Compressible spin models for plastic crystals

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We study a compressible spin model with two different species of spin variables on each lattice site. The integration of elastic degrees of freedom produces mixed biquadratic couplings in addition to the usual single-species tetralinear terms. We consider three different ways of accounting for the lattice vibrations and discuss the occurrence of first-order transitions. The results are analyzed in the context of plastic crystals.

Plastic crystals are characterized by the interplay of rotational and translational degrees of freedom.[1] Lowering the temperature from the liquid phase, these compounds undergo a first-order phase transition to an intermediate, thermodynamically stable, plastic phase, where rotational disorder coexists with a translationally ordered state. At lower temperatures there is another phase transition, usually of first order, to the solid phase. Much effort has been devoted to the study of both the plastic phase and the solid-plastic transition.[2] Due to steric hindrances, the coupling between translational and rotational degrees of freedom is expected to play a fundamental role in the onset of these transitions. Earlier works, which were restricted to the description of the solid-plastic transition.[3,4] included only rotational degrees of freedom explicitly. Lattice vibrations were used to account for the translational degrees of freedom, and a bilinear coupling was assumed between rotations and vibrations. In more recent works, some spin models have been proposed to describe the global phase diagram by explicitly including both rotational and translational degrees of freedom.[5,6] Bilinear translational-rotational couplings were considered together with random fields coupled to rotations.[5] More recently, tetralinear translational-rotational couplings were also assumed without random fields.[6] However, rigid lattices were used in both cases.

According to the previuos investigations, the theoretical phase diagram of plastic crystals is strongly dependent on the *ad hoc* form of the couplings between the various kinds of degrees of freedom involved in this problem. A more physical approach should consist indeed in the derivation of these couplings from a model that accounts for the three separate ingredients of the problem, that is, translational, rotational, and elastic degrees of freedom, without *a priori* assumptions about the form of mixed couplings. Steric hindrances being expected to be instrumental in the interplay of rotations and translations, and elastic degrees of freedom being not critical, it is natural to tackle the problem of translation-rotation couplings by considering compressible systems.

The critical behavior of compressible Ising models has been the subject of many investigations.[7–15] First, it is interesting to consider two very schematic models: (i) The elastic mean-field, or Domb, model, in which the elastic fluctuations are taken into account as an average, and shear forces are overemphasized;[7,9] (ii) The shearless model, where only compression forces are taken into account, and which lends itself to an exact solution.[8,15] In the pressure ensemble, Domb's model leads to an effective spin Hamiltonian with long-range four-spin interactions which turn the transition first order. The effective Hamiltonian of the shearless model, however, in a suitable field ensemble yields a standard second-order transition with renormalized critical exponents. In a seminal paper, Larkin and Pikin[10] considered a more realistic continuum compressible model, embedded in an elastically isotropic medium. In the pressure ensemble, the effective spin Hamiltonian includes again long-range four-spin interactions, as in Domb's model, which turn the transition first order except in the limit of no shear forces. This work has been later extended, and considered in the framework of the renormalization group, by Sak,[11] Bergman and Halperin,[12] and several other authors.[13,14]

In the present paper we extend earlier works on compressible spin systems by considering two specie of spins on each lattice site of the same elastic medium. Once elastic vibrations are integrated out there appear new mixed biquadratic couplings between the two species of spin, in addition to the usual tetralinear terms. Various models of including the effects of elasticity lead to different effective Hamiltonians. The elastic mean-field version of a system of two compressible Ising models gives rise to two first-order transitions. In the pressure ensemble, besides long-range four-spin interactions among the same set of spin variables, there exist also mixed long-range couplings between spin variables of different types. We then consider a system of two compressible models without shear forces. In the pressure ensemble, there exist only short-range mixed biquadratic couplings, as in the spin model of Ref. 6. The transitions may be either continuous or first order, with a tricritical point. Finally, we also consider a more realistic model, including isotropic compression and shear forces, which generate both short and long-range tetralinear couplings. The results are discussed with respect to the form of translation-rotation couplings in plastic crystals.

Let us first consider a compressible spin model with two spin species per site and nearest-neighbor interactions, given by Hamiltonian

$$\mathcal{H} = -J_R(v)\sum_{(ij)} \sigma_i\sigma_j - J_T(v)\sum_{(ij)} t_i t_j + N\phi(v) , \tag{1}$$

where the coupling coefficients, J_R and J_T, and the elastic potential, ϕ, are functions of the average volume per particle v. A set of general spin variables, σ_i, for all sites $i=1,2,\ldots,N$, has been introduced to represent the rotational degrees of freedom, and an extra set, t_i, has been used to mimic the melting transition. In this first case, the effect of elastic vibrations is taken into account in a global, or mean field, way. Local elastic fluctuations are totally ignored. From the canonical partition function,

$$Z(T,v,N) = Z_R[\beta J_R(v)] Z_T[\beta J_T(v)] \exp[-\beta N_\phi(v)] , \tag{2}$$

where $\beta=(k_B T)^{-1}$, we calculate expressions for the Helmholtz free energy, the pressure and the compressibility. It can be shown that, if the rigid models display diverging specific heats at criticality, there is a mechanical instability which turns the transition into first order.[7,9] Writing the partition function in the pressure ensemble,

$$Y(T,p,N) = \int_0^\infty dv\, e^{-\beta N p v} Z(T,v,N) = \mathrm{Tr}\, e^{-\beta \mathcal{H}_{\mathrm{eff}}} , \tag{3}$$

where the trace is a sum over all spin variables, we obtain an effective spin Hamiltonian, $\mathcal{H}_{\mathrm{eff}}$, in terms of the field variables T and p. For simplicity, let us assume the linear forms

$$J_R(v) = J_{R0} - J_{R1}(v - v_0) , \tag{4a}$$

and

$$J_T(v) = J_{T0} - J_{T1}(v - v_0) , \tag{4b}$$

for the exchange terms, and the quadratic form,

$$\phi(v) = \phi_0 + \tfrac{1}{2}\phi_2 (v - v_0)^2 , \tag{5}$$

for the elastic potential. Discarding a smooth function of p, the effective Hamiltonian is given by

$$\mathcal{H}_{\mathrm{eff}} = -\tilde{J}_R(p)\sum_{(ij)} \sigma_i\sigma_j - \tilde{J}_T(p)\sum_{(ij)} t_i t_j - \frac{1}{2\phi_2 N}\left[J_{R1}\sum_{(ij)}\sigma_i\sigma_j + J_{T1}\sum_{(ij)} t_i t_j\right]^2 , \tag{6}$$

where

$$\tilde{J}_R(p) = J_{R0} + \frac{pJ_{R1}}{\phi_2} \tag{7a}$$

and

$$\tilde{J}_T(p) = J_{T0} + \frac{pJ_{T1}}{\phi_2} . \tag{7b}$$

As in the model of Ref. 6, the effective Hamiltonian of Eq. (6) includes mixed biquadratic coupling terms. In the present work, however, instead of displaying a short-range character, these couplings are long ranged. Moreover, the first-order nature of the transitions is associated with the long-range character of the couplings,[15] without depending on the assumption of more complex degrees of freedom.[6]

To go beyond the elastic mean-field approach, we have to include the effects of the local microscopic fluctuations. The Hamiltonian should then be written in the form

$$\mathcal{H} = -\sum_{(ij)} J_R(\mathbf{R}_1 - \mathbf{R}_j)\sigma_i\sigma_j - \sum_{(ij)} J_T(\mathbf{R}_i - \mathbf{R}_j) t_i t_j + \sum_{(ij)} \phi_{ij} , \tag{8}$$

where $\mathbf{R}_i$ is the position of site i, and the sums are restricted to nearest neighbors on a cubic lattice. At this stage, it is very hard to integrate over the elastic degrees of freedom. We can, however, neglect all shear forces, and consider elastic compression terms between nearest neighbors only. The problem is then drastically simplified, as the model, from the elastic point of view, is reduced to a set of decoupled one-dimensional chains.[8,15] Now it is easier to work directly in the pressure ensemble. To integrate the elastic degrees of freedom, let us consider a decoupled elastic chain, along the x direction, described by the Hamiltonian

$$\mathcal{H}_{jx} = -\sum_i J_R(X_{j+1} - X_i)\sigma_{ij}\sigma_{i+i,j} - \sum_i J_T(X_{i+1} - X_i) t_{ij} t_{i+1,j} + \sum_i \phi(X_{i+1} - X_i) + p\sum_i (X_{i+1} - X_i) , \tag{9}$$

where the subscript j refers to the y or z directions, and the force p plays the role of the external pressure. For simplicity, let us again assume that J_R and J_T are linear and ϕ is quadratic in the lattice displacements, as in Eqs. (4) and (5). Discarding a smooth function of p, we have the effective spin Hamiltonian in the pressure ensemble,

$$\mathcal{H}_{\mathrm{eff}} = -\tilde{J}_R(p)\sum_{(ij)} \sigma_i\sigma_j - \tilde{J}_T(p)\sum_{(ij)} t_i t_j - \frac{J_{R1}^2}{2\phi_2}\sum_{(ij)}\sigma_i^2\sigma_j^2 - \frac{J_{T1}^2}{2\phi_2}\sum_{(ij)} t_i^2 t_j^2 - \frac{J_{T1}J_{R1}}{\phi_2}\sum_{(ij)}\sigma_i t_i \sigma_j t_j , \tag{10}$$

where $\tilde{J}_R$ and $\tilde{J}_T$ are given by Eq. (7). For Ising spin variables, $\sigma_i=\pm1$, and $t_i=\pm1$ for all i, this effective Hamiltonian displays the nearest-neighbor tetralinear couplings considered by Galam and Gabay.[6] It corresponds indeed to the asymmetric Ashkin-Teller model.[11] For small tetralinear couplings, which corresponds to small elastic effects, mean-field calculations for the Ashkin-Teller model indicate that there are two second-order transitions.[16,17] For larger couplings, however, the transitions may turn first order and the phase diagram in much more complex. The study of this global phase diagram is left for a future work.

At this point, to get one step further towards considering realistic elastic effects, we introduce some shear forces by the inclusion of second-neighbor interactions in the elastic potential of Eq. (8). It is convenient to write the small displacements from equilibrium and the spin variables in terms of their Fourier components. After some long and straightforward manipulations, we obtain an effective spin Hamiltonian of the form

$$\mathcal{H}_{\text{eff}}=\mathcal{H}_{SR}+\mathcal{H}_{LR} , \tag{11}$$

where, up to lowest orders in k, we have

$$\begin{aligned}\mathcal{H}_{SR}=&-\sum_k[(A_R-B_Rk^2)\hat{\sigma}_k\hat{\sigma}_{-k}+(A_T-B_Tk^2)\hat{t}_k\hat{t}_{-k}]\\&-C\sum_{k_1,k_2,k_3}[J_{R1}\hat{\sigma}_{k_1}\hat{\sigma}_{k_2}\hat{\sigma}_{k_3}\hat{\sigma}_{-k_1-k_2-k_3}\\&\qquad+2J_{R1}J_{T1}\hat{\sigma}_{k_1}\hat{\sigma}_{k_2}\hat{t}_{k_3}\hat{t}_{-k_1-k_2-k_3}\\&\qquad+J_{T1}\hat{t}_{k_1}\hat{t}_{k_2}\hat{t}_{k_3}\hat{t}_{-k_1-k_2-k_3}] ,\end{aligned} \tag{12}$$

and

$$\mathcal{H}_{LR}=-D\left[\sum_k(J_{R1}\hat{\sigma}_k\hat{\sigma}_{-k}+J_{T1}\hat{t}_k\hat{t}_{-k})\right]^2 , \tag{13}$$

where prefactors C and D are positive and depend on the elastic parameters. The long-range term $\mathcal{H}_{LR}$ corresponds to the Fourier representation of tetralinear couplings in the effective spin Hamiltonian of the elastic mean-field model. Equation (12), for $\mathcal{H}_{SR}$, corresponds to the short-range couplings of the shearless case. The detailed study of the model Hamiltonian of Eq. (11) is in progress. It seems, however, that the long-range terms will dominate and the transitions will be discontinuous. Considering one single set of spin variables, we regain the results of Bergman and Halperin[12] for the case of an elastically isotropic medium.

Finally, to emphasize the connection between our work and the physics of plastic crystals, it is worth making some comments on the validity of using discrete variables to describe continuous rotations. In plastic crystals, the interplay between the symmetries of both the lattice and the molecular groups generates the existence of a discrete set of equivalent orientations in the plastic phase. Due to steric hindrances, the dynamics of reorientations is rather complex. However, at first approximation, it is reasonable to assume instantaneous jumps between discrete orientations,[3] thus making appropriate the use of Ising variables. On the other hand, Heisenberg variables would require the introduction of additional anisotropic exchange couplings. The problem becomes then more difficult and is out the scope of the present work.

In conclusion, we have shown that elastic degrees of freedom are instrumental to generate couplings between translational and rotational degrees of freedom in models for plastic crystals. The mixed couplings are found to be always biquadratic, but their specific form depends on the way elasticity is included. A mean-field elastic model produces long-range coupling terms which drive the transition first order. In contrast, a shearless model, which overemphasizes microscopic position fluctuations, produces couplings that are always short ranged. The transitions are then continuous or discontinuous with a tricritical point. Finally, a more realistic model, which takes into account some shear forces, generates both short and long-range tetralinear couplings. The study of the competition between these interactions is required to determine the nature of the associated transitions. However, it is reasonable to expect that long-range terms will dominate and the transition will turn into first-order always.

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