}(\partial H_{\rm I}/\partial H)_{\rm coex}, \qquad (3)$$

where $E_{\rm I}=(1/N)<\sum_{\langle ij\rangle}s_is_j\rangle_{\rm I}$ is the nearest-neighbor correlation and $M_{\rm I}=\langle s_i\rangle_{\rm I}$ is the magnetization of the Ising model at the "coexistence" condition $H_{\rm I}=0$. With the fluid-magnet correspondence invoked, the densities in the two outer branches are $\rho_{\pm}=(1+M_{\pm})/2$, so that the diameter anomaly arises from that part of the *internal energy* $E_{\rm I}$ which varies as $t^{1-\alpha}$, and thus requires an effective coupling $K_{\rm I}$ which depends on the bare one-body field H.

These arguments suggest that the crucial difference between the effective interactions in metallic and insulating fluids also distinguishes the *amplitudes* of the singularities in their diameters. The interactions screened by delocalized electrons in a liquid metal are manifestly *functions of thermodynamic state,* while in nonmetals, state-independent interactions such as fluctuating-dipole forces generally provide quite accurate descriptions of their structure and thermodynamics over most of the phase diagram. Of course, both types of interactions are sufficiently short ranged to lead to critical exponents in the Ising-model universality class.

Recent experiments[12] on metals near the liquid-vapor critical points have shown that there are profound changes in their electronic structure in that region, as evidenced by dielectric anomalies and a roughly exponential variation in electrical conductivity with density. These changes may be viewed as a consequence of a polarization catastrophe accompanying the impending insulator-metal transition, and to the extent that the particle interactions reflect the nature of the changing electronic states, they will be functions of thermodynamic fields in the vicinity of the critical point.

In either phase, insulating or metallic, the system is described by a single fundamental Hamiltonian, and any analysis is best carried through in the grand canonical ensemble by considering a liquid metal to be a two-component system of ions and valence electrons. The free energy $\Xi=-\beta^{-1}\ln Z_{\rm tot}$ of this system is given by the grand partition function

$$Z_{\rm tot}=\underset{\{i\}}{\rm Tr_C}\ \underset{\{e\}}{\rm Tr_Q}\exp\{-\beta[\hat{T}_i+\hat{T}_e+U_{\rm tot}(\{\mathbf{R}_i\},\{\mathbf{r}_e\}]-\mu_i\hat{N}_i-\mu_e\hat{N}_e\}, \qquad (4)$$

where $\hat{T}_i$ and $\hat{T}_e$ are the ion and electron kinetic energy operators, and μ_i and μ_e their chemical potentials. The total potential energy $U_{\rm tot}(\{\mathbf{R}_i\},\{\mathbf{r}_e\})$ is a function of the ion and electron coordinates, $\{\mathbf{R}_i\}$ and $\{\mathbf{r}_e\}$, respectively. The standard adiabatic separation allows the quantum trace ($\rm Tr_Q$) over electron states[13] to be performed for fixed $\{\mathbf{R}_i\}$, thereby reducing the partition function to a classical trace ($\rm Tr_C$) of a one-component system (ions), interacting through an *effective* potential $U(\{\mathbf{R}_i\};\mu_e,T)$. This potential incorporates the characteristic screened interactions in a metal, and is viewed as fundamentally a function of μ_e,[14] rather than that of the electron density ρ_e, as the latter enters into the screening wave vector in the usual zero-temperature correspondence.

The procedure of tracing over the electron coordinates is formally no different from the usual averaging carried out in a multicomponent system. However, in a metal the ion and electron chemical potentials are linked through the requirement of overall electroneutrality. This rigorous neutrality constraint,[15] a consequence of the long-range Coulomb forces, implies that the composite system of electrons and ions is equivalent[16] to a one-component system of ions alone, but one which is governed by an effective ion chemical potential $\bar{\mu}=\mu_i+z_i\mu_e$, where z_i is the ion valency. It is μ to which the experimentally observable density is conjugate.

Quite generally, we may write the total effective potential as a sum of n-body potentials,

$$U=\textstyle\sum_i\Phi^{(1)}(r_i)+\sum_{i<j}\Phi^{(2)}(r_{ij})+\ldots,$$

where all structure-independent contributions have been absorbed into $\Phi^{(1)}$. When we take the derivative of the effective one-component grand free energy with respect to $\bar{\mu}$, the thermodynamic density has a form analogous to that of the lattice models and scaling theory, namely,

$$\rho=\rho^{(1)}\frac{\partial\Phi^{(1)}}{\partial\bar{\mu}}+(\rho^{(1)})^2\int d^3r\,g(r)\frac{\partial\Phi^{(2)}(r)}{\partial\bar{\mu}}+\ldots,$$

where $\rho^{(1)}$ is the average of the one-body operator, $g(r)$ is the pair correlation function, and translational invariance has been assumed. The second (and higher-order) terms involving the n-body correlation functions contain the temperature singularity of the internal energy, so that there appears[17] a term in the mean density varying as $t^{1-\alpha}$ whose amplitude is governed by the state dependence of the n-body potentials.[18]

The electron states which dominate the quantum trace clearly reflect the physical properties of the system. In insulators and dilute metallic vapors with localized electrons, the trace would normally be taken over tight-binding-like orbitals for which the multipole expansion of U is appropriate (van der Waals interactions at long range then being the leading terms). However, the metal is characterized by the presence of itinerant electrons in a band of states, and the electron trace leads to thermodynamic-state–dependent and structure-independent one-body terms in U, as well as to specifically state-dependent pair and multicenter interactions.[19] It is important to reemphasize that, in passing through the critical region, the character of these states changes rapidly from one to the other, the resulting free charge density varying dramatically with the total density. This is to be contrasted with the situation in typical electrolyte solutions, where, as can be readily seen from Debye-Hückel theory, the screening is weakly state dependent, the free charge density varying slowly with the concentration of ionizable species. These systems do not exhibit the vast qualitative change in the form of the interaction which occurs at the metal-nonmetal transition.

In metals, the characteristic dependence of the screened pair potential $\Phi^{(2)}(r;\mu_e,T)$ on μ_e can be seen with linear-response theory in the pseudopotential formalism. In Fourier space, the standard result is[19]

$$\Phi^{(2)}(q;\mu_e,T)=(z_i)^2 v_C(q)+[v_{ps}(q)]^2\Pi(q;\mu_e,T),$$

where $v_C(q)$ and $v_{ps}(q)$ are the transforms of the Coulomb and electron-ion potentials, and $\Pi=(\epsilon^{-1}-1)/v_C(q)$ is the static polarizability function. In a single-electron picture the dielectric function $\epsilon(q;\mu_e,T)$ depends on the electron chemical potential through the Fermi-Dirac distribution function. Now we see immediately that the *scale* of the μ dependence of $\Phi^{(2)}$ is that of the screening interaction, which is comparable to the bare ion-ion Coulomb energy in liquid metals. In contrast, any chemical-potential dependence of fluctuating-dipole forces should be related to the degree to which continuum states (i.e., those involving charge separation) enter the electron trace. Since the statistical weight of such states is suppressed by the Boltzmann factor $\exp(-I/2kT)$, where I is the ionization potential, this is clearly negligible for typical insulating systems in which the effective ionization potential is essentially constant in the critical region.

We note that the tracing out of the electrons which yields the state dependence is schematically very similar to the decimation transformation[20] of a decorated-lattice calculation (Fig. 1). However, the breaking of particle-hole symmetry and the singular diameter in such models arise from the structure of the lattice (two inequivalent sublattices with different coordination numbers),[4] while the electron gas is a fundamental feature of metallic systems at the level of the Hamiltonian.[21]

Finally, the present analysis may also apply to other systems which exhibit closely related[22] electronic and

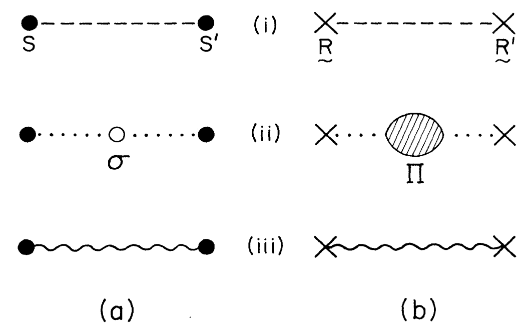

FIG. 1. Similarity of the decorated-lattice decimation and the inclusion of screening effects in a metal. (a) The coupling between spin s and s' (i) is a constant, but the effective interaction (iii) acquires a state dependence from the trace over the decorating spin, which is coupled to the primary sites (ii). (b) The bare Coulomb interaction between ions at $\mathbf{R}$ and $\mathbf{R}'$ in a metal (i) is modified by the electron gas [e.g., the simplest polarization effect, as in (ii)], yielding a state-dependent screened interaction (iii).

structural transitions. In particular, the solubility gap in metal-ammonia solutions has a distinct asymmetry which has been attributed[23] to the change in the range of the screened interactions near the consolute point, and the associated metal-insulator transition. The detailed properties of the coexistence-curve diameter have not been assessed to our knowledge, but may provide evidence for a singularity.

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