Suppression of the Order Parameter Correlation Length by Inhomogeneous Strains

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Very recently we presented puzzling results of diffuse neutron scattering experiments on KSCN and RbSCN. The data yield an increase of the diffuse intensity with increasing temperature below T_c, whereas the width remains constant. Using molecular dynamics and 3D Monte Carlo simulations, we have shown that below T_c the width of the correlation functions can be stabilized by strain fields originating from the order parameter strain interactions. Here we construct a novel analytic model which predicts the existence of a second characteristic length scale and explains the suppression of the growth of precursor clusters by the influence of inhomogeneous strain fields.

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A qualitative and quantitative understanding of the role of inhomogeneous strains in phase transitions is of vital interest for the physics of minerals [1,2], alloys [3], molecular crystals [4], high-T_c superconductors [5], as well as the analysis of structural phase transitions in general. Strain effects influence the behavior of materials in an essential way, both on a macroscopic scale, i.e., the thermodynamic behavior [6] as well as the mesoscopic structure, i.e., domains and domain walls, phase boundaries, or nucleation near a phase transition. Especially, there is a long tradition of studying the effects of elastic interactions, e.g., on the morphology and growth of precipitates [7] in phase separating alloys. In a simple but quite useful Landau-Ginzburg approach solids are often treated as elastic *continua*. On the other hand, it is well known that for understanding phenomena like the formation of small precipitates in alloys, e.g., Guinier-Preston zones, discreteness effects are essential and dispersion of the elastic energy must be taken into account [8]. Unfortunately, even if the elastic energy is calculated exactly for 3D lattices of simple structure, the resulting discrete models are as a rule analytically intractable and one has to resort to computer simulations [7].

The present work is based on a simple, general, transparent and ready-to-use *analytic* approach without reference to a particular lattice symmetry, which is suitable for both qualitative and quantitative discussions. This model was constructed following a detailed analysis of transitional precursor effects in KSCN and RbSCN found in diffuse neutron scattering [9–11], accompanied by both molecular dynamics [11] and 3D Monte Carlo [12] simulations. Both crystals exhibit order-disorder phase transitions with reorientations of SCN molecules at $T_c = 415$ K (KSCN) and 440 K (RbSCN) from a tetragonal to an orthorhombic structure. For both substances the temperature dependence of the superstructure Bragg peak $I_B(\mathbf{q}_c) \propto \eta^2$ can be well fitted by a compressible pseudospin model [13] over a large temperature region below T_c, exhibiting a strong coupling between the order parameter (η) and the strains (ϵ), which, due to symmetry, is of the type $\eta^2\epsilon$.

However, the interpretation of the diffuse scattering below T_c is by no means straightforward. The diffuse neutron scattering measurements were done in the vicinity of the critical wave vector $\mathbf{q}_c = (2\pi/a, 0, 0)$ and equivalent points, i.e., for $\mathbf{Q}_1 = (2\pi/a + q_x, 0, 0)$, $\mathbf{Q}_2 = (2\pi/a, q_y, 0)$, and $\mathbf{Q}_3 = (2\pi/a, 0, q_z)$, where a is the lattice constant. In both phases we have found diffuse scattering intensities $I_d(\mathbf{Q}_i)$ centered around these points which increase when approaching T_c. Above T_c the inverse widths of the peaks also increase, but *below T_c the width of the diffuse scattering remains constant* (Fig. 1). This behavior, which is confirmed by the molecular-dynamics simulations (Fig. 2), is in sharp contrast to what is expected from a standard Landau theory description. For $i = 1, 3$ it suffices [14] to compute $k_B T \chi_{11}(\mathbf{q}) = \langle \eta_{1\mathbf{q}} \eta_{1-\mathbf{q}} \rangle \propto I_d(\mathbf{Q}_i)$. In doing so, the Landau free energy is usually altered by order parameter gradient terms to account for spatial fluctuations, yielding a Lorentzian shape of $\chi_{11}(\mathbf{q})$. However, from such a standard theory one obtains the result [15] that *the* $(\mathbf{q} = \mathbf{0})$ *component of the diffuse intensity*

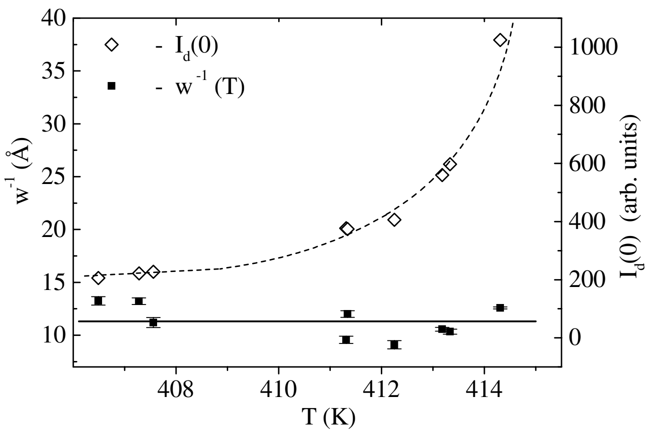

FIG. 1. Measured T dependence of $I_d(\mathbf{0})$ and $w^{-1}(T)$ below T_c.

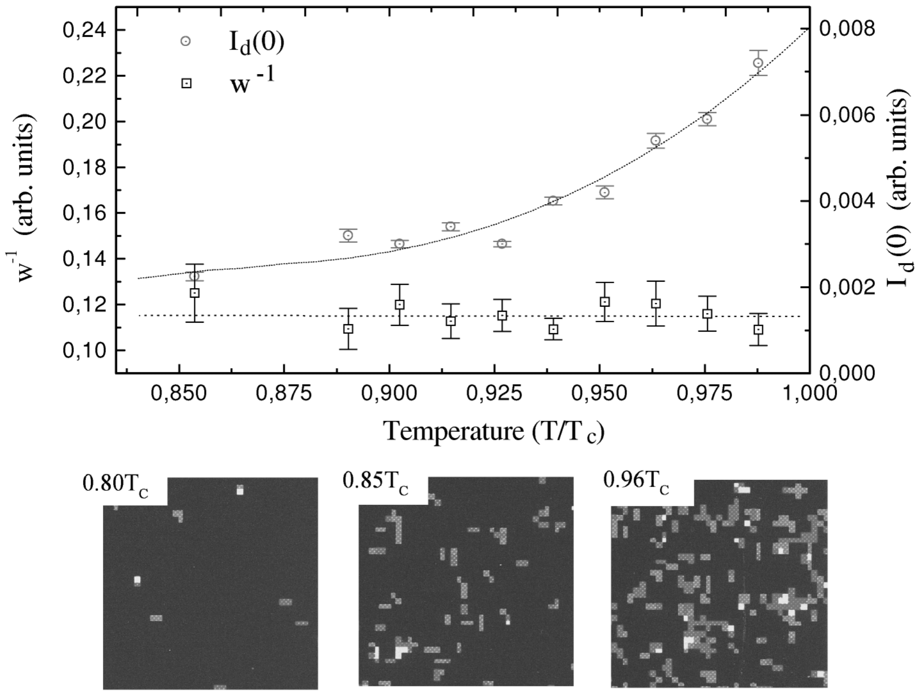

FIG. 2. Molecular-dynamics simulation of $I_d(\mathbf{0})$ and $w^{-1}(T)$ below T_c. Fluctuations into the four different domain states are indicated by different gray scales.

should follow the same temperature dependence as the square of the order parameter correlation length. Below T_c, this clearly contradicts the results of both experiment and computer simulations. This puzzling discrepancy, an immediate consequence of the Lorentzian type of correlation function calculated in $\mathbf{q}$ space, represents a long-standing problem [9]. The precursor clusters seem to be prevented from growing in size in the ordered phase, whereas their number increases when approaching T_c from below. In contrast, note that both the size and the number of the clusters do increase approaching T_c from above. In this Letter we show that the elastic energy stored in the cluster formation is responsible for the effects described above. This is already indicated by our observations in models using molecular dynamics [11] and Monte Carlo simulations [12]. However, from these simulations it is difficult to disentangle the various contributions of the order parameter strain interactions, and the actual mechanism of how the elastic interactions really stabilize the average cluster size is far from being transparent.

To explain the deviation from the standard behavior $\chi_{11}(T)/\xi^2(T) = \text{const}$, significant additional gradient-type terms must play a prominent role, leading to a more complicated T-dependent wave-vector contribution to the susceptibility. In fact, as was pointed out in [16], for example, the quadratic-linear strain coupling does lead to an additional $\mathbf{q}$ dependence of $\chi_{11}(\mathbf{q})$—however, this contribution depends only on the *direction* of $\mathbf{q}$, whereas here a nontrivial $|\mathbf{q}|$ dependence is observed. Comparing the order of magnitude of $w^{-1}(T)$ experimentally obtained in Ref. [9] to the KSCN lattice constants, one realizes that the discrete nature of the system should play a noticeable role in the problem.

To account for the discreteness of the solid, the first correction to a continuous strain field is the inclusion of an additional strain gradient term in the free energy. We are therefore led to study models of the following general type: Let $\eta(\mathbf{x}) := [\eta_1(\mathbf{x}), \ldots, \eta_d(\mathbf{x})]$ denote a d-component order parameter field, $\epsilon_{ij}(\mathbf{x}) = \frac{1}{2}(\frac{\partial u_i}{\partial x_j} + \frac{\partial uj}{\partial x_i})(\mathbf{x})$ the strain tensor field resulting from a displacement vector field $\mathbf{u}(\mathbf{x})$. We consider the Landau-Ginzburg-type density

$$\mathcal{H}[\eta, \epsilon] := \frac{1}{\Omega} \int_x \bigg(\frac{1}{2}\,\kappa(\eta)\,(x) + \Phi[\eta(\mathbf{x}), \epsilon(\mathbf{x})] + \frac{1}{2} \sum_{\alpha\beta mn} \gamma_{\alpha\beta mn} \times \nabla_m \epsilon_\alpha(\mathbf{x}) \nabla_m \epsilon_\beta(\mathbf{x}) \bigg), \qquad (1)$$

where $\frac{1}{2}\kappa(\eta)(\mathbf{x}) = \frac{1}{2}\sum_{\mu,\nu=1}^{d} \sum_{i,j=1}^{3} \kappa_{\mu\nu}^{ij} \partial_i \eta_\mu(\mathbf{x}) \times \partial_j \eta_\nu(\mathbf{x})$ and Ω is the system volume. Decomposing $\eta_\mu(\mathbf{x}) = \overline{\eta}_\mu + \sum_{\mathbf{q}} \delta\eta_{\mu\mathbf{q}} e^{i\mathbf{x}\mathbf{q}}$ and $\epsilon_\alpha(\mathbf{x}) = \overline{\epsilon}_\alpha + \sum_{\mathbf{q}} \times \delta\tilde{\epsilon}_\alpha(\mathbf{q}) e^{i\mathbf{q}\mathbf{x}}$ into mean field and fluctuating degrees of freedom, making use of the mean-field equilibrium conditions $\partial\Phi/\partial\eta_\mu|_{(\overline{\eta},\overline{\epsilon})} = \partial\Phi/\partial\epsilon_\alpha|_{(\overline{\eta},\overline{\epsilon})} = 0$ and suppressing anharmonic higher order terms, we obtain an expansion of $\mathcal{H}(\eta, \epsilon)$ into homogeneous and harmonic parts with respect to the Fourier modes of $\eta(\mathbf{x})$ and $\epsilon_{ij}(\mathbf{x})$. For $\mathbf{q} \neq \mathbf{0}$, however, the inhomogeneous strain contributions $\tilde{\epsilon}_\alpha(\mathbf{q})$ are not proper degrees of freedom of the system [17]. Instead, the modes $\tilde{\epsilon}_\alpha(\mathbf{q} \neq \mathbf{0})$ must be further decomposed in terms of the displacement Fourier modes according to $\delta\tilde{\epsilon}_{ij}(\mathbf{q}\neq\mathbf{0}) = -\frac{i}{2}[q_i\tilde{u}_j(\mathbf{q}) + q_j\tilde{u}_i(\mathbf{q})]$. Introducing the formal vectors $\phi := [\eta_{1\mathbf{0}},\ldots,\eta_{d\mathbf{0}},\tilde{\epsilon}_1(\mathbf{0}),\ldots,\tilde{\epsilon}_6(\mathbf{0})]$ and $\psi(\mathbf{q}) := [\eta_{1\mathbf{q}},\ldots,\eta_{d\mathbf{q}},\tilde{u}_1(\mathbf{q}),\tilde{u}_2(\mathbf{q}),\tilde{u}_3(\mathbf{q})]$, the abbreviation $\kappa_{\mu\nu}(\mathbf{q}) := \sum_{i,j}\kappa_{\mu\nu}^{ij}q_iq_j$ and the Voigt symbol $v(i\,|\,j) := 2-\delta_{ij}$, the resulting decomposition is

$$\mathcal{H}[\eta,\epsilon] = \Phi(\overline{\eta},\overline{\epsilon}) + \frac{1}{2}\sum_{i,j=1}^{d+6}N_{ij}(\overline{\eta},\overline{\epsilon})\phi_i\phi_j + \frac{1}{2}\sum_{i,j=1}^{d+3}M_{ij}(\mathbf{q};\overline{\eta},\overline{\epsilon})\psi_i(\mathbf{q})\psi_j(-\mathbf{q}) + \cdots. \quad (2)$$

The matrix $\mathbf{M}(\mathbf{q};\overline{\eta},\overline{\epsilon}) = [M_{ik}(\mathbf{q};\overline{\eta},\overline{\epsilon})]_{i,k=0}^{d+3}$ with submatrix $\widehat{\mathbf{M}}(\mathbf{q};\overline{\eta},\overline{\epsilon}) = [M_{d+i,d+k}(\mathbf{q};\overline{\eta},\overline{\epsilon})]_{i,k=1}^{3}$ is defined as [18]

$$M_{\mu\nu}(\mathbf{q};\overline{\eta},\overline{\epsilon}) = \kappa_{\mu\nu}(\mathbf{q}) + \frac{\partial^2\Phi}{\partial\eta_\mu\partial\eta_\nu}\bigg|_{(\overline{\eta},\overline{\epsilon})}, \quad \mu,\nu = 1,\ldots,d. \quad (3)$$

$$\widehat{M}_{ik}(\mathbf{q};\overline{\eta},\overline{\epsilon}) = \sum_{jl}\left(\sum_{mn}\gamma_{ijklmn}q_mq_n + \frac{\partial^2\Phi}{\partial\epsilon_{ij}\partial\epsilon_{kl}}\bigg|_{(\overline{\eta},\overline{\epsilon})}\right) \times \frac{q_jq_l}{v(i\,|\,j)v(k\,|\,l)}, \quad (4)$$

$$M_{d+i,\nu}(\mathbf{q};\overline{\eta},\overline{\epsilon}) = \sum_{l=1}^{3}\frac{1}{v(i\,|\,l)}\frac{\partial^2\Phi}{\partial\eta_\nu\partial\epsilon_{il}}\bigg|_{(\overline{\eta},\overline{\epsilon})} iq_l, \quad (5)$$

$$M_{\mu,d+k}(\mathbf{q};\overline{\eta},\overline{\epsilon}) = \sum_{j=1}^{3}\frac{1}{v(k\,|\,j)}\frac{\partial^2\Phi}{\partial\eta_\mu\partial\epsilon_{jk}}\bigg|_{(\overline{\eta},\overline{\epsilon})}(-iq_j). \quad (6)$$

$\widehat{\mathbf{M}}(\mathbf{q};\overline{\eta},\overline{\epsilon})$ can be regarded as a *generalized dynamical phonon matrix.* From these completely general equations it is straightforward to deduce the order parameter susceptibilities within mean-field approximation as $\chi_{\mu\nu}(\mathbf{q}\neq\mathbf{0}) = \langle\eta_{\mu\mathbf{q}}\eta_{\nu-\mathbf{q}}\rangle/(k_BT) = M_{\mu\nu}^{-1}(\mathbf{q};\overline{\eta},\overline{\epsilon})$. For instance, in case of a scalar order parameter η (i.e., $d=1$) this yields

$$\chi^{-1}(\mathbf{q}\neq\mathbf{0}) = \kappa(\mathbf{q}) + \frac{\partial^2\Phi}{\partial\eta^2}\bigg|_{(\overline{\eta},\overline{\epsilon})} - \sum_{ijkl}\frac{q_jq_l}{v(i\,|\,l)v(k\,|\,j)} \times \frac{\partial^2\Phi}{\partial\eta\partial\epsilon_{il}}\bigg|_{(\overline{\eta},\overline{\epsilon})} \times \widehat{M}_{ik}^{-1}(\mathbf{q};\overline{\eta},\overline{\epsilon})\frac{\partial^2\Phi}{\partial\eta\partial\epsilon_{jk}}\bigg|_{(\overline{\eta},\overline{\epsilon})}. \quad (7)$$

Let us study the consequences of this result for the simplest yet analytically tractable model that still contains all the basic features. Consider an isotropic cubic ($C_{1111} - C_{1122} = 2C_{1212}$) system where $\kappa(\mathbf{q}) = D\mathbf{q}^2$, $\gamma_{ijklmn} = g\delta_{ik}\delta_{jl}\delta_{mn}v(i\,|\,j)v(k\,|\,l)$, yielding a strain gradient density of $g\sum_{ijm}[v(i\,|\,j)\nabla_m\epsilon_{ij}(\mathbf{x})]^2$, and $\Phi(\eta,\epsilon) = V(\eta) + b\eta^2\sum_{i=1}^{3}\epsilon_i + \frac{1}{2}\sum_{i,j=1}^{6}C_{ij}\epsilon_i\epsilon_j$, assuming $D,g,b>0$. Then [19]

$$\chi^{-1}(\mathbf{q}) = D\mathbf{q}^2 + V''(\overline{\eta}) - \frac{6b^2\overline{\eta}^2}{C_{1111}+2C_{1122}} - \frac{4b^2\overline{\eta}^2}{g\mathbf{q}^2 + C_{1111}}. \quad (8)$$

Obviously, below T_c this function is non-Lorentzian. Therefore one must not confuse its inverse half-width $w^{-1}(T)$ with the order parameter correlation length $\xi(T)$. Instead, $\chi(\mathbf{q})$ can actually be split into a sum of two Lorentzians below T_c. Using the abbreviations $e := 4b^2\overline{\eta}^2, v = V''(\overline{\eta}) - 6b^2\eta^2/(C_{1111}+2C_{1122})$, $c := C_{1111}$, we have $\chi(\mathbf{q}) = \lambda_+(\mathbf{q}) + \lambda_-(\mathbf{q}) = \frac{x_+}{\alpha+q^2+1} + \frac{x_-}{a-q^2+1}$, where

$$x_\pm := \frac{1}{2(v-e/c)}\left[1 \mp \frac{gv - cD - 2ge/c}{\sqrt{(gv-cD)^2 + 4egD}}\right], \quad (9)$$

$$\alpha_\pm := \frac{1}{2(cv-e)}\left[gv + cD \pm \sqrt{(gv-cD)^2 + 4egD}\right]. \quad (10)$$

This defines two characteristic length scales $\xi_\pm(T) = \sqrt{a_\pm}$ for the model. We have $\lambda_+(\mathbf{0}) > \lambda_-(\mathbf{0})$ as long as $g(v-2e/c) < cD$. For $g\to 0$, $\lambda_+(\mathbf{q}) \to \frac{1}{Dq^2+v-e/c}$ and, consistent with this, $\xi_+(T)$ reduces to the usual Lorentzian correlation length $\sqrt{D/(v-e/c)}$, while $\xi_-\to 0$ together with $\lambda_-(\mathbf{q})\to 0$. Certainly $\xi_+(T) > \xi_-(T)$ for all stable systems. But this implies [20] that $\xi_+(T) \equiv \xi(T)$ is to be identified with the true order parameter correlation length.

To study the qualitative consequences of the above analysis, we reconsider our previous example for $V(\eta) := \frac{A_0}{2}(T-T_0) + \frac{B}{4}\eta^4$, where A_0, $B - 6b^2/(C_{1111} + 2C_{1122}) > 0$. The resulting mean-field model predicts a continuous phase transition at $T_c = T_0$. For $T \nearrow T_c$

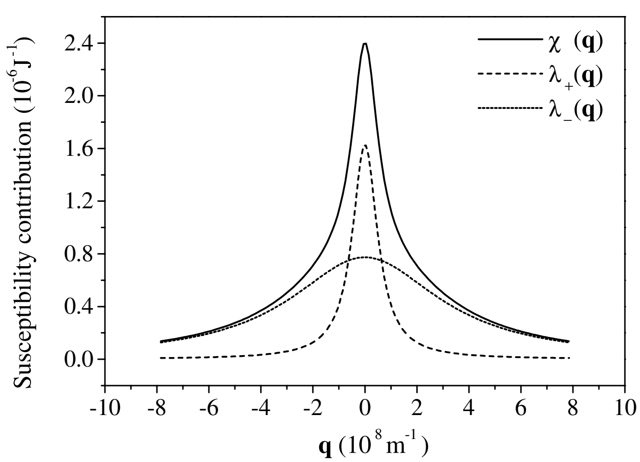

FIG. 3. Example: Decomposition of susceptibility according to $\chi(\mathbf{0}) = \lambda_+(\mathbf{0}) + \lambda_-(\mathbf{0})$ at $T = 412$ K. Parameters as in Fig. 4.

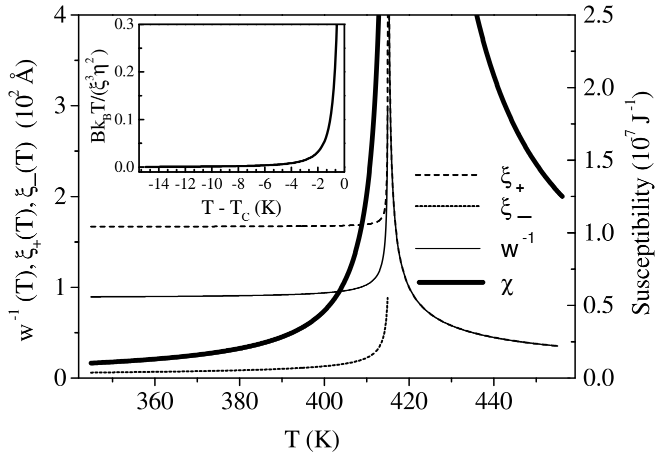

FIG. 4. Results according to Eqs. (8)–(10) using the model parameters $A_0 = 2 \times 10^4\,\mathrm{J\,K^{-1}}$, $T_0 = 415$ K, $B = 3.125 \times 10^6$ J, $C_{1111} = 10^{10}$ J, $C_{1122} = 5.7 \times 10^9$ J, $b = 10^8$ J, $D = 10^{-11}\,\mathrm{m^2\,J}$, and $g = 10^{-6}\,\mathrm{m^2\,J}$. Inset: Plot of the corresponding Levanyuk-Ginzburg criterion $Bk_BT/[\xi^3(T)\eta^2(T)] \ll 1$.

we have $\lambda_+(\mathbf{q}) \to \frac{1}{Dq^2}$, while $\lambda_-(\mathbf{q}) \to 0$, reaching its maximum below but close to T_c. λ_- and ξ_- can thus be regarded as describing a process which has its origin in the presence of strain gradient energy and, depending on the value of parameters, can be significant well below T_c but becomes insignificant for $T \to T_c$ only after passing through a maximum value. It seems tempting to interpret this process as the formation of strain from the surface of η-precursor clusters, since the surface influence may be significant for small cluster size $\xi_+(T)$ while becoming negligible for $\xi_+ \to \infty$. In essence, these additional strain contributions accompanying order parameter fluctuations may lead to a significant rise of the diffuse background to be identified with λ_-. Also, for certain parameter values we observe *simultaneous stabilization of both correlation length* $\xi_+(T)$ *and width* $w^{-1}(T)$ *up to temperatures quite close to* T_c. Moreover, notice that while the experimental determination of $w^{-1}(T)$ from measurement of $\chi(\mathbf{q})$ is certainly not strongly affected by a particular choice of fitting function, below T_c the actual order of magnitude $\xi_+(T)$ of the average cluster size as calculated from a susceptibility of type (7) may be much larger than $w^{-1}(T)$.

We illustrate our main results in Figs. 3 and 4, ensuring the self-consistency of our mean-field approximation below T_c outside a narrow critical region by a plot of the Levanyuk-Ginzburg criterion $Bk_BT/[\xi^3(T)\eta^2(T)] \ll 1$. While the effects discussed can in fact be reproduced using a large variety of parameters, we used a sample of parameters representative [13] of KSCN in order of magnitude. The qualitative agreement with scattering data obtained both experimentally and from computer simulations is excellent. As to the detailed quantitative interpretation of experimental results, analysis of the full anisotropic model constructed above is in progress.

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[14] Indeed, consider the eigenvector of the dynamical phonon matrix that corresponds to the critical pattern of displacements in the unit cell. Inspecting its contribution to the neutron scattering structure factor, one realizes that $\mathbf{Q}_1$ and $\mathbf{Q}_3$ probe purely antiphase fluctuations, whereas for $\mathbf{Q}_2$ scans both antiphase and orientational fluctuations contribute to the diffuse scattering.

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[18] The matrix $\mathbf{N}(\overline{\eta}, \overline{\epsilon})$, which determines the $(\mathbf{q} = \mathbf{0})$ part of $\tilde{G}_{ij}(\mathbf{q})$ is not explicitly listed since it is not of interest here. In fact it is well known that correlation functions turn out to be discontinuous at $\mathbf{q} = \mathbf{0}$ in systems with elastic couplings due to the influence of inhomogeneous shear strains. [*Proceedings of the Conference on Light Scattering Near Phase Transitions,* edited by H. Z. Cummins and A. P. Levanyuk (North-Holland, Amsterdam, 1983)]. See also Ref. [16].

[19] We set $\chi(\mathbf{0}) := \lim_{q \to 0} \chi(\mathbf{q})$ in view of Ref. [18].

[20] Recall that ξ is defined asymptotically by $\langle \eta(\mathbf{x})\eta(\mathbf{0})\rangle \sim \mathrm{const}|\mathbf{x}|^{-1} \exp(-|\mathbf{x}|/\xi)$ for $|\mathbf{x}| \to \infty$.