Volume-change phase transition in solids at valence instability

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Volume changes at the valence phase transition occur as a macroscopic mechanical instability, where only a single mode representing homogeneous expansion becomes unstable without critical phonon enhancement. As a consequence, the Landau theory of phase transitions holds exactly at the critical point in describing the transition phenomenologically. However, there is a new possibility: If crystals are allowed to change their shapes in only one direction, the acoustic mode in that direction can become critical at the transition. We examine macroscopic dynamics near the transition and point out the resemblance between the valence transition and the swelling transition in gels. The frequency-dependent specific heat is also proposed.

Cowley examined general conditions of observing a phase transition in solids in which the volume (or the lattice constant) is the order parameter and there are no critical fluctuations with wavelengths shorter than the crystal dimension. In such cases, an instability is triggered without critical enhancement of acoustic modes when the bulk modulus $K = -V(\partial p/\partial V)_{T}$ tends to zero, $V$ being the volume and $p$ being the pressure. In cubic crystals this condition is written as $K = (C_{11} + 2C_{12})/3 \to 0$ and $C_{12} < 0$. Hereafter, $C_{ij}$ are the usual elastic moduli. Notice that if $C_{12} > 0$, an acoustic mode becomes unstable at $C_{11} - C_{12} \to 0$ before $K$ tends to zero. Examples are given by rare-earth compounds such as solid solutions of Sm$_{1-x}$Y$_x$S or Ce$_{1-x}$Th$_x$ at the valence transition. They undergo isomorphic transitions without any change of symmetry. The transition is usually of first order but can be made of second order by changing the pressure or the alloy composition. On the $p-V$ phase diagram of such materials, $V$ jumps discontinuously at first-order transitions and the isothermal compressibility $K^{-1} = -V^{-1} \times (\partial V/\partial p)_T$ can be nearly infinite near the critical point. Note that, even if $K \equiv 0$, no critical scattering from phonons has been observed.

Here I point out that an analogous phase transition belonging to the same universality class has been studied for over a decade in polymer gels as the volume phase (or swelling) transition by Tanaka's group. There, if gels are immersed in a solvent, they can swell or shrink discontinuously as a first-order phase transition upon a change of an external parameter such as the temperature. Moreover, the discontinuity at the transition can even be diminished to zero by changing the degree of ionization of the network. Then we have continuous phase transition where the bulk modulus $K = -V(\partial \Pi/\partial V)_T$ vanishes, $\Pi$ being the osmotic pressure. We notice a striking resemblance between $V-T$ or $V-p$ curves for solids near the valence transition and those for gels near the swelling transition. At this critical point, however, Tanaka claimed that critical enhancement of the scattered light intensity was observed. Recently, I have shown that the spinodal curve, on which the scattering diverges, is given by $K + \frac{4}{3} \mu = 0$, $\mu$ being the shear modulus. Namely, the spinodal curve is separated from the critical point and is located in an unstable region $K < 0$. The difference of the temperature at which $K = 0$ and the temperature at which $K + \frac{4}{3} \mu = 0$ can be estimated to have been of order 1 K and the experiment was not precise enough to detect it.

The aim of this paper is to examine the phase transition in the case of cubic solids in some detail on the basis of the results for gels. (i) We show that as $K \to 0$ only a single mode representing homogeneous expansion becomes marginal while fluctuations with wavelengths much less than the system size are still suppressed by the finite shear modulus $C_{44}$ for the cubic case. This means that the critical exponents are exactly given by the mean-field values. In Ref. 4, the resistivity anomaly was shown to be described by the mean-field exponents. Although they attributed it to a long-range force, our view is that this should arise from the discrete nature of the transition. (ii) However, interestingly, the specific heat at constant pressure $C_p$ diverges according to the following thermodynamic relation:

$$C_p = C_V + VT \left( \frac{\partial p}{\partial T} \right)_V \sqrt{K}. \quad (1)$$

We assume that the specific heat at constant volume $C_V$ and the thermodynamic derivative $(\partial p/\partial T)_V$ have no singularity at the point $K = 0$. Obviously, the thermal expansion coefficient $\beta_p = V^{-1}(\partial V/\partial T)_p = (\partial p/\partial T)_V K^{-1}$ also diverges like $K^{-1}$. (iii) As in the gel case the phase transition can be drastically altered if the sample is clamped and allowed to change its shape in only one or two directions. Particularly, in the one-dimensional (1D) case, the valence instability can occur at an instability point of the acoustic mode propagating in the stretched (or shrunken) direction, thus accompanied by critical fluctuations. However, the instability point of the 1D case and that of the usual 3D case should be greatly separated due to the large sizes of $|C_{12}|$ and $C_{44}$ in solids in contrast to the gel case where the two points can be very close.

In the cubic-crystal case the stress tensor $\sigma_{ij}$ is related to the spatial derivatives of the displacement vector $u_i$.
\[
\begin{align*}
\sigma_{ii} &= C_{11} \frac{\partial}{\partial x_i} u_i + C_{12} \left( \mathbf{\nabla} \cdot \mathbf{u} - \frac{\partial}{\partial x_i} u_i \right), \\
\sigma_{ij} &= C_{44} \left( \frac{\partial}{\partial x_i} u_j + \frac{\partial}{\partial x_j} u_i \right) \text{ for } i \neq j.
\end{align*}
\]

The elastic free energy is given by
\[
F_{el} = \frac{1}{2} \int_V d\mathbf{r} \sum_{i,j} \left( \frac{\partial u_i}{\partial x_j} \right) \sigma_{ij} = \int_V d\mathbf{r} \left[ \left( C_{11} - C_{12} \right) \sum_i \left( \frac{\partial}{\partial x_i} u_i \right) \right]^2 + \frac{1}{2} C_{12} (\mathbf{\nabla} \cdot \mathbf{u})^2 + \frac{1}{2} C_{44} \left( u^2_{x_1} + u^2_{x_2} + u^2_{x_3} \right),
\]

where \( u_{ij} = \partial u_i / \partial x_j + \partial u_j / \partial x_i \). On the boundary the stress-free condition is required:
\[
\sum_j \sigma_{ij} n_j = (C_{11} - C_{12} - 2 C_{44}) n_i \left( \frac{\partial}{\partial x_i} u_i \right) + C_{12} n_i (\mathbf{\nabla} \cdot \mathbf{u}) \]
\[
+ C_{44} \left( \mathbf{n} \cdot \mathbf{\nabla} u_i + \sum_j n_j \frac{\partial}{\partial x_j} u_j \right) = 0,
\]

when \( n \) is the outward normal to the surface of the system. The equation of motion is of the form
\[
\rho \frac{\partial^2}{\partial t^2} u_i = - \frac{\partial}{\partial u_i} F_{el} = \sum_j \frac{\partial}{\partial x_j} \sigma_{ij},
\]

where \( \rho \) is the mass density and the dissipative effects are neglected. Then we consider the following eigenvalue problem:
\[
\sum_j \frac{\partial}{\partial x_j} \sigma_{ij} = (C_{11} - C_{12} - 2 C_{44}) \frac{\partial^2}{\partial x_i^2} u_i \]
\[
+ (C_{12} + C_{44}) \frac{\partial}{\partial x_i} (\mathbf{\nabla} \cdot \mathbf{u}) + C_{44} \nabla^2 u_i = - \lambda u_i.
\]

Let \( \hat{u}_p \) and \( \lambda_p \) with \( p = 0, 1, 2, \ldots \), be the eigenfunctions and the eigenvalues to (7) under the boundary condition
\[
\hat{u}_p = \chi - \frac{i}{2} (C_{11} + 2 C_{12}) / C_{44} \]
\[
\times \left[ \frac{1}{2} x^2 + \frac{1}{3} (C_{44}/C_{11}) x^3 \right] / R^2 + \cdots.
\]

The ratio of the second term to the first term is of order \( K / C_{44} \) at \( r = R \) and is surely small for \( |K| / C_{44} \ll 1 \). The lowest eigenvalue \( \lambda_0 \) is obtained from (7) in the form
\[
\lambda_0 = 5 (C_{11} + 2 C_{12}) / R^2 + \cdots.
\]

To treat the problem more generally we introduce an Hermitian form for two vectors \( \mathbf{u} \) and \( \mathbf{v} \) by
\[
\langle \mathbf{u}, \mathbf{v} \rangle = \int_V d\mathbf{r} \left[ \left( C_{11} - C_{12} \right) \sum_i \left( \frac{\partial}{\partial x_i} u_i \right) \left( \frac{\partial}{\partial x_i} v_i \right) + C_{12} \sum_i \left( \frac{\partial}{\partial x_i} u_i \right) \sum_j \left( \frac{\partial}{\partial x_j} v_j \right) \right],
\]

where \( \mathbf{u} \) and \( \mathbf{v} \) both satisfy the boundary condition (5). Some manipulations lead to
\[
\langle \mathbf{u}, \mathbf{v} \rangle = - \int_V d\mathbf{r} \sum_i u_i \frac{\partial}{\partial x_i} \sigma_{ii},
\]

where \( \sigma_{ii} \) are related to \( u_i \) by (2) and (3). Then we find
\[
\lambda_0 = \langle \hat{u}_0, \hat{u}_0 \rangle / \int_V d\mathbf{r} |\hat{u}_0|^2 = 3 (C_{11} + C_{12}) / R^2,
\]

where \( R \) is the gyration radius defined by \( VR^2 = \int_V d\mathbf{r} x^2 \), the origin of the reference frame being at the center-of-mass from \( \int_V d\mathbf{r} \hat{u}_0 = 0 \). It follows the relation
\[
\int_V d\mathbf{r} \hat{u}_p = 0 \text{ from (5) and (7)}.
\]

Next we express \( F_{el} \) [see Eq. (4)] by expanding \( u_i \) as (8):
\[
F_{el} = \frac{1}{2} \langle \mathbf{u}, \mathbf{u} \rangle = \frac{1}{2} \sum_p (\lambda_p N_p) A_p^2,
\]

where \( N_p = \int_V d\mathbf{r} |\hat{u}_p|^2 \). Particularly, \( N_0 = VR^2 \) and \( \lambda_0 N_0 = 9KV \). The variables \( A_p \) are independently Gaussian with variance \( k_B T / (\lambda_p N_p) \) near equilibrium. The correlation function of \( u_i \) can be formally expressed as
\[
\langle u_i(r_1) u_j(r_2) \rangle = - k_B T \sum_{p=0} N_p \lambda_p \int_V d\mathbf{r} \hat{u}_p(r_1) \hat{u}_p(r_2)
\]
\[
- (k_B T / 9KV) x_{i1} x_{j2} \text{ as } K \to 0.
\]
On the second line of this equation, only the first mode \( p = 0 \) is retained. As \( K \to 0 \), (16) is consistent with the thermodynamic relation \( \langle |\delta V|^2 \rangle = k_B T V / K \), \( \delta V \) being the total-volume fluctuation. However, to the correlation function of the local-density fluctuation \( \delta \rho (r) \equiv -\rho (V \cdot u) \), the first mode gives rise to a nearly homogeneous contribution inversely proportional to \( V \) \((-k_B T / V K)\). Therefore, it is irrelevant to scattering experiments in which fluctuations with sizes of the order of light (or neutron) wavelengths are detected. On such spatial scales much shorter than the system size, the correlation function should be insensitive to the boundary conditions and hence, it may be calculated by pushing the system size to infinity. Then from (4) we find for the Fourier component \( u_{ik} \):

\[
\langle u_{ik} u_{kj} \rangle = \frac{1}{W_i k^2} \delta_{ij} - \frac{C_{12} + C_{44}}{1 + (C_{12} + C_{44}) G} W_i W_j k^4 \, ,
\]

(17)

where

\[
W_i = C_{44} + (C_{11} - C_{12} - 2 C_{44}) k_i^2 / k^2 \, ,
\]

(18)

\[
G = \frac{2}{k} k_i^2 / (k^2 W_i) \, .
\]

(19)

We expect that the contribution from large \( p \) in (16) should be insensitive to the boundary conditions with its dominant part being the inverse Fourier transform of (17). The correlation function for \( \delta \rho \) with \( \delta \rho \) is of the form

\[
\langle |\delta \rho_k|^2 \rangle = \rho^2 G / [1 + (C_{12} + C_{44}) G] \, .
\]

(20)

The above results can be used only when the wavelength \( 2 \pi / k \) is much shorter than the system size and much longer than any microscopic lengths. We can easily check that the correlation functions (17) and (20) remain finite even for \( K = 0 \) if \( C_{12} < 0 \), implying no critical scattering. However, if we set \( C_{44} = 0 \), we find \( \langle |\delta \rho_k|^2 \rangle = \rho^2 / K \) as in fluids. This means that the finite shear modulus \( C_{44} \) serves to suppress the fluctuations with sizes less than the system size.

Obviously the mean-field theory holds exactly at the critical point of the valence transition. The Landau expansion is allowed for the free energy near the critical point,

\[
F / V = \frac{1}{2} K A_0 + b A_0^2 - h A_0 + \frac{1}{2} (T / c_v) (\rho \delta s - a A_0)^2 \, ,
\]

(21)

where \( A_0 \) is the deviation measured from the critical value and is related to the volume deviation \( \delta V \) by \( A_0 \approx \delta V / 3 V \), \( \delta s \) is the entropy deviation (per unit mass), and \( c_v \) is the specific heat per unit volume at constant volume. The coefficients \( b \) and \( h \) have the usual meaning. Here the system is assumed to be nearly homogeneous and, to be precise, \( \delta s \) should be taken to be the spatial average of the entropy deviation. The coupling constant \( a \) is equal to \( 3 (d \rho / d T) \). Then the deviation of the total entropy, \( \delta S = V \rho \delta s \), obeys a distribution with variance \( k_B T \), where \( C_p \) is given by (1). The temperature variation \( \delta T \) is the thermodynamic force to \( \rho \delta s \) and hence, \( \delta T = (T / c_v) (\rho \delta s - a A_0) \).

(22)

We can now consider the time development of the volume of the system when \( |K| \ll C_{12} \sim C_{44} \). Taking into account the dissipative effect, we assume that the amplitude \( A_0 \) of the first mode \( p = 0 \) obeys

\[
\rho \left( \frac{\partial^2}{\partial t^2} + \gamma_0 \frac{\partial}{\partial t} \right) A_0 = -\frac{1}{N_0} \frac{\partial F}{\partial A_0} = -\frac{1}{R_g^2} [9 K + 4 b A_0^2] A_0 - a \delta T - h \, .
\]

(23)

Here use has been made of (21) and (22) and the volume deviation \( \delta V \) is nearly equal to \( 3 A_0 V \). The decay rate \( \gamma_0 \) will be the following order:

\[
\gamma_0 \sim \xi \rho^{-1} R_g^{-2} \, ,
\]

(24)

where \( \xi \) is the bulk viscosity independent of the system size. To the linear order and under isothermal conditions, by assuming \( A_0 \propto e^{-\alpha t} \), we find

\[
\Omega = \frac{1}{2} \gamma_0 \pm i \lambda_0 (\rho_0 - \frac{1}{2} \gamma_0^2)^{1/2} \, .
\]

(25)

The mode becomes overdamped for \( 0 < \lambda_0 < \frac{1}{2} \gamma_0^2 \) or for \( (K / \rho)^{1/2} R_g < \text{const} (\sim \xi) \). The system is unstable for \( K < 0 \). However, the isothermal condition is satisfied only when the time scale of the heat exchange at the boundary is much faster than \( 1 / \Omega \). In the reverse case \( \Omega \) should be determined under the adiabatic condition \( \delta T = 0 \) before the heat exchange occurs.

It is also worth noting that the frequency-dependent specific heat \( C_p (\omega) \) should be measurable in solids and gels near the transition as in the case of supercooled liquids near the glass transition, because the volume change occurs slowly for \( K = 0 \). Then (1) can be used more generally as the relation between \( C_p (\omega) \) and the frequency-dependent bulk modulus \( K (\omega) \). This can be shown as follows: In response to small changes of the temperature and the volume, \( \delta T \) and \( \delta V \), respectively, under constant pressure, the heat absorbed by the system is given by

\[
\delta Q = T \delta S = C_v \delta T + \left[ \frac{\delta S}{\delta V} \right]_p \delta V \, .
\]

(26)

In our case, the volume change occurs very slowly as

\[
\rho \left( \frac{\partial^2}{\partial t^2} + \gamma_0 \frac{\partial}{\partial t} \right) \delta V = -\lambda_0 \left[ \delta V - \frac{\delta V}{\delta T} \frac{\partial T}{\partial T} \right] \, ,
\]

(27)

which is the linearized version of (23). The thermal diffusion process is assumed to take place quickly. If all time dependences are taken as \( \exp (i \omega t) \), we obtain

\[
C_p (\omega) = \delta Q / \delta T = C_v + \nu T \left[ \frac{\partial^2}{\partial T^2} \right]_p \, ,
\]

(28)
where $K(\omega)$ is the frequency-dependent bulk modulus

$$K(\omega) = K[1 + i\omega \gamma_0 / \lambda_0 - \rho \omega^2 / \lambda_0]$$

$$= K + \frac{1}{15} \rho R_k^2 (i\omega \gamma_0 - \omega^2).$$

Finally, in summary we have examined the macroscopic behavior of solids in which the order parameter is the volume itself. This aspect seems to have not been studied seriously so far, probably because it has appeared rather trivial. However, it would be interesting to induce the valence transition with phonon softening by using clamped solids expandable in only one direction.

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8. T. Tanaka, Physica A 140, 261 (1986), and references quoted therein.
10. A. Onuki, Phys. Rev. A 38, 2192 (1988). Usually $K$ is supposed to be positive in elastic theories. In gels $K$ can be made negative transiently because the time scale of swelling is very slow due to the friction between the network and the solvent. In principle, $K / \mu$ can be negative with no instability in any materials if deformations are allowed in only one or two directions (Ref. 12).
11. In the gel case $(\partial p / \partial T)_{\nu}$ should be replaced by $(\partial \Pi / \partial T)_{\nu}$. I am not aware of measurements of $C_p$ in solids near the critical point of the valence transition, whereas the specific heat at zero osmotic pressure in gels near the critical point is now being measured at the Massachusetts Institute of Technology (T. Tanaka, private communication).