On the Importance of Fluctuations in Weakly First-Order Metal–Insulator Transitions

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Metal-insulator transitions (MITs) —remain theoretically mysterious. In addition to the lack of an obvious order parameter, these phase transformations demonstrate singular behavior in their response functions in addition to large discontinuities in some extensive variables like the entropy. This has made their classification as either first or second-order transitions difficult. It is hypothesized that the emergence of pseudoscaling behavior at an otherwise first order transition may be due to the addition of long-range interactions for systems that are near tricritical points. Therefore, the importance of fluctuations around the saddle point for otherwise first-order phase transitions will be investigated. Renormalization group techniques will be used to examine the effects of the addition of long-range interactions near the phase transition. We will demonstrate that such long-range interactions may alter the order of the phase transition upon renormalization.

I. INTRODUCTION

Metal-insulator transitions occur when electrons delocalize from insulating states into otherwise free charge carriers. This transition often manifests as a change in the magnitude of the electrical conductivity from oxide ($<10^{-2}$ Ω^{-1}m^{-1}) to metallic ($>10^{2}$ Ω^{-1}m^{-1}) [1]. Such transitions notably occur in the insulating oxides VO_2 and NbO_2 solely as as function of temperature and are considered first order because they have large discontinuities in the entropy at their phase transition[1–3]. It is worth mentioning that other extensive quantities, like the volume, change as little as 0.2%.

The theoretical picture has been muddied by significant ongoing debate over whether MITs are driven by changes in the electronic degrees of freedom, the phonon density of states from a concomitant structural transformation, or both [1, 4–8]. Recent work suggests there may exist a description of such transitions in the previously unevaluable electronic entropy from electronic transport property measurements [8]. Our study will thus confine itself to systems for whom this thermodynamic description is valid.

Because the theoretical descriptions of metals and insulators can vary dramatically, an appropriate (and quantitatively useful) Hamiltonian to describe the system is lacking. Taken together, this has made the identification of a relevant order parameter for theses systems difficult.

There are several other important features of these transitions that have hindered theoretical work. The range of transition temperatures is significant, magnetite undergoes the famous Verwey MIT in Fe_3O_4 at 125 K, NbO_2 has a T_c of roughly 1100 K. This essentially rules out electronic structure calculation methods as a viable way to probe the thermodynamics of these transitions. These materials also tend to exhibit seemingly singular behavior in their response functions at the phase transition temperature. This type of behavior would indicate if not a diverging correlation length ,ξ, at-least a large, finite ξ near the phase transition, as has been observed in some high-dimensional Monte Carlo models [9]. Previous experimental work has sought to avoid this trouble all together by either doping or applying pressure to otherwise first-order MITs until they become second order so that they may be evaluated using classical field theory tools[10–12].

Because of the inherent difficulties in providing a quantum mechanical picture of the transition, a Landau theory could prove useful in providing a thermodynamic picture for the near singular behavior of the free energy of the metal and insulating phases as they approach the first order phase transformation.

To establish the possibility that there may exist a pseudoscaling universality class for such transitions (and in the absence of a clear order parameter) we propose to examine mean heat capacity and entropy data for two oxides insulting oxides that undergo MITs. We will apply mean field Landau theory, consider fluctuations about the saddle point in the limit that we are near a tricritical point, and examine the effects of the addition of long range interactions under renormalization.

II. ELECTRONIC ENTROPY

The electronic entropy can be accessed from measurable electronic transport properties. It has been demonstrated that the partial molar entropy of a conduction electron can be related to the Seebeck coefficient from [13].

$$\left(\frac{\mathrm{dS}}{dn_e}\right)_{T,P,n_j} = -\alpha F \tag{1}$$

where α is the Seebeck coefficient and F is Faraday constant.

The integral form was implemented for metal-insulator transitions by [8] and resulted in the electronic state entropy:

$$S_{\mathrm{e}} = -n_e e \alpha_e \tag{2}$$

TABLE I. Electronic entropies of transition for VO_2 and NbO_2.

Material	T_c (K)	ΔS^{T} (J/molK)	ΔS^{elec} (J/molK)
VO_2	340	14.7[14]	9.2[8]
NbO_2	1100	10 [3]	7.9 (this work)

TABLE II. Critical exponents of the heat capacity near the first-order transition temperature from above (+) and below (-).

Material	α+	α-
VO_2	-0.32	-2.5
NbO_2	-0.22	-0.24

where e is the fundamental charge constant, n is the number of free charge carriers (here electrons). The electonic entropy has been evaluated for VO_2 and NbO_2. In both cases, the electronic entropy calculated using Eq. (2) accounts for 60-70% of the total observed entropy and is listed in Table 1. This suggests that the fundamental nature of these transitions may be similar.

III. CRITICAL BEHAVIOR

The starting point for an evaluation of pseudoscaling behavior of the electronic free energy is the critical exponent of the heat capacity given in the equation

$$C_{\text{singular}} \propto (T - T_c)^{\alpha} \tag{3}$$

The critical exponent of the heat capacity ,α, is independent of the chosen order parameter, therefore serving as a useful starting point for examining the universal nature of the MIT. The critical behavior of the oxides of interest were examined from data on both sides of the phase transition in Table 2, with the data coming from below the VO_2 largely relying on extrapolation [3, 15]. Table 2 otherwise suggests that the listed oxides may exhibit some similarities in their pseudoscaling behavior.

A plot of the heat capacity as NbO_2 approaches the critical point is presented in Fig.1.The shape of the heat capacity as a function of temperature is reminiscent of a λ transition, although it does not seem to belong to the superfluid He universality class, as the scaling law coefficient in that case is $\alpha_{superfluid} \approx 0.01$.

IV. MEAN FIELD THEORY

Previous work has examined MITs from the perspective of second-order phase transitions, and employed *2-4* polynomials for the Landau free energy[11]. We propose

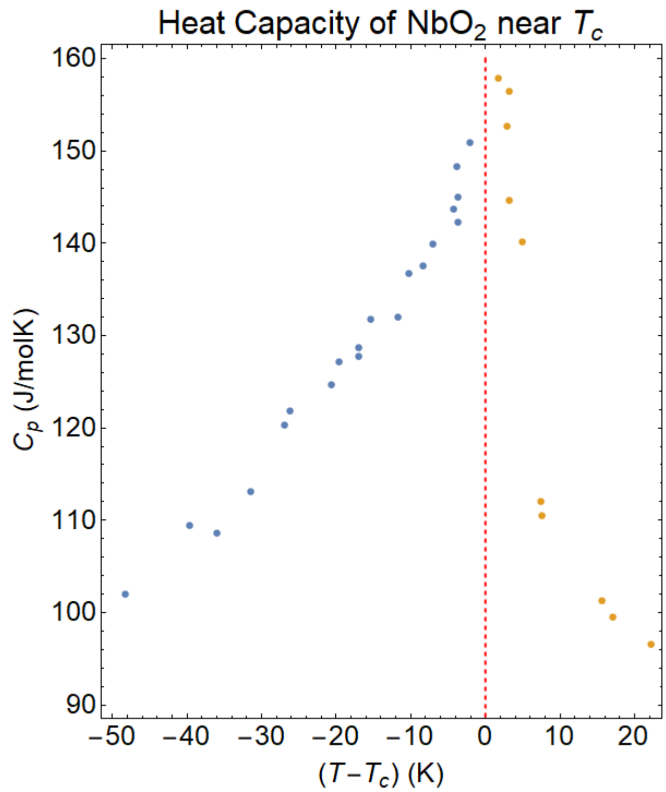

FIG. 1. Variation of the heat capacity of NbO_2 as a function of the temperature relative to the critical point. Reproduced from ref. [3]

a *2-4-6* polynomial which should satisfy these requirements as:

$$\Psi(m) = \int \frac{K}{2}\nabla^2(m) + \frac{t}{2}m^2 + um^4 + vm^6 \tag{4}$$

where the coefficients to the order parameter m are phenomenological parameters.

A first order phase transition occurs for the conditions[16]:

$$u < 0,\ \bar{t} = \frac{u^2}{2v} \tag{5}$$

However it can be demonstrated that in the absence of fluctuations, such a formulation yields a divergence in the heat capacity only from below with an effective $\alpha = 0.5$ and no such divergence coming from above, at odds with experimental observation. Additionally, the case in which $u = 0$ describes a tricritical point. While it may be simple to say that a weakly first-order transition involves both $u < 0$ and $\lim_{u\to 0}$, in addition to evaluating the effects of fluctuations, we will examine the possibility that long-range interactions may be driving an otherwise strongly first order transition towards second order. We believe this is relevant considering the magnitude changes in the entropy are quite large for these transitions to be considered "weak". We will implement both Gaussian theory and momentum-space renormalization group methods to examine the relevancy of u with the introduction of such long-range interactions.

V. FLUCTUATIONS

Transverse and longitudinal fluctuations are introduced as

$$m(x) = (\bar{m} + \phi_l(x))\hat{e_l} + \sum_{\alpha=2}^{n} \phi(x)_t^\alpha \hat{e_\alpha} \tag{6}$$

Keeping fluctuation contributions to second order, we find expressions for the free energy to be:

$$f(\phi_l, \phi_t^\alpha) = f(0,0) + \int d^d x \left[\frac{K}{2}(\nabla\phi_l)^2 + \frac{\phi_l^2}{2}(t + 12\bar{m}^2 u + 30\bar{m}^4 v) + \sum_{\alpha=2}^{n} \left(\frac{K}{2}(\nabla\phi_t^\alpha)^2 + \frac{(\phi_t^\alpha)^2}{2}(t + 6\bar{m}^4 v) \right) \right] \tag{7}$$

$$= f(0,0) + \begin{cases} \frac{n}{2} \int \frac{d^d q}{2\pi^d} ln(kq^2 + t) & \text{if } t > 0 \\ \frac{n}{2} \int \frac{d^d q}{2\pi^d} ln(kq^2 - 4t) & \text{if } t < 0 \end{cases} \tag{8}$$

Where we have converted to Fourier representation of the free energy in equation (8). The heat capacity is given by $C_v = -T\frac{d^2 f}{dT^2}$ and so therefore the contributions from fluctuations and the saddle point are given by

$$C_{fl.} = C - C_{s.p.} \propto K^{-d/2}|t|^{\frac{d}{2}-2} \tag{9}$$

$$C_{s.p.} \propto (-vt)^{\frac{1}{2}} \tag{10}$$

Where s.p. refers to the saddle point result and fl. to the fluctuations. We have induced critical behavior on both sides of the transition and note a reduction in the upper critical dimension, d_u, from 4 in the case of the second-order transition to 3 in the first order. The value of the fluctuations are still given by $\alpha = 0.5$ in $d = 3$. While the qualitative behavior has been repaired, this still does not offer a satisfying explanation for the emergence of singular like behavior near the phase transition in otherwise first-order systems.

VI. LONG RANGE INTERACTIONS

We postulated earlier that the addition of long range interactions near the phase transition may be modulating the weakly first-order behavior and perhaps the relevancy of u. We shall explore this possibility utilizing momentum-space renormalization. An example of such an interaction is given by:

$$\int d^d x \int d^d y \frac{K\, m(x) \cdot m(y)}{|x-y|^{d+\sigma}} \tag{11}$$

Where K is a constant interaction parameter between spin states.The K associated with the long-range interaction will be reffered to as K_σ going forward to avoid confusion with equation (4). This inclusion alters the Fourier space representation of the hamiltonian as

$$\begin{aligned} \beta H = & \int \frac{d^d q}{(2\pi)^d} \frac{t + Kq^2 + K_\sigma q^\sigma + ...}{2} m(q)\cdot m(-q) + \\ & u \int \frac{d^d q_1 d^d q_2 d^d q_3}{(2\pi)^{3d}} m(q_1)m(q_2)m(q_3)m(-q_1 - q_2 - q_3) + \\ & v \int \frac{d^d q_1 d^d q_2 d^d q_3 d^d q_4 d^d q_5}{(2\pi)^{5d}} m(q_1)m(q_2)m(q_3)m(q_4)m(q_5)m(-q_1 - q_2 - q_3 - q_4 - q_5) \end{aligned} \tag{12}$$

Under renoramlization, we can define the rescaling parameters as $q^{'} = bq$ and the order parameter $m^{'} = m/z$. This allows us to read off the first order recursion relations from equation (12) as :

$$\begin{cases} t^{'} = b^{-d} z^2 t \\ K^{'} = b^{-d-2} z^2 K \\ K_\sigma^{'} = b^{-d-\sigma} z^2 K_\sigma \\ u^{'} = b^{-3d} z^4 u \\ v^{'} = v^{-5d} z^6 v \end{cases} \tag{13}$$

The interesting behavior relevant to us occurs when $u \neq 0$ and in which we are at a fixed point where K_σ is the scale invariant interaction, leading to $z^2 = b^{d+\sigma}$ and $u^{'} = b^{2\sigma-d}u$. In $d = 3$, $\sigma > \frac{d}{2}$ suggests the Gaussian results are invalid and that u remains relevant upon renormalization, whereas the converse demonstrates that u is relevant (and necessary) for the transition to remain first-order. This suggests that long-range interactions can push us from a first to second-order transition, and that it is possible that weakly first-order transitions may correspond to the crossover case of $\sigma = 2$ upon which the magnitude of such an interaction may become important and compete directly with other short range interactions like K.

One can now try to imagine how such interactions may emerge during a first order transition. Perhaps these interactions occur at the meso-scale and are associated with nanometer sized phases in close contact with each other. We can only conjecture about the mechanism behind this interaction, but if we examine the case of σ =2 and in which u is marginal, the real space representation of the potential would be proportional to $\frac{1}{r^5}$, slightly longer ranged than a typical Lennard-Jones. This type of interaction has been speculated about but not widely treated, perhaps because it only becomes relevant near a first-order transition[17].

A more sophisticated treatment should explore the thermodynamic effects of the finite size of such phases. This may be possible numerically with $q \geq 3$ Potts models, which have demonstrated large (but finite) correlation lengths in otherwise first-order phase transformations for $d = 3$ [18].

VII. ORDER PARAMETER

It was originally hypothesized that eq (2). could prove useful in providing an order paramter because it can be related mathematically as

$$\Delta S = -n_e e \alpha_e = -\frac{1}{2} m^2 a_o \tag{14}$$

Where we have assumed that

$$t \propto a_0 (T - T_c),\ a_o > 0 \tag{15}$$

For materials with electron dominated conductivity, this results in an imaginary order parameter. However, considering our expansion in even powers of m, this can be overlooked. What is more concerning is that the metallic phase can be considered to have the nonzero value of eq (2)., but that the order-parameter should fall to zero as would eq (2) for an insulator. We consider this to be a sign that order parameters reminiscent of the electrical conductivity (at least in the Drude approximation) while seemingly the natural choice for such a problem, do not provide a useful description of the order parameter for metal-insulator transitions.

Topological treatments akin to the XY model have also been used to replicate MITs, but they focus on purely second-order phenomena[16].It may be worth examining what kinds of perturbations are necessary to cause a weakly first-order transition in such models, in which case the order parameter again may becomes more clear.

VIII. CONCLUSION

We have examined the weakly first-order nature of metal-insulator transitions and demonstrated the importance of fluctuations near a tricritical point in recovering some pseudoscaling behavior of the heat capacity. Through the use of first-order renormalization, we derived recursion relations for the Landau phenomenological parameters and demonstrate that long-range interactions may weaken otherwise strong first-order phase transformations. Such interactions arising near the critical point may account for the nearly singular beheavior in the heat capacity in otherwise first order transitions.

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