Elastic Singularities at the Peierls Transition

Joseph A. Aronovitz,[a] Paul Goldbart, and George Mozurkewich
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801
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We consider the elastic softening of quasi-one-dimensional materials near the Peierls transition caused by critical fluctuations in the charge-density-wave order parameter. Singularities in the elastic constants and thermal expansion are related to those in the specific heat. Our analysis suggests that a correction to scaling dominates the asymptotic critical behavior over the observed range of temperatures. Experimental data are used to estimate the width of the critical region according to the Ginzburg criterion.

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Young's moduli in quasi-one-dimensional crystals are observed to soften near the Peierls transition temperature T_c by as much as 1.5%,[1] with a temperature dependence which appears to be either a cusp or divergence, rounded very close to T_c. Such singular elastic properties should be expected near the transition to an incommensurate charge-density-wave (CDW) state, since the long-wavelength phonons are coupled to the critically fluctuating CDW degrees of freedom. The associated singularity in the speed of sound has been examined theoretically by Nakane[2] using a microscopic approach. Working in a self-consistent one-loop approximation, Nakane finds that the singular part of the speed of sound varies like $|T-T_c|^{-1/2}$. However, this approximation scheme does not treat the effects of critical fluctuations accurately and, consequently, is inadequate near the critical point. The importance of a full treatment of the critical regime has been made apparent by recent experiments on the blue bronze $K_{0.3}MoO_3$: x-ray scattering data by Girault, Moudden, and Pouget[3] and specific-heat measurements by Kwok and Brown[4] and by Johnston[5] suggest that this material exhibits x-y-like critical behavior within an observable range of temperatures near T_c. These experiments raise the possibility of observing critical effects in the elastic properties, a possibility which motivates us to explore further the elastic properties near the Peierls transition.

In this Letter, we give a renormalization-group treatment of the effect near the Peierls transition of coupling between elastic and CDW degrees of freedom in quasi-one-dimensional crystals. At long wavelengths, we find that the problem is equivalent to that of an elastic ferromagnet, up to irrelevant operators. Such magnetoelastic systems have been studied thoroughly,[6,7] and we borrow from these investigations the result that the elastic degrees of freedom are irrelevant near T_c, allowing us to show that the singular contribution to a typical elastic constant λ takes the form

$$\delta\lambda \equiv \lambda - \lambda_0 \sim \lambda_1 C(\tau)\,, \tag{1}$$

where $\tau \equiv (T-T_c)/T_c$, the factor $C(\tau)$ is the singular contribution to the specific heat, λ_0 is the bare elastic constant, and λ_1 is a known function of the bare phonon-CDW coupling constants, to be given below in Eq. (6). As the specific-heat exponent α satisfies $-1<\alpha<0$, the singularities in $C(\tau)$ are cusps. Crystalline symmetry dictates, through the factor λ_1, that only certain elastic constants acquire these cusps in their temperature dependence. Our analysis also implies that the tensor of thermal-expansion coefficients shows cusps as functions of temperature with the same exponents. This specific-heat-type singularity in elastic constants and thermal expansion, induced by the CDW, has a magnetic counterpart predicted in recent work by Chandra.[8] Estimating the Ginzburg criterion using experimental data, we conclude that the critical region should be observable, in agreement with the experiments of Girault, Moudden, and Pouget, as should be the elastic singularities described here.

We begin by assuming that the critical behavior of the complex CDW order parameter ψ may be adequately modeled, in the absence of elastic deformations, by a coarse-grained free energy

$$F=\int d^dx \left\{ \frac{r}{2}|\psi|^2 + \tfrac{1}{2}[(\nabla_a + ik_a)\psi^*]g_{ab}[(\nabla_b - ik_b)\psi] + \frac{w}{4!}|\psi|^4 \right\}, \tag{2}$$

where $\mathbf{k}$ is the CDW wave vector (whose magnitude is $2k_F$), and the tensor g_{ab} reflects the symmetry properties of the underlying undistorted crystal. We couple the CDW order parameter ψ to the local displacement vector[9] $\mathbf{u}(\mathbf{x})$ by replacing all constant parameters in F by functions of $\mathbf{u}$, and augmenting F by adding the elastic term F^{el}, obtaining the total free energy $F^{\mathrm{tot}} \equiv F + F^{\mathrm{el}}$, where

$$F^{\mathrm{el}} = \tfrac{1}{2}\int d^dx\, \lambda_{abcd} u_{ab} u_{cd}\,. \tag{3}$$

In Eq. (3), $u_{ab} \equiv (\partial_a u_b + \partial_b u_a + \partial_a u_c \partial_b u_c)/2$ is the strain tensor, and λ_{abcd} is the tensor of bare elastic constants. We work in Lagrangian coordinates so that $\mathbf{x}$ always refers to positions in the undistorted system. As the free energy is invariant under translations and rotations, the quantities r, $\mathbf{k}$, w, and g_{ab} can only depend on the displacement field $\mathbf{u}(\mathbf{x})$ through the strain tensor $u_{ab}(\mathbf{x})$ and, thus, can be expanded in the form $r=r^{(0)}+r_{ab}^{(1)}u_{ab}+r_{abcd}^{(2)}u_{ab}u_{cd}+\cdots$.

First, we examine how the coupling of the CDW to elasticity affects the fixed-point structure of the system. After completely expanding the free energy in powers of the displacement field $\mathbf{u}(\mathbf{x})$, power counting shows that the only relevant nonlinear coupling induced by the elastic degrees of freedom has the form $r_{ab}^{(1)}u_{ab}|\psi|^2$. In determining relevance, we are operating within the context of the momentum-space renormalization group and the ϵ expansion. To determine the critical properties of the coupled system it is thus sufficient to consider the relevant free energy

$$F^{\mathrm{rel}}=\int d^dx\left(\frac{r^{(0)}}{2}|\psi|^2+\tfrac{1}{2}\nabla_a\psi^* g_{ab}^{(0)}\nabla_b\psi+\frac{w^{(0)}}{4!}|\psi|^4\right)+\tfrac{1}{2}\int d^dx\,\lambda_{abcd}u_{ab}u_{cd}+\tfrac{1}{2}\int d^dx\,r_{ab}^{(1)}u_{ab}|\psi|^2. \quad (4)$$

In Eq. (4), we have made the gauge transformation $\psi\to\exp(i\mathbf{k}^{(0)}\cdot\mathbf{x})\psi$ to eliminate $\mathbf{k}^{(0)}$ and have replaced the strain tensor by its linearized version, $u_{ab}=(\partial_a u_b+\partial_b u_a)/2$.

We now orient the coordinate axes so as to diagonalize $g_{ab}^{(0)}$, and then suitably rescale the spatial axes and displacement field $\mathbf{u}$ to transform $g_{ab}^{(0)}$ into δ_{ab}. The resulting free energy is identical in form to Eq. (4), except that $g_{ab}^{(0)}$ is replaced by δ_{ab}. It is then equivalent to the free energy of the anisotropic elastic ferromagnet studied by de Moura *et al.*[6] Their work shows that elasticity is irrelevant near the Peierls transition whenever the specific-heat exponent α of the rigid system is negative, as is the case for the three-dimensional x-y model, i.e., Eq. (4) decoupled from the displacement field.[10]

Accordingly, it is permissible to extract the singular parts of the renormalized elastic constants and the thermal-expansion tensor α_{ab} from an effective free energy $F^{\mathrm{eff}}[u_{ab}]$ which is computed using the following prescription: Expand $\exp(-F)$ in powers of the linearized strain tensor u_{ab} to quadratic order; integrate over ψ; and reexponentiate, while keeping all singular terms to leading order in a gradient expansion.[11] By *singular terms* we will henceforth mean terms which produce either cusps or divergences in either elastic constants or thermal-expansion coefficients at T_c. We thus obtain the singular corrections to F^{el} due to the fluctuations in ψ. This procedure leads to the effective free energy

$$F^{\mathrm{eff}}[u_{ab}]=\int d^3x\left[\tfrac{1}{2}(\lambda_{abcd}+\delta\lambda_{abcd})u_{ab}u_{cd}+\sigma_{ab}u_{ab}\right], \quad (5)$$

where

$$\delta\lambda_{abcd}=-r_{ab}^{(1)}r_{cd}^{(1)}C(\tau),\quad \sigma_{ab}=r_{ab}^{(1)}D(\tau),$$

$$C(\tau)=\lim_{k\to 0}\int\frac{d^3k'}{(2\pi)^3}\left\langle\frac{|\hat\psi|_{\mathbf{k}}^2}{2}\frac{|\hat\psi|_{\mathbf{k}'}^2}{2}\right\rangle, \quad (6)$$

$$D(\tau)=\left\langle\frac{|\psi(\mathbf{x})|^2}{2}\right\rangle,$$

$\langle\cdot\rangle$ is an average over ψ in the rigid theory, $C(\tau)$ is the singular part of the specific heat, and $|\hat\psi|_{\mathbf{k}}^2$ is the Fourier transform of $|\psi(\mathbf{x})|^2$. It is sufficient to treat $F^{\mathrm{eff}}[u_{ab}]$ in mean-field theory. Accordingly, we can read off the renormalized elastic constants $\lambda_{abcd}^{\mathrm{eff}}=\lambda_{abcd}+\delta\lambda_{abcd}$, up to nonsingular corrections. The fluctuation-induced stress tensor σ_{ab} generates a nonzero equilibrium value $\langle u_{ab}\rangle$ for the strain tensor. The rate of change with temperature of $\langle u_{ab}\rangle$ determines the singular part of the thermal-expansion tensor $\delta\alpha_{ab}$ through $\delta\alpha_{ab}=d\langle u_{ab}\rangle/dT$, the most singular part of which is given by

$$\delta\alpha_{ab}=\frac{\hat r^{(0)}}{T_c}C(\tau)\tilde\lambda_{abcd}r_{cd}^{(1)}, \quad (7)$$

where $\tilde\lambda_{abcd}$ is the compliance tensor conjugate to λ_{abcd}, $\hat r^{(0)}\equiv r^{(0)}/\tau$, and we have used the fact that up to nonsingular terms, $dD(\tau)/d\tau=-\hat r^{(0)}C(\tau)$. From the renormalization group, it is known that for τ in the critical regime,

$$C(\tau)\sim C_\pm|\tau|^{-\alpha}(1+\tilde C_\pm|\tau|^{\nu\omega})+\text{non-cusp-producing terms}. \quad (8)$$

The theoretical values of $-\alpha$ and $\nu\omega$ are 0.008 ± 0.003 and 0.521 ± 0.005, respectively.[10] The experimental values of these exponents have been measured for the superfluid transition in ^{4}He giving values in agreement with theory.[12] From Eq. (8) we see that for τ asymptotically close to zero, $C\sim|\tau|^{0.01}$, while at currently experimentally accessible values of τ we expect this term to be dominated by the correction to scaling, so that one sees $C\sim|\tau|^{0.53}$.

Equations (6) and (7) are the principal results of this Letter and have several observable consequences. First, the specific heat, elastic constants, and thermal expansion all share the same additive singular temperature dependence, $C(\tau)$, which would be observed to scale as $|\tau|^{0.53}$. Also, the amplitude ratios

$$A=\begin{cases}C_+/C_-, & \text{for } \tau \text{ very small},\\ C_+\tilde C_+/\tilde C_-C_-, & \text{for } \tau \text{ small},\end{cases} \quad (9)$$

can be independently extracted from the temperature dependence near T_c of any given elastic constant (such as $\delta\lambda_{1111}$), any element of the thermal-expansion tensor, or the specific heat itself, which provides a consistency check. In the event that experiment can probe the true asymptotic behavior, $C(\tau)\sim|\tau|^{-\alpha}$, the ratio $A=C_+/$

C_- is universal, with a theoretical value[13] $A \approx 1-4\alpha \approx 1.03 \pm 0.01$.

Second, in ratios of the form $\delta\lambda_{abcd}(\tau)/\delta\lambda_{a'b'c'd'}(\tau)$, the factor $C(\tau)$ cancels, leaving the ratio of unrenormalized microscopic parameters,

$$r_{ab}^{(1)} r_{cd}^{(1)} / r_{a'b'}^{(1)} r_{c'd'}^{(1)} . \tag{10}$$

Similarly, taking the ratio $\delta\alpha_{ab}(\tau)/\delta\alpha_{a'b'}(\tau)$ leaves $\tilde{\lambda}_{abcd} r_{cd}^{(1)} / \tilde{\lambda}_{a'b'c'd'} r_{c'd'}^{(1)}$, with the compliance tensor $\tilde{\lambda}_{abcd}$ readily computable from the background elastic constants λ_{abcd}. Thus, for this CDW system, one can extract quantitative microscopic information from critical properties.

Third, crystalline symmetry introduces constraints. For example, in the orthorhombic coordinate system appropriate to TaS_3, $r_{ab}^{(1)}$ is diagonal and only the longitudinal elastic constants λ_{aaaa} and λ_{aabb} would acquire cusps.[14]

Fourth, for temperatures outside the critical region, the fluctuation corrections to the elastic constants and thermal expansion would be controlled by Gaussian-fluctuation corrections to the specific heat, i.e., $C(\tau) \sim |\tau|^{-1/2}$. This is the regime of applicability of Chandra's analysis[8] of the magnetic susceptibility, in which she predicts that the derivative of the magnetic susceptibility $d\chi/dT$ acquires the singularity associated with the Gaussian specific heat, i.e., $d\chi/dT \sim |\tau|^{-1/2}$.

The critical singularities in elastic constants and thermal-expansion coefficients predicted in Eqs. (6) and (7) represent departures from a mean-field behavior. Their observability depends on the width ΔT of the fluctuation-dominated critical regime. Traditionally, this range is characterized by the Ginzburg criterion,[15]

$$\frac{\Delta T}{T_c} = \frac{k_B^2}{\xi^6 \Delta C^2} , \tag{11}$$

in which ξ is the correlation length of the fluctuations at temperatures well above T_c, and ΔC is the mean-field specific-heat jump. This form of the Ginzburg criterion gives reasonable results for the superfluid transition in ^{4}He. Furthermore, it is built exclusively from experimentally accessible quantities. Ginzburg-Landau theories can be derived from microscopic models in certain cases such as the BCS superconductor[16] and the single-chain CDW.[17] Then the Ginzburg criteria can be reexpressed in terms of microscopic parameters in the form $\Delta T/T_c \sim (T_c/E_F)^4$, where E_F is the Fermi energy. However, for the real three-dimensional CDW transition, this specialized form cannot be appropriate because the single-chain Ginzburg-Landau theory does not correctly account for interchain coupling.

We now apply Eq. (11) to $K_{0.3}MoO_3$. From Girault, Moudden, and Pouget,[3] the correlation volume at 300 K, constructed from correlation lengths in three perpendicular directions, is $\xi^3 = 480$ Å^3. ΔC for $K_{0.3}MoO_3$ is uncertain because it must be estimated from data which are influenced by fluctuations, and because measurements by several groups vary substantially. Kwok and Brown[4] found 3.6 J mol^{-1}K^{-1}, Konate[18] quotes 2 J mol^{-1}K^{-1}, and from Johnston[5] we estimate 1.3 J mol^{-1}K^{-1}. These values give widths ΔT of 15, 20, and 120 K, respectively. In light of the approximate nature of Eq. (11) these numbers should not be taken too seriously; however, they suggest that the critical regime should be observable near a Peierls transition and, with it, the elastic singularities predicted above.

Recent experiments[19] measuring Young's modulus of TaS_3 seem to be consistent with our prediction of a cusp with power-law $|\tau|^{0.53}$ over a temperature range with half-width $\Delta T \sim 10$ K.

In summary, we have analyzed the critical behavior near the Peierls transition in quasi-one-dimensional materials within the framework of the renormalization group and find that the elastic constants and thermal-expansion coefficients have the same critical behavior as the specific heat. The asymptotic critical behavior is dominated over a particularly narrow range of temperatures because the specific-heat exponent is close to zero. On the other hand, experimental data suggest that the critical region is rather wide. Therefore, we expect that the observable singular behavior will be dominated by corrections to scaling. Finally, the results presented here may also be applicable to elastic anomalies near the transition to the conventional superconducting state,[20] should the critical regime be observable.

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[a]Current address: MIT Lincoln Laboratory, 244 Wood Street, Lexington, MA 02173.

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