Asymmetry Induced Phase Transformations

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Abstract. Special class of one-dimensional (1D) lattice systems with asymmetric on-site potential can exhibit a sequence of phase conversions. Whereas this result is exact in 1D, one can ask if a sequence of phase transformations may evolve into a sequence of phase transitions in higher dimensional systems, where exact results are not available. In this paper we discuss such a problem: of a presence of a sequence of phase transitions in 3D systems with asymmetric on-site potential.

1. Motivation

In the thermodynamic regime, one-dimensional (1D) lattice systems with degenerated vacuum, reveal the coexistence of localized and extended excitations, kinks and phonons, respectively, that is accompanied by characteristic hump developed in a specific heat \cite{1}, \cite{2}. Such systems in higher dimensions, 2D and/or 3D, exhibit phase transitions of second order - in fact it is the most simple manifestation of spontaneously broken (discrete) symmetry.

It has been shown recently \cite{3}, \cite{4} that 1D or quasi one-dimensional, strongly non-linear systems, with non-degenerated vacuum exhibit interesting behavior. Such systems with local asymmetric, double-well or triple-well potential exhibit rich structure of the specific heat. In particular circumstances, of a “shape asymmetry”, there appears two-peak structure in specific heat corresponding to the sequence of two phase conversions. One can ask whether such a double-peak structure of specific heat, would lead, in higher dimensions, to a sequence of the phase transitions (of the first order).

In this paper we discuss the problem of 2D and 3D system with multistable, triple-well, on-site potential where a sequence of phase transitions may occur. The paper is organized as follows. In section 2, dimensional systems revealing two phase conversions is addressed. In section 3, their three-dimensional versions are investigated, exhibiting a sequence of phase transitions.

2. Sequence of phase conversions - 1D systems

Let us consider one component system of harmonically coupled atoms with a local multistability represented by a triple-well potential, described by the Hamiltonian of the form \cite{1}, \cite{2}, \cite{3}:

\begin{equation}
H = \frac{m\omega_0}{\alpha^2} \left[ \sum_{l} \left( \frac{1}{2} x_l^2 + V(x_l) \right) + \frac{1}{4} \sum_{l' \neq \nu} \varphi \omega (x_{l} - x_{l'})^2 \right],
\end{equation}
where $a$ - denotes the characteristic inverse distance, $\omega_0$ - characteristic frequency, and $m$ is the characteristic mass i.e. mass of single atom in chain; $\dot{x}_l$ denotes (dimensionless) time derivative, and $a$ is dimensionless coupling. On-site potential $V(x)$ is composed of a central well (CW) and double-well (DW) arranged in such a way that CW is narrower and deeper than symmetric side wells (DW) (see Fig. 1). Thermodynamics of such a lattice system in one dimension, may be found by means of the transfer integral method. In continuum classical limit with nearest neighbour interaction described by coupling constant $k$ [2], [3], [4], it exhibits interesting behavior. Namely, if we take on-site potential $V(x)$ as composed of the double-Morse potential $V_{DM}$ as DW, and the CW as Pöshl-Teller potential $V_{P-T}$ (see Fig. 1),

\[ V(x) = V_{DM}(x) + V_{P-T}(x), \]  

\[ V_{DM}(x) = V_1 \left\{ \exp \left[ -2\alpha(x + p) \right] - 2 \exp \left[ -\alpha(x + p) \right] \right\} + V_2 \left\{ \exp \left[ -2\beta(x - p) \right] - 2 \exp \left[ -\beta(x - p) \right] \right\}, \]  

\[ V_{P-T}(x) = \frac{-U}{\cosh^2(\kappa x)}, \]

where $V_1$, $V_2$ sets depth, $\alpha$, $\beta$ tunes the shape, and $p$ sets positions of minima for DM; parameter $U$ and $\kappa$ have respectively analogous meaning for CW, where position of minimum is fixed at $x = 0$. The detailed analysis of the on-site potential (2) is a bit lengthy and will be done in another paper. Here we will consider a sub-class of potentials $V(x) = V(-x)$, so that symmetric DM potentials, $V_1 = V_2$ and $\alpha = \beta$ setting symmetric DW, and observe shape transformations only by changing values of $U$, and $\kappa$. Such a typical $U - \kappa$ plane divided into sections of special shapes, namely: single well (SW), double well (DW), and triple well (TW), is presented in Fig. 2. For large $\kappa$, where CW is very narrow the TW shape is dominant, only for large values of $U$ the SW class is available. In a range of moderate $\kappa$ values, where specific fitting of CW shape to DM’s potential barrier takes place, one can observe drastic lowering of $U$ values, where SW class dominates. Finally, for small values of $\kappa$, where CW is crucially wide comparing to the width of DM potential ($\sim 2p$), the DW shape is available. It come from the fact, that in this interval CW is wide, leading to the shift of DM potential. For very large values of $U$, where the variation of CW can’t be ignored, the SW domain is again available.
Figure 2. Plane of $U - \kappa$ parameters divided into domains of specific shapes of on-site potential (2) occurrence: single well (SW), double well (DW), and triple well (TW), with $V_{DM}$ fixed parameters: $V_1 = V_2 = 0.6$, $\alpha = \beta = 0.7$, and $p = 10$.

The thermodynamic properties of one dimensional version of system (1) with Hamiltonian

$$H = \frac{m\omega_0}{a^2} \left[ \sum_l \left( \frac{1}{2} \dot{x}_l^2 + V(x_l) + \frac{k}{2}(x_l - x_{l+1})^2 \right) \right],$$

are described in terms of the pseudo-Schrödinger eigenvalue problem [5]:

$$\left( -\frac{1}{2m^*} \frac{d^2}{dx^2} + V(x) + V_0(T) \right) \Psi_i(x) = E_i \Psi_i(x),$$

$$m^* = kT^{-2}, \quad V_0(T) = -\frac{T}{2} \ln \left( \frac{2\pi T}{k} \right),$$

where $T = k_B\theta/m\omega_0^2$ is dimensionless temperature ($k_B$ - Boltzmann constant, $\theta$ - temperature). Configuration part of free energy is expressed via ground state “energy” of the eigenvalue problem (6)

$$F_{con} \simeq E_0(T), \text{ for } k \gg 1.$$ 

Specific heat function is presented in Fig. 3. Asymmetry of the local potential leads to a particular form of a specific heat: apart of smooth hump, sharp and intensive peak, manifesting dramatic change in the system is developed in this case. Interpretation of such a shape of a specific heat is the following. Particles occupying at low temperature range stable position in CW of local on-site potential perform radical jump to a shallower, side well of DW structure; this jump corresponds to a sharp peak of specific heat. The RTCT (Real Trajectories in Complex Time) [3], [4] approach indicates that: free energy of a more stable phase, corresponding to lower energy within CW, is increasing faster than the free energy of the less stable phase, corresponding to higher energy within DWs. Intersection of corresponding ground state ”energy levels” at some temperature $T_0$, results in a narrow peak of specific heat. Above that temperature, DW phase is a dominant one (lower free energy). The following phase conversation is related to the hump of specific heat: particles are performing large amplitude fluctuations about central, $x = 0$, position. This picture is confirmed by means of numerical tools. First, the temperature of first phase conversion corresponds to the (avoided) crossing of the free energies of CW and DW phases (“energy level crossing”, see [3], [4], and Fig. 4). The narrow peak in the specific heat arises at the temperature $T_0 \simeq 2.822$ (Fig. 3) of energy level crossing (see Fig. 4). Second, analyzing
Figure 3. Specific-heat \( C \) versus temperature \( T \) for \( k = 10.0 \), and with on-site potential parameters as in Fig. 1.

Figure 4. The ground “energy” levels crossing for on-site potential: \( V_{DM} - \text{solid line} \), \( V_{P-T} - \text{dashed line} \) for \( k = 10.0 \), and with parameters as in Fig. 1.

the specific heat structure one can notice that it is composed of three distinct contributions, see (Fig. 5). In the low temperature regime and in the high temperature regime, it reveals the shape characteristic of CW (a). In the intermediate temperatures range a hump corresponding to a double-well structure (though shifted) is formed (b). As added together, these three parts fit to the specific heat of the system (c) - sharp and narrow peak is missing as it arises when the central well and one of the side wells are present. Interpretation of the double peak structure of the specific heat becomes evident when one removes one of the side wells. Then, one only small quantitative correction are found, Fig. 6.

3. Sequence of phase conversions - 3D systems

Phase transformations manifested in specific heat of one dimensional systems would evolve into phase transitions in higher dimensions. There we shall consider 3D lattice system (1) with on-site triple-well asymmetric potential \( V(x) \) of shape asymmetry, composed of the double-well \( \phi^4 \)-type potential \( V_{\phi^4}(x) \), and the central, inverted Gaussian well \( V_G(x) \) (see also [6]):

\[
V(x) = V_{\phi^4}(x) + V_G(x),
\]  

(8a)
Figure 5. Specific heat $C$ versus temperature $T$ with distinct contributions. (a) – dashed line $V_{P-T}$, (b) – dash-dot-dotted line $V_{DM}$, (c) – solid line full $V(x)$ for $k = 10.0$, and on-site potentials parameters: $V_{DM}$: $V_1 = V_2 = 0.75$, $\alpha = \beta = 0.7$, $p = 10.0$, $V_{P-T}$: $U = 1.0$ $\kappa = 2.0$.

Figure 6. Specific heat $C$ versus temperature $T$ for: full $V(x)$ (solid line), and one with one removed side-well $V_{cut}(x)$ (dashed) for $k = 10.0$, and on-site potentials parameters: $V(x)$ as in Fig. 1, and $V_{cut}(x)$ as given by $V_{DM}$: $V_1 = 0$, $V_2 = 0.6$, $\alpha = 0$, $\beta = 0.7$, $p = 10.0$, and $V_{P-T}$: $U = 1.0$ $\kappa = 2.0$. Inset: Plot of the $V_{cut}(x)$ on-site potential with above parameters.

\[ V_{g4}(x) = -\frac{1}{2}x^2 + \frac{1}{4}x^4, \quad \text{(8b)} \]

\[ V_G(x) = -\gamma \exp \left( -\frac{x^2}{2\delta^2} \right), \quad \text{(8c)} \]

\[ f_0 = \sum_{l,l'} \varphi_{l'}w, \quad \text{(8d)} \]

Introduced above alternative form of $V(x)$ on-site potential, written in dimensionless units depends on two parameters $\gamma > 0$ and $\delta > 0$, which tune single central Gaussian well. The $\gamma$ parameter adjust depth, with $V_G(0) = -\gamma$, and $\delta$ – sets width of central well. The invariant component of (8a), double-well $V_{g4}(x)$ has fixed minima at $x_0 = \pm 1$, with depth $V_{g4}(x_0) = -1/4$. Manipulating with these two parameters $\gamma, \delta > 0$, similarly as in the case of potential (2), on-site potential (8a) may take a form of: single well (SW), double well (DW), and triple well (TW).
Figure 7. Plane $\gamma - \delta$ divided on regions of particular form of on-site potential equ. (8a) occurrence: SW – single well, DW – double-well, TW – triple-well, and TSV – shape asymmetry subregion of TW region. Dashed line: $\gamma = \delta^2$, dash-dotted line: $\gamma = 2\delta^4 \exp(-1 + 1/(2\delta^2))$.

The $\gamma - \delta$ plane with marked out domains of potential particular types occurrence is given in Fig. 7. We restrict our interest to the TW case; Some of its properties are following. Central well is placed, naturally in $x = 0$, while the side wells are arranged at

$$x_{\text{min}}^2 = 1 + 2\delta^4 W_0 \left( -\frac{\gamma}{2\delta^2} e^{\frac{1}{2\delta^2}} \right), \quad (9)$$

and a summits of potential barrier between wells are placed in

$$x_{\text{max}}^2 = 1 + 2\delta^4 W_{-1} \left( -\frac{\gamma}{2\delta^2} e^{\frac{1}{2\delta^2}} \right), \quad (10)$$

where $W_0, W_{-1}$ are the Lambert-W functions. The sector of TW (see Fig. 7) may be divided into two half-planes:

- $0 < \gamma < \frac{\pi}{8}$, where TW region is bordered only from bottom by $\gamma = \delta^2$, which comes form the condition for appearance of the central well.
- $\gamma > \frac{\pi}{8}$, where TW region is additionally bordered from top by $\gamma = 2\delta^4 \exp(-1 + 1/(2\delta^2))$ in interval $0 < \delta < \sqrt{\frac{1}{2}}$, which comes from the condition for existence of side wells.

In some part of TW region, on-site potential 8a belongs to the class of shape asymmetry, which is determined by thermodynamic properties of three dimensional version of the system (1). In fact, in this range of parameters, in 1D version, one can observe energy levels intersection, corresponding to the narrow peak appearance, followed by the moderate peak in specific heat. Considering the thermodynamic properties of three dimensional version of such a system one can find a confirmation of our hypothesis about the sequence of the phase transitions in shape asymmetry case. Indeed, in the mean field approximation the system shows two phase transitions and existence of an ordered phase, in the finite temperature range, see Fig. 8. Both phase transitions are of the first order. By pointing out a region of parameters $\gamma-\delta$, where those two transitions are present we can identify the subregion of TW half-plane, where on-site potential (8a) takes the form of shape asymmetry, namely TSV region on Fig.7.

The detailed discussion of the asymmetry driven phase transition in model (8) will be given in a subsequent papers [7], [8].
Figure 8. Square of order parameter $\eta^2$ vs temperature $T$ for $f_0 = 20$, and on-site potential $V(x)$ equ. (8a) with parameters: $\gamma = 0.28$, $\delta = 0.185$ – solid line; $\gamma = 0.30$, $\delta = 0.14$ – dashed line; $\gamma = 0.32$, $\delta = 0.15$ – dash-dotted line.

4. Conclusions
We are reporting a possibility of new type of structural phase transitions. Multistable on-site potential, considered in a form of a symmetric double-well, is usually associated with the spontaneously broken symmetry phenomena. Multistable asymmetric on-site potential may lead to interesting phenomena in one-dimensional systems, e.g. resulting in a sequence of phase transformations. It is argued here that particular type of asymmetry of multistable on-site potential may result in a sequence of phase transitions in three-dimensional systems. We have proposed triple-well potential of specific shape ("large asymmetry") leading to the sequence of two consecutive, first-order phase transitions.

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