Solid-solid volume collapse transitions are zeroth order

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We present an exactly solvable non-linear elastic model of a volume collapse transition in an
isotropic solid. Integrity of the lattice through the transition leads to an infinite-range density-
density interaction, which drives classical critical behavior. Nucleation is forbidden within a pres-
sure window leading to intrinsic hysteresis and an unavoidable discontinuity of the thermodynamic
potential (zeroth order transition). The window shrinks with increasing temperature ending at a
critical point at a temperature related to the shear modulus. Mixed phases behave non-extensively
and show negative compressibility. We discuss the implications for Ce, SmS, and related systems.

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Room temperature γ Cerium shows a well known tran-
sition to isostructural α Cerium at ~ 0.8GPa with a
17% reduction of the volume. Similar (though not neces-
sarily isostructural) transitions occur in other f-electron
systems. Volume-collapse transitions were also pre-
dicted to occur in colloidal systems and close to first
order electronic transitions when mesoscopic inhomoge-
neous electronic states are frustrated by the long-range
Coulomb interaction.

Consider one of these systems which is driven across
the volume-collapse transition by adiabatically changing
the average volume. In analogy with the van der Waals
liquid-gas transition one expects a range of average vol-
ume values for which there is phase coexistence at a con-
stant equilibrium pressure. This presents an interesting
nucleation problem. Within purely energetic considera-
tions the mixed phase consists of a region of the sample
with the small unit cell volume and a region with the
large unit cell volume separated by a flat surface so as
to minimize the interface boundary energy. The lattice
mismatch at the interface can be seen as a line of dislo-
cations. However dislocations are very difficult to nuclae-
ate in a solid since they require the breaking of chemical
bonds. Indeed it is customary to assume on solid-solid
transitions that the lattice integrity is preserved.

Under this hypothesis the thermodynamic ground state
is frustrated from the onset, and the question arises of
how the system minimizes its free energy, preserving the
integrity constraints. To answer this question we solve a
non-linear elastic model of a volume-collapse transition
in an isotropic solid assuming lattice integrity (no dislo-
cations). The latter condition leads to the well known
St. Venant compatibility constraints among the differ-
ent components of the strain tensor and allows the free
energy to be expressed as a function of the order parame-
ter (OP) alone, with long-range interactions. This
kind of approach has been shown to lead to anomalous
nucleation in volume conserving transitions.

We find that compatibility constraints induce a dis-

cance-independent density-density interaction and thus
mean-field (MF) theory becomes exact and the model results to be trivially solvable at all temperatures
in the absence of short-range interactions. Critical ex-
ponents are MF like even in the presence of short-range
interactions. In the mixed phase the system behaves non
extensively and violates usual stability criteria for ex-
tensive systems. In particular, it possesses negative com-
pressibility. For an experiment in which the pressure acts
as the control variable we show that usual nucleation is
forbidden within a finite pressure window. This pressure
window implies an intrinsic hysteresis loop in a pressure
controlled experiment. Outside the pressure window the
transition can occur, but only irreversibly with an in-
trinsic jump of the thermodynamic potential. Since the
discontinuity occurs in the thermodynamic potential it-
self rather than in its first derivative the transition can be
called of zeroth order (instead of first) as done with sim-
ilar phenomena in gravitational systems. The extent
of the hysteresis loop reduces as a function of tempera-
ture, vanishing at a critical point. The temperature of
the critical point is related to the shear modulus of the
material.

Model The OP is taken to be the dilation strain $\epsilon_1 \equiv \sum_i^d \epsilon_{ii}/\sqrt{d}$ where $\epsilon_{ij}$ are the components of the infinitesimal strain tensor $\epsilon$ and $d$ is the dimensionality
of the system. Our starting point is a coarse grained elas-
tic Hamiltonian $H \equiv H_1 + H_h$ with $H_1$ a non-linear
Ginzburg-Landau like double-well term:

\begin{equation}
H_1 = \int d^d x \left( ae_1 - \frac{b}{2} e_1^2 + \frac{c}{4} e_1^4 + \frac{\kappa}{2} |\nabla e_1|^2 \right),
\end{equation}

The remaining $d(d+1)/2 - 1$ independent components of the strain tensor give the harmonic contribution:

\begin{equation}
H_h = \mu \int d^d x \sum_{i,j=1}^d \bar{e}_{ij}^2.
\end{equation}
where $\mu$ is the shear modulus of the material, and the (traceless) ‘accommodation strains’ tensor $\tilde{\epsilon}_{ij} \equiv \epsilon_{ij} - \delta_{ij}\epsilon_1/\sqrt{d}$ has been defined.

Zero temperature theory. In the absence of dislocations and in order to be physical the strain tensor must fulfill the St. Venant compatibility condition $^{[3]}$

$$\text{curl \, \text{curl} \, \epsilon = 0} \quad (3)$$

which leads to constraints between $\epsilon_1$ and $\tilde{\epsilon}_{ij}$. A uniform strain satisfies Eq. (3) trivially and therefore it is unconstrained. Thus the $k = 0$ term in the Fourier decomposition of $H_h$, corresponding to uniform accommodation strains, can be minimized by choosing $\tilde{\epsilon}_{ij}(k = 0) = 0$. For $k \neq 0$ the accommodation strains can be eliminated in favor of $\epsilon_1$ by minimizing $H_h$ with respect to $\tilde{\epsilon}_{ij}$, and enforcing the constraints in Eq. (3) by Lagrange multipliers $^{[4]}$. The resulting equilibrium equations together with Eq. (4) allow Eq. (2) to be written as a function of $\epsilon_1$ alone:

$$H_h = (d - 1)\mu \frac{1}{L^d} \sum_{k \neq 0} \epsilon_1(k)\epsilon_1(-k).$$

Here $L$ is the linear dimension of the system. A crucial point is that the $k = 0$ term is excluded from the sum. We can extend the sum to all $k$ by explicitly subtracting the missing term. We obtain in real space:

$$H_h/[(d - 1)\mu] = \int d^d x [\epsilon_1(x) - \tilde{\epsilon}_1]^2 \quad (4)$$

$$= \int d^d x \int d^d x' \left[ \delta(x - x') - \frac{1}{L^d} \right] \epsilon_1(x)\epsilon_1(x').$$

with $\tilde{\epsilon}_1 \equiv \int d^d x\epsilon_1/L^d$. The accommodation strains induce a local term that increases the stiffness at all wave vectors, and a distance independent “ferro” like interaction in $\epsilon_1$ that decreases the uniform stiffness alone, i.e., the stiffness at finite wave vector is larger than at zero wave vector, a well known result that holds also for linear elastic solids $^{[10]}$. A similar result has been obtained in $d = 2$ in the context of the dislocation mediated melting problem close to an isostructural critical point $^{[11]}$.

We define $\phi \equiv \epsilon_1 \sqrt{c/b}$, $m \equiv 4(d - 1)\mu/b$ and $\gamma \equiv 2k/b$. Up to an additive constant the coarse grained energy density $h$ [from Eqs. (1) and (4)] in units of the height of the double well barrier $[b^2/(4c)]$ reads:

$$h(\phi, \bar{\phi}) = h_0(\phi) + \gamma|\nabla \phi|^2 + m(\phi - \bar{\phi})^2$$

with $h_0(\phi) \equiv (1 - \phi^2)^2$ being the double well in the dimensionless volume $\phi$. The term linear in the OP has been eliminated by redefining the origin of pressure. The parameter $\gamma$ fixes the width of the interface between the low and high volume phases in a mixed state.

We first discuss the $\gamma = 0$ case and generalize for a finite $\gamma$ below. The energy density Eq. (1) couples the values of $\phi$ at different spatial positions only through $\phi$, namely it corresponds effectively to a MF. We stress however, that this is the exact energy of the model.

Mixed phase solutions for a constrained total volume obey the familiar common tangent construction: $\partial h(\phi, \bar{\phi})/\partial \phi|_{\phi = \phi_+} = \partial h(\phi, \bar{\phi})/\partial \phi|_{\phi = \phi_-} = [h(\phi_+, \bar{\phi}) - h(\phi_-, \bar{\phi})]/(\phi_+ - \phi_-)$ where $\phi_\pm = \pm \sqrt{1 - m/2}$ and the $+ (-)$ corresponds to the OP of the expanded (collapsed) phase. The only difference with a conventional phase separation computation is that the construction is $\phi$-dependent because $h$ depends on the global variable $\phi$ [see Fig. 1(a)]. This dependence makes the total energy of the mixture non additive. In Fig. 1(b) we report the resulting average energy density $\bar{h}(\phi)$. For $m > 2$ the mixed solution does not exist and the system remains always uniform. We have checked these results with direct analytical computations assuming specific shapes for the coexisting phases and different boundary conditions. In all cases the maximum shear strain is of the same order as the relative volume mismatch. As long as the volume mismatch is small (a few percent) the shear strain will behave elastically. For large volume mismatch glide of atomic planes may take place and our theory becomes approximate. In any case the transition will be irreversible.

For a pressure controlled experiment the physical pressure is given by $P = p\sqrt{b^2/(16cd)} - a/\sqrt{d}$ with $p$ the dimensionless pressure: $p = -\partial h(\phi)/\partial \phi$ at $T = 0$. In the mixed phase the free energy has negative curvature so the compressibility is negative [Fig. 1(b)]. This thermodynamic state is stable at constant volume with the pinned boundary conditions of Ref. $^{[12]}$. This violation of usual stability criteria is common in non-extensive systems $^{[3]}$.

In Fig. 2 we show the values of $\phi$ and the Gibbs free energy density $g(p) \equiv \bar{h}(\phi(p)) + p\phi(p)$ as a function of $p$.
remains uniform until p phase at low pressure and increasing pm < phase. Consider now a pressure controlled experiment for tion of this solution in Fig. 2(a) corresponds to the mixed solution line intersects the uniform solution. At this point the small volume phase nucleates spontaneously since γ = 0. It is easy to show that the mixed state is mechanically unstable at constant pressure due to the negative compressibility, so the volume collapses and the system jumps to the lower branch of the curve following the vertical line. Decreasing the pressure the process is reverted and the volume suddenly expands at p↑(= −p↓) producing the hysteresis loop indicated in the figure. A conventional first-order phase transition driven by pressure at a very low rate (so that nucleation occurs) would follow a vertical line at p = 0 in the top panel. This is not possible here because the infinite range interaction makes the critical drop radius diverge, and the nucleation energy-barrier to scale as the volume of the system.

In the case m > 4/3 the compressibility of the uniform solution diverges at the spinodal points [full dots in Fig. 2(b) and (d)]. The transition proceeds by a k = 0 instability at p↓ = −p↑ = 8/(3√3), independent of m and with no energy barrier. The lower panels in Fig. 2 show that the transition involves an unavoidable jump in the thermodynamic potential for all m ≠ 0 justifying calling this transition ‘zeroth order’.

Finite temperature theory Using MF theory it is straightforward to obtain the exact partition function for γ = 0, and the exact ̸ − p dependence at different temperatures. In Fig. 3 we show the isotherms in the ̸ − p plane for m = 0.6 for different values of a dimensionless temperature t (units are restored below). The pressure width (Δp) and volume width (Δ̸) of the hysteresis loop is reduced at finite temperatures up to the point where it vanishes, which determines the critical point coordinates (pγc, Tγc(m)). The pressure width as a function of temperature determines a wedge of forbidden nucleation [shown in Fig. 3(b) for different values of m] around the critical pressure pγc.

For m < 4/3 the singularities at p = ±p± of the T = 0 isotherm become rounded at finite temperature [Fig. 3(a)] due to the thermally induced spatial fluctuations of the OP. This implies that the compressibility will show precursor effects for all m > 0, diverging at the transition.

The solution in the case of finite γ and m is given implicitly by ̸ = ̸0(p + m̸) where ̸0(p) is the equation of state of the same model except that m = 0, i.e., the well studied φ4-model which has the universality class of the short-range Ising model. If m > 4/3 the qualitative description of the forbidden nucleation region are completely equivalent to the γ = 0 case. For m < 4/3 a region of normal nucleation and growth appears around the wedge of forbidden nucleation at low temperatures and the divergence of the compressibility gets a cutoff. These effects never reach the critical point. Both for γ = 0 and γ > 0 we find that critical exponents are given exactly by MF. This is also in agreement with the d = 2 theoretical analysis of Ref. [11].

Comparison with experiments A wedge where nucleation does not occur is observed in Ce[1, 2], SmS[3] and related systems. Interestingly it is also observed in a volume-collapse transition in amorphous ice[4]. However without detailed studies it is difficult to be sure that it does not arise from usual hysteresis due to a finite driving rate, as occurring in other first order transitions. Other indicators however, point more strongly to the applicability of our theory.

In agreement with the present theory MF critical exponents have been observed[2]. The connection between MF critical behavior and long-range strains has long been
In contrast with usual first-order phase transitions, where hysteresis is not intrinsic, one can define here a critical exponent for the pressure width of the hysteresis loop: \( \Delta p \propto |t - t_c|^{3/2} \). We are not aware of detailed measures of this critical exponent, however the curvature of the boundaries found in Ref. \[12\] for Gd doped SmS are compatible with this exponent. We hope our work will stimulate further experimental work.

Also in contrast with usual first-order transitions, critical behavior (although classic like) can be easily observed far from the critical point. The divergence of the compressibility discussed above implies that the bulk modulus vanishes at \( p > p_c \) and jumps discontinuously to a finite value for \( p > p^* \). Decreasing pressure the jump and the square root singularity change side and occur at \( p^* \). Similar behavior is found as a function of temperature.

An anomaly measured in YbInCu\(_4\) on cooling resembles our prediction when plotted in an appropriate scale (see inset of Fig. 4 in Ref. \[13\]). This also explains the appearance of precursor effects which have been very puzzling in the mixed valence literature and have led some authors to interpret the transition as second order\[15\].

In mixed valence systems the double well is attributed to the anomalous contribution of \( f\)-electrons to the crystal binding\[16\]. For a realistic description it may be necessary to take the parameters in Eq. (1) to depend on \( T \) and \( v \) (see inset of Fig. 4 in Ref. \[15\]). This also explains the appearance of precursor effects which have been very puzzling in the mixed valence literature and have led some authors to interpret the transition as second order\[15\].

The temperature dependence of \( a \) does not affect the critical temperature, but \( b \) does. Indeed in current explanations of the critical point in \( f\)-electron systems this electronic effect is crucial whereas the shear rigidity does not play a relevant role\[16\]. To check the relevance of the temperature scale set by the shear modulus on determining real values of \( T_c \) we take the opposite point of view, i.e., we neglect the temperature dependence of the coefficients in Eq. (1) and take into account the effect of the shear rigidity alone. Restoring dimensions, the critical temperature is given by: \( k_B T_c = t_c(m) v_b^2 / (4c) \) where \( m \) is the minimum volume in the system allowed to fluctuate independently. For the case \( \gamma = 0 \) this volume should be assimilated to the atomic volume. In the case \( \gamma > 0 \), this volume can be greater depending on the strength of the short distance interactions parametrized by \( \gamma \). In any case we expect it to be of the order of a few atomic volumes. The parameters \( b, c \) and \( m \) can be fixed by fitting the observed pressure and volume with of the hysteresis loop at a given temperature and from the measured value of the shear modulus\[11,12\]. Within the experimental uncertainties this procedure gives the right value of \( T_c \) for Ce (\( \sim 550 K \))\[11,12\] and SmS (\( \sim 750 K \))\[13\] if we assume \( v_0 \sim 2v_f \) where \( v_f \) is the volume associated with one formula unit. Since the relation between \( v_0 \) and \( v_f \) go beyond our model we cannot exclude temperature effects on the coefficients of Eq. (1) contributing to \( T_c \), however the fact that we obtain the right order of magnitude with a \( v_0 \) on the order of \( v_f \) implies that the scale set by the shear modulus can not be neglected in the determination of \( T_c \).

In conclusion we have presented an exactly solvable model of an isostructural volume collapse transition, the solid-state analog of the van der Waals transition. Unlike the fluid counterpart the thermodynamics is very anomalous due to the presence of infinite range interactions. In particular, the transition is intrinsically irreversible with a discontinuity of the thermodynamic potential making of it a laboratory example of a class of phase transitions, namely zero order transitions, first discussed in the context of gravitational systems\[9\].

Despite the simplicity of our model, which assumes an isotropic solid, we believe the present features are quite robust. Indeed our findings are in good agreement with the behavior of real anisotropic systems\[11,12,13,15\]. In these mixed valence systems the unexpected thermodynamics is a consequence of the interplay between strong correlations, determining the double well potential\[16\], and long-range strains. The present approach can be seen as a first step to understand this interplay in more complex non-isostructural transitions like the magnetoresistant manganites\[2\] which also show volume mismatch among different phases and irreversibility\[13\].

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