THERMODYNAMIC PROPERTIES OF THE DISCOMMENSURATION POINT FOR INCOMMENSURATE STRUCTURES: A "THIRD-ORDER" PHASE TRANSITION

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The consequences of the opening of a phason gap in incommensurate systems are studied on a simple model, the discrete frustrated $\phi^4$-model. Analytical considerations and numerical results show that there is a very weak phase transition that can be characterized as third order.

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INTRODUCTION

It is well known that the modulation function of an incommensurate modulated phase is smooth at the transition from disordered to incommensurate, and that it may become discontinuous further from the transition line. In the incommensurate phase it marks the transition from a simple modulation to a structure that is locally like the commensurate structure that usually appears at another phase transition from incommensurate to commensurate modulation. The phenomenon of the appearance of a discontinuity is often called the transition by breaking of analyticity [1] or the discommensuration transition [2], the latter because at the transition the structure is locally periodic but with domain walls, called discommensuration. The transition is accompanied by an opening of a gap in the phason frequencies [3]. It has been studied on several models [2-9], like the discrete frustrated $\phi^4$-model (DIFFOUR), the Frenkel-Kontorova model and a double chain model for incommensurate composites.

From these studies the qualitative change in the modulation and the phason gap opening have been well established. It is not so clear whether the transition is a transition in the thermodynamic sense, and whether there are discontinuities in the thermodynamic quantities. To that end we analyze the situation for a displacively modulated structure using the DIFFOUR model. First the ground state properties are analyzed. Then temperature effects are studied. The analytical results are checked with numerical calculations.

DEFINITIONS AND GROUND-STATE PROPERTIES OF THE MODEL

The model under consideration is the 3D DIFFOUR array. It is a cubic lattice of 2-4 anharmonic double well oscillators, with a harmonic coupling. Each atom is coupled with 6 nearest neighbours and 2 next-nearest neighbours in the $z$-direction. The potential energy of the model is expressed as

$$V = -\frac{A}{2} \sum_n x_n^2 + \frac{B}{4} \sum_n x_n^4 + C \sum_{n,m} (x_n - x_m)^2 + D \sum_{n,m} (x_n - x_m)^2.$$  \hspace{1cm} (1)

Here $A, B, C, D$ are constants. The third sum (marked with a prime) runs over all pairs of the nearest neighbours $n$ and $m$, and the last sum (with a double-prime) is over the pairs of the next-nearest neighbours in the $z$-direction.

The ground-state properties of the model depend on the two dimensionless combinations: $a = -A/C$ and $d = D/C$. Along a line in the $a-d$ plane, the modulated phase with an incommensurate modulation period becomes energetically favourable:

$$x_n = f(z),$$  \hspace{1cm} (2)

where $f$ is a periodic function with, generally, an irrational period. For a small $a$, $f(z)$ is a sinus-like continuous function. With an increase of $a$ the modulation function becomes less smooth and at certain temperature can loss the continuity ("breaking of analyticity" or discommensuration transition). The part of the ground-state "phase diagram", containing the incommensurate phase, is schematically shown in Fig.1. Typical profiles of the modulation function are shown in Fig. 2. The plateaus at the discontinuous curve correspond to a locally periodic structure with discommensuration.
One can note that even the discontinuous modulation function roughly resembles the graph of sinus. Therefore it is reasonable first to consider a sinusoidal trial modulation \( f_0(z) = x_0 \sin kz \). The minimisation of the potential energy gives \( \cos k = -\frac{C}{4D}, \quad x_0^2 = \frac{4}{3}(A - \frac{C^2}{4D} - 4C - 8D) \).

The following procedure allows to describe qualitatively the appearance of the discontinuities. Let us use \( f_0(z) \) as a starting point, and find a function \( f_1(z) \) that minimises the potential energy of each layer in the fixed field of its neighbours:

\[
V_1(z) \equiv \frac{Bf_1^4(z)}{4} + (-A + 4C + 4D)\frac{f_1^2(z)}{2} - 2f_1(z)(Cf_0(z + 1) + Cf_0(z - 1) + Df_0(z + 2) + Df_0(z - 2)) = \min. \tag{3}
\]

One can consider this expression as the first iteration in the determination of the modulation function for a fixed period of modulation. However, we shall consider only the first iteration. Physically, this is a condition for the ground-state state of an anharmonic oscillator in the given external field formed by the neighbouring particles. The value of the field passes through zero at \( z = 0 \) and at \( z = \pi/k \). The qualitative behaviour of \( f_1(z) \) is determined by the sign of \( -A + 4C + 4D \). If this combination is positive, \( f_1(z) \) is a continuous function. Otherwise, discontinuous steps from \( -\sqrt{A - 4C - 4D} \) to \( \sqrt{A - 4C - 4D} \) appear at \( z = 0 \) and at \( z = l/2 \).

The situation at the points of discontinuity resembles quite much the Landau scenario of second-order phase transitions. Thus the contribution to the ground-state energy from these two points is of the Landau type - for example, it shows a discontinuity in the second derivative with respect to \( A \). However, to obtain the total energy, one should integrate over the modulation period. It is useful to consider the derivative of the ground-state en-

\[
\frac{dV_{gs}}{dA} = \frac{\partial V_{gs}}{\partial A} \propto \int f_1^2(z) \frac{dz}{2} \tag{4}
\]

To establish this formula we took into account that \( \frac{\partial V_{gs}}{\partial x_m} = 0 \), as \( V_{gs} \) should be minimised with respect to \( x_m \). The behaviour in the transition point with \( f = f_1(z) \) can be analysed by means of the expansion in powers of \( (-A + 4C + 4D) \). It turns out that both \( dV_{gs}/dA \) and \( d^2V_{gs}/dA^2 \) are continuous, and only the third derivative shows a step.

Quantitatively, the approach described above is very inaccurate. For example, for \( D = -0.4C \) it predicts the breaking of continuity at \( A = 2.4C \), whereas actually it takes place at \( A \approx 0.6C \). One can increase the accuracy, considering instead of \( f_0^2 \) the minimum of each three neighbouring layers in a given field of the surround-
normalisation is the function \( V \) of the eigenvalues of the 3 \( \times \) 3 matrix of the second derivatives of \( V_3(0) \) becomes zero. This gives the following condition for the breaking of continuity: 

\[
-\Delta + 4C + 3D - \sqrt{8 + (D - 3f_1^2(1))^2} + 3f_1^2(1)/2 = 0.
\]

The prediction for the \( D = -0.4C \) system is now much better: \( A \approx 1.0C \).

It should be noted also that the continuity of the modulation function actually breaks down not at the single point \( z = 0 \). Indeed, the exactly calculated modulation function is a fixed point of the transformation \( f \rightarrow C f_1(z + 2) + D f_0(z + 3) \).

Although the above approach is very simplified, it clearly shows the physical picture of the breaking of continuity. The qualitative prediction about the continuity of \( d^2V_{gs}/dA^2 \) seems to be correct as well. Fig. 3 shows a numerical result for this quantity, which is a smooth line.

At the same time, it is worth to note that the "breaking of continuity" affects the spectrum of elementary excitations essentially. For a continuous modulation function, a phason branch is present in the spectrum \([2, 3, 9]\).

It shows a linear (phonon-like) dispersion, with a phase velocity \( v \propto \langle f(z) (\partial f/\partial z)^2 dz \rangle^{-1/2} \). The zero-frequency Goldstone mode corresponds to the uniform shift of the modulation phase; its eigenfunction is \( u_0 \propto v f/\partial z \) (the normalisation is \( \int u^2 dz = 1 \)). For a discontinuous \( f(z) \), the integral for \( v \) diverges, indicating the presence of a gap at the beginning of the spectrum. This regime can be described as follows. Formally, one can still calculate \( u_0 \) from the above formula. For a modulation function \( f \), one obtains that \( u_0 \) becomes the two singular peaks at \( z = 0, \pi/k \). Physically, this means that the low-lying excitations are the vibrations of atoms only in the points where the modulation is broken. Therefore, their frequency is determined by the second derivative of \( V_1 \), \( \omega_0^2 \propto d^2V_1/dz^2 \). One can interpret these vibrations as domain wall oscillations. Consequently, the presented model predicts a gap, which is proportional to the square of the discontinuity of the modulation.

\[
\begin{align*}
V_3 &\equiv (f_1^2(z) + f_1^2(z + 1) + f_1^2(z - 1))/4 + (-\Delta + 4C + 4D)(f_1^2(z) + f_1^2(z + 1) + f_1^2(z - 1))/2 \\
&- 2Cf_1(z)f_1(z + 1) - 2DF_1(z)f_1(z + 1) \\
&- 2DF_1(z)f_0(z + 2) + f_0(z - 2) - 2f_1(z + 1)(Cf_0(z + 2) + Df_0(z + 3)) \\
&- 2f_1(z - 1)(Cf_0(z - 2) + Df_0(z - 3)) = \text{min}.
\end{align*}
\]

\[
\begin{align*}
\text{FIG. 3: The second derivative of the ground-state potential energy with respect to } a \text{ for the system with } d = -0.4. \text{ There is a step at } a = -0.45, \text{ corresponding to the transition from para-phase to the incommensurate state. No singularities at the breaking of continuity point } (a \approx 0.6) \text{ are observed.}
\end{align*}
\]

\[
Z = \int \exp(-V/T) dx_1 \ldots dx_n
\]

(Boltzmann constant is equal to unity).

In the mean-field consideration, the inter-atomic correlations are neglected, so that the average position of an on-site oscillator \( \bar{x}(z) \) is given by a self-consistent equation

\[
\bar{x}(z) = \bar{x}(f(z)) = \frac{\partial F(f(z))}{\partial f}
\]

\[
F(f(z)) \equiv -T \ln \int \exp \left( \frac{1}{T} \left( \frac{x^4}{4} + \frac{(-\Delta + 12C + 4D)x^2}{2} - f(z)x \right) \right) dx;
\]

\[
f(z) = 2C(4\bar{x}(z) + \bar{x}(z - 1) + \bar{x}(z + 1)) + 2D(\bar{x}(z - 2) + \bar{x}(z + 2)).
\]

\[
\begin{align*}
\text{FINITE TEMPERATURE: THE MEAN-FIELD APPROACH AND MONTE CARLO RESULTS}
\end{align*}
\]
Here \( f(z) \) is an average force acting on the oscillator from its neighbours.

Note that these equations determine the one-to-one correspondence between \( \tilde{x}(z) \) and \( f(z) \), so that one can construct a function \( f(\tilde{x}) \). It can be checked that equations (4) are the minimum conditions for the function

\[
F_{MF} = \sum_n \left( F(f(x_n)) - F(0) + x_n f(x_n) - (6C + 2D)x_n^2 \right) + C \sum_{n,m} (x_n - x_m)^2 + D \sum_{n,m} (x_n - x_m)^2.
\]

Thus in the mean-field approximation the problem at a finite temperature is replaced by the problem for the ground-state on an effective system [5]. The on-site potential of this effective system depends on temperature. The value of \( F_{MF} \) can be interpreted as a mean-field expression for the free energy of the system. As the temperature goes to zero, [5] tends to [1], if \( A \) is not too large (\( A < 12C + 4D \)).

The breaking of continuity of the modulation function occurs at a certain critical temperature \( T_c \). The considerations from the previous section can directly be applied here. In particular, the heat capacity, being the second derivative of the free energy, does not show a discontinuity at \( T_c \).

To go beyond the mean-field approach, it is necessary to consider the role of the fluctuations. Here we discuss, if the fluctuation phenomena can destroy the phase with a broken continuity. As it is demonstrated, the breaking of continuity occurs due to the appearance of the effective double-well potential for the layer with \( z = 0 \) (formula [3]). To incorporate the fluctuation in this model, it is natural to suppose that in the zeroth approximation the problem at a finite temperature is replaced by the problem for the ground-state [10] placed in an external field. The dependence of the heat capacity, being the second derivative of the modulated and disordered phase. The breaking of

\[
\sum_i \frac{x_i^4}{4} + \frac{(-A + 4C + 4D)x_i^2}{2} + \sum_{i,j} C(x_i - x_j)^2 - 2 \sum_i x_i(Cf_0(z + 1) + Cf_0(z - 1) + Df_0(z + 2) + Df_0(z - 2))
\]

Here the indices run over the layer with a given \( z \)-coordinate. The layer is in fact the 2D discrete \( \phi^4 \) model [10] placed in an external field. The dependence of the average of \( x_i \) on the value of the external field is discontinuous, if the layer without the external field shows a phase transition. Since a phase transition occurs in the 2D discrete \( \phi^4 \) model indeed, we conclude that fluctuations do not destroy the discontinuity of the modulation function for the model under consideration. It can be noted that for a 2D DIFFOUR model this is not true. In fact, in this case we would come to the 1D discrete \( \phi^4 \) chain, which does not show a phase transition.

To check the conclusion about the thermal behaviour of the heat capacity, we performed a Monte Carlo simulation of the system with a modulated ground state with a discontinuous modulation function. The system was studied for \( a = 1.5, d = -0.4 \). A slab of \( 8 \times 8 \times 557 \) atoms with periodic boundary conditions and the standard Metropolis algorithm was used. Initially we put the system in its ground-state, and set the temperature to be small. Then the temperature was slowly increased (about \( 3 \cdot 10^9 \) Monte Carlo trial steps were used for each value of temperature). The average potential energy \( \langle E \rangle \) was calculated at each point. Afterwards, the thermal capacity \( d < E > /dT \) was obtained. Thermal behaviour of this quantity is presented in Fig. 4. There is a clear peak at \( TB/C^2 \approx 3.7 \) corresponding to the transition between the modulated and disordered phase. The breaking of

\[
\text{FIG. 4: Monte Carlo result for the heat capacity of the system} \quad a = 1.5, d = -0.4. \text{ The ground state of this system is incommensurate with a broken continuity. The data shows a clear peak at the transition to the disordered phase} \quad (TB/C^2 \approx 3.7) \text{ and no other pronounced features.}
\]

continuity of the modulation function occurs at a lower temperature, but it does not result in any remarkable feature of \( d\langle E(T)\rangle/dT \).
CONCLUDING REMARKS

In several model systems for aperiodic crystals there is a transition from a smooth modulation function to a modulation function with discontinuities. This transition has been called the discommensuration transition of the transition by breaking of analyticity or continuity. In the phase space region where the modulation function is continuous there is in these models a phason excitation of zero frequency. In the other region there is a phason gap. However, neither the structural transition nor the opening of a phason gap has been observed in experiment. There are even few systems where a gap-less phason or phason with very low frequency has been found. Generally this is attributed to pinning by defects, or other friction mechanisms [11]. Another possible method to check the existence of the transition is by measuring thermodynamic quantities. In the model studied here, the DIFFOUR model, the transition is very weak. It can be called to be of third order. The conclusion is that the transition could only be observed by a precise structure determination. However, in general the discontinuity will be not strong enough to be seen.

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