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COMMENT

Comment on 'Bifurcation behaviour in structural phase transitions with multi-well potentials'

Kazuyuki Itoh and Chikako Moriyoshi

Department of Materials Science, Faculty of Science, Hiroshima University, Higashi-Hiroshima 724, Japan

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Abstract. Normand and co-workers predicted anomalous temperature dependence of a few thermal averages induced by the bifurcation behaviour or the local breaking of symmetry. Against their prediction, based on the ϕ^4 atom potential model, the double-quadratic-well (DQW) potential model leads to different temperature dependences on the specific heat and the mean square displacement. It turns out that the anomalous temperature dependence of the ϕ^4 model arises from the anharmonic character of the potential barrier as well as the bifurcation behaviour. Making a distinction between the two kinds of anomaly, we present a plausible temperature variation of the bifurcation behaviour on the basis of the DQW model of the above two quantities.

Recently, Normand *et al* (1990) predicted that some physical quantities such as the mean square thermal displacement, the specific heat and the collective frequencies of lattice vibrations display an anomalous temperature variation when the thermal energy approaches the barrier height h of the disordered atom potential. They showed that this effect is induced at around the temperature $T_0 = h/k_B$. Noting that the atom bifurcates at two sites when below T_0 as a reflection of the local breaking of symmetry, they called the effect the bifurcation behaviour or the quasi-transition. Although this effect is irrelevant to the phase transition in the fluctuating sense, the prediction has attracted much attention for the following reasons. (i) The effect causes a deviation of physical quantities from normal values. (ii) The effect is observable for many different quantities in addition to those mentioned above. (iii) We must distinguish the effect from the phase transition. (iv) The effect provides information about the form of the atom potential through the local breaking of symmetry.

Normand *et al* (1990) calculated the temperature dependence of the above quantities in the high-temperature regime on the basis of the ϕ^4 atom potential model. The potential function is expressed by

$$V(x) = \alpha x^2 + \beta x^4$$

where x is the atomic displacement from the centre. Here, we consider $\alpha < 0$ because the bifurcation behaviour is crucial for the double-well potential case. It should be mentioned that the ϕ^4 potential has a third-order term about the equilibrium position. This implies that the pronounced anharmonicity leads to biased values of the thermal

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averages; even so the ϕ^4 potential is suited for dynamical problems (see, for example, Bruce and Cowley 1981). Therefore, to study the nature of the effect, it is necessary to investigate to what extent the ϕ^4 potential gives feasible thermal averages. The aim of this comment is to estimate a more plausible temperature variation induced by the bifurcation behaviour with respect to the specific heat and the mean square thermal displacement, and to gain a deeper understanding of this effect.

We calculate the thermal averages based on the double-quadratic-well (DQW) potential model, which, in contrast to the ϕ^4 atom potential model, yields a harmonic character about the equilibrium positions. The DQW potential function is expressed as a function of the atomic displacement x from the origin by

$$V(x) = \tfrac{1}{2}c(x - x_0)^2 \qquad (x_1 \leqslant x)$$
$$V(x) = \tfrac{1}{2}ax^2 + h \qquad (-x_1 \leqslant x < x_1)$$
$$V(x) = \tfrac{1}{2}c(x + x_0)^2 \qquad (x < -x_1).$$

$V(x)$ is a smooth function at x_1. h and a specify the barrier form and are expressed in terms of parameters of the equilibrium positions by $a = c(1 - x_0/x_1)/2$ and $h = cx_0^2(1 - x_1/x_0)/2$. As in the earlier study, we calculate thermal averages assuming the high-temperature regime.

The temperature dependence of the specific heat is given in figure 1. The DQW atom potential is shown in the inset. The results are shown by the solid lines (1)–(4). For comparison, the previous result of the ϕ^4 model is also shown by the dotted line (5). Here, $r = x_1/x_0$ $(0 \leqslant r < 1)$ in the DQW model is a measure of the deviation from the quadratic potential form, i.e. a measure of the anharmonic character of the potential barrier. In contrast to the ϕ^4 model prediction, the peak at around $T/T_0 \sim 0.2$ becomes small with decreasing r and, in practice, disappears for small values of r, such as $r = 0.2$ in the figure. Only an extrapolated curve is given for the $r = 0.0$ case. The r dependence is readily explained by the fact that, to raise the temperature in the region $T/T_0 < 1.0$, the deviation from the quadratic potential form requires an additional increment of the internal energy. The peak around $T/T_0 \sim 0.2$ is, therefore, not due to the bifurcation behaviour but due to this deviation. On the other hand, the dip in the specific heat at around $T/T_0 \sim 1.0$ is induced by the bifurcation behaviour because the potential barrier hardly contributes to the increment of the internal energy in the region $T/T_0 > 1.0$. We may regard the peak as the precursor of the intrinsic bifurcation behaviour. At higher temperatures, the specific heat returns to the harmonic value, $C/k_B = 0.5$.

We conclude that the specific heat peak does not always appear clearly and, as is suggested later, the peak would hardly be observed in practice. In addition, we are aware of a few mechanisms which cause an extra specific heat peak such as a two-level-type excitation. It is, therefore, impossible to regard the peak simply as the precursor of the bifurcation behaviour. Along these lines, we think that the cusp-like anomaly of the specific heat observed in $Pb_3(P_{1-x}As_xO_4)_2$ at $T_t \simeq 490$ K (Salje and Wruck 1983) is, contrary to the opinion of Norman *et al* (1990), not necessarily associated with the bifurcation behaviour. The proof is not given until the dip is found around $T \sim 2500$ K, where we assume $T_t/T_0 \sim 0.2$. It should be said that if the crystal has n atoms in a structural formula, $1/n$ is a measure of the ease of observation of the specific heat anomaly. Therefore, we can expect to observe the dip of the specific heat for crystals having simple crystal structures.

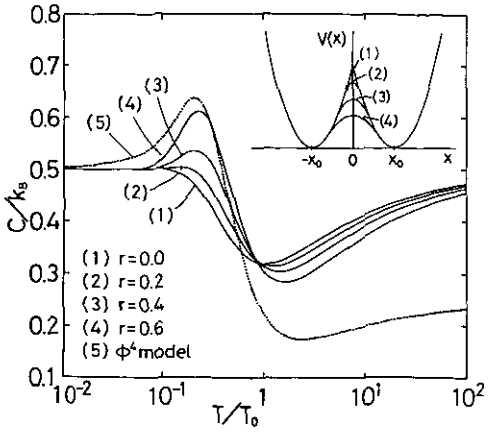

Figure 1. Temperature variation of the specific heat C/k_B calculated from the DOW model as a function of $r = x_1/x_0$ from (1) to (4). The dotted curve (5) is the result of the ϕ^4 model. The DOW potential is depicted in the inset.

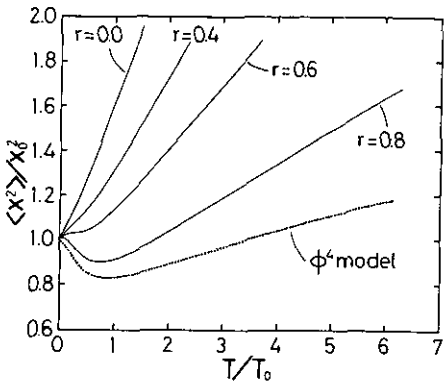

Figure 2. Temperature variation of the mean square thermal displacement $\langle x^2\rangle/x_0^2$ calculated from the DOW model as a function of $r = x_1/x_0$. The dotted curve is the result of the ϕ^4 model.

Figure 2 shows the temperature dependence of the mean square thermal displacement. Normand *et al* (1990) have pointed out, on the basis of the ϕ^4 model, that the anomalous increase of $\langle x^2\rangle$ in the low-temperature region is due to the bifurcation behaviour. However, as is shown in figure 2, the magnitude of the anomaly depends on r indicating that the anomaly is induced by the deviation from the quadratic potential form. The bifurcation behaviour, which emerges plainly in the limiting case of $r = 0.0$, can only be recognized by a slight change in the inclination of the temperature dependence curve around $T/T_0 \sim 0.5$. Therefore, it is rather difficult to observe the effect with respect to $\langle x^2\rangle$, in contrast to what is found in the specific heat case. To our knowledge, the linear-like temperature dependence of $\langle x^2\rangle$ in the disordered phase (Itoh and Fujihara 1991) is displayed by a large number of ferroelectric compounds. This experimental result indicates that $r \ll 1.0$ in most cases, which also suggests an absence of the specific heat peak. In any event, it is very unusual to find the anomaly of $\langle x^2\rangle$ arising from the deviation from the quadratic potential form as well as the bifurcation behaviour.

It seems that the bifurcation behaviour exhibits a variety of temperature dependences for respective thermal averages. It is important to pay attention to how the bifurcation behaviour predicted by Normand *et al* (1990) influences the measured values.

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