Thermodynamics of the asymmetric double sinh-Gordon theory in 1+1 dimensions

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Classical thermodynamics of the $(1+1)$-dimensional asymmetric double sinh-Gordon system is investigated. The pseudo-Schrödinger equation resulting from the transfer integral method is solved numerically and within the semiclassical approximation; the exact results are also given at several temperatures. It is found that the specific heat exhibits a characteristic hump resembling a similar one observed in the systems with a symmetric potential; in some structures, extremely narrow and extremely high peak is developed. The interpretation for this behavior is given.

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A lot of effort has been made to study the statistical mechanics of nonlinear coherent structures in low dimensions. These studies, focused on the phenomena related to the kink dynamics and nucleation, have found a wide range of applications, e.g., in conducting polymer physics [1] and DNA [2,3]. Most of theoretical approaches were based on the structures with a local *symmetric* double well potential; recently it was shown that some progress may be made when the local φ^4 potential is replaced by its quasiexactly solvable (QES) counterpart [4], the double sinh-Gordon potential, also called the double Morse (DM) potential. The main reasons to study the properties of structures with an *asymmetric* potential are the following: First, a local asymmetric double well potential is an inherent feature not only in hydrogen bonded chains but, as it has been explained, it is a common one for the wide class of systems exhibiting the so-called photoinduced phase transitions [5–9]. Second, while in the systems with a symmetric potential the coexistence of extended excitations, phonons and localized excitations, kinks, is well understood and described in terms of the WKB approximation, in the case of systems with an asymmetric potential neither phenomenology of phonons and bell shapes (localized excitations) nor semiclassical description has been proposed. In this paper we report on the essential progress made in the description and understanding of the thermodynamic properties of the classical, one dimensional, nonlinear systems with a local *asymmetric* double well potential. We apply a modified WKB approximation to the QES model with the asymmetric DM potential and thus we are able to obtain a consistent description of its thermodynamic properties. Thermodynamics is studied in the usual way by using the transfer integral method and solving the Schrödingerlike equation–its ground state eigenvalue and eigenfunction correspond to the free energy and probability distribution function (PDF) (see Ref. [4]), respectively. We find that the specific heat reveals a characteristic hump; the shape of this hump, its magnitude, and its width depend on the interplay of the model parameters. Another interesting phenomenon is the nearly singular character of the specific heat in some systems that appears to be associated with the ‘‘avoided level crossing.’’

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The classical partition function Z_{cl} of a one-dimensional one-component system described by the Hamiltonian

$$H=\sum_n Al\left[\frac{1}{2}\dot{\varphi}_n^2+\frac{1}{2}\frac{c_0^2}{l^2}(\varphi_{n+1}-\varphi_n)^2+\omega_0^2V(\varphi_n)\right], \quad (1)$$

where l — lattice constant, c_0 — speed of sound, A — a certain constant, in the continuum limit takes the form

$$Z_{\text{cl}}=\left[\frac{2\pi l}{\beta h c_0}\right]^N\sum_n \exp[-\beta NlA\omega_0^2E_n]. \quad (2)$$

E_n are the eigenvalues of the Schrödingerlike equation

$$\left[-\frac{1}{2}\frac{1}{m^*}\frac{\partial^2}{\partial\varphi^2}+V(\varphi)\right]\Psi_n(\varphi)=E_n\Psi_n(\varphi), \quad (3)$$

$$m^*=\beta^2A^2c_0^2\omega_0^2.$$

Let us consider the asymmetric version of the local DM potential [10]

$$V(\varphi)=(B\cosh\varphi-n)^2+2BC\sinh\varphi, \qquad B<n, \quad (4)$$

which is composed of two mirror copies of the Morse potential shifted against each other. This potential belongs to the QES class and the exact results for the free energy [4,11,12] may be given at several temperatures. There are two types of excitations in such a system:

(a) extended, phonons, with spectrum $\Omega_q^2\approx\omega_0^2+c_0^2q^2$;

(b) localized bell-shaped excitations (hereafter bell shapes), the form and the energy of a resting bell shape are given, respectively, by the equations

$$\frac{1}{2}\varphi'^2_{\text{BS}}-V(\varphi)=-V_0, \quad (5)$$

$$E_{\text{BS}}=2\int_{\varphi_0}^{\varphi_1}\sqrt{2(V-V_0)}\,d\varphi. \quad (6)$$

The main difference between the kinks, appearing in the systems with a symmetric double well potential, and the bell shapes is that the former are stable excitations whereas the latter are not: the bell shapes in the system (1) are obviously

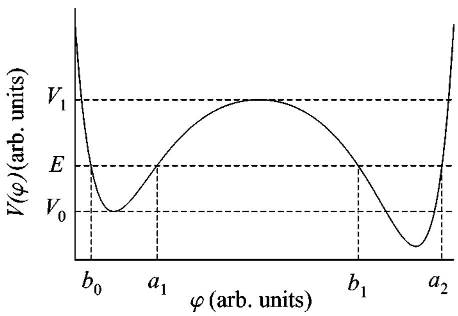

FIG. 1. The asymmetric double-Morse potential.

unstable (see [13,14]). Despite that, the bell shapes should affect the thermodynamic properties of the system and this problem may be discussed within the semiclassical approach. The standard WKB approximation cannot be applied in that case, but the alternative semiclassical approximation, called *real trajectories in complex time* (RTCT), [15] proved itself to be a reliable approach in a wide range of potentials [11]. Energy levels [see Eq. (3)], being the poles of the appropriate Green's function, are determined as the solutions of the equation (see Ref. [11])

$$\cos(W_1)\cos(W_2)-\frac{1}{4}\Gamma^2\sin(W_1)\sin(W_2)=0, \qquad (7)$$

where (see Fig. 1),

$$W_i(E)=\int_{b_{i-1}}^{a_i} d\varphi \sqrt{2m^*[E-V(\varphi)]}, \qquad (8)$$

$$\Gamma(E)=\exp\left[-\int_{a_1}^{b_1} d\varphi \sqrt{2m^*[V(\varphi)-E]}\right]. \qquad (9)$$

In Figs. 2 and 3 we show the plot of the free energy and the specific heat for some chosen model parameters. The RTCT results are compared with the exact numerical results and with the analytical ones at the discrete set of temperatures where they are available. The agreement between the exact and RTCT plots of the specific heat, a function sensitive to the smallest inaccuracies (cf. Ref. [4]), shown in Fig. 3, confirms the reliability of the latter method. In order to investigate the origin of the hump in the specific heat let us identify the following temperature regimes.

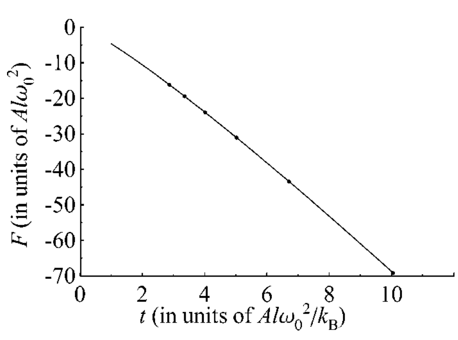

FIG. 2. Free energy as a function of temperature t for $B=0.1$, $C=-0.07$: RTCT result (solid line) and analytical results (dots).

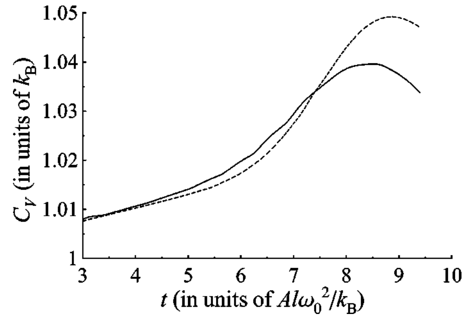

FIG. 3. Specific heat for $B=0.1$, $C=-0.07$: numerical results (solid line) and RTCT approximation (dashed line).

At low temperatures, where the effective mass m^* is large enough, the ground state eigenvalue lies below the bottom of the higher well (see Fig. 1)

$$E_0 \approx \frac{1}{2}(\beta A c_0 \omega_0)^{-1} \leqslant V_0.$$

The corresponding wave function, whose normalized module equals to PDF, is expected to be localized in the lower potential well.

At high temperatures, where the effective mass is small enough, the ground state eigenvalue lies well above the potential barrier,

$$W_1(E_0)=\frac{1}{2}\pi, \qquad E_0>V_1.$$

The PDF is expected to be localized at the center of the local potential. In the intermediate temperature regime various types of behavior are revealed, depending on the interplay of such model parameters as depth and width of the two wells.

(1) Small asymmetry. Two Morse potentials, left and right, are slightly shifted up against each other, $|C| \ll B$. The two lowest solutions of Eq. (7) are expressed via the left well (E_0^L) and right well (E_0^R) ground states,

$$E_0^{\pm}=E_0^R+\Delta E_0^{\pm} \equiv E_0^L-\delta E_0+\Delta E_0^{\pm},$$

$$\Delta E_0^{\pm}=\frac{1}{2}[(\delta E_0)\pm\sqrt{(\delta E_0)^2+\Gamma^2(E_0)\nu_1\nu_2}],$$

$$\nu_{1(2)}=\left[\frac{\partial}{\partial E}W_{1(2)}(E_0^{L(R)})\right]^{-1}.$$

In some small temperature range, when the lowest energy levels are close to the top of the potential barrier

$$\delta E_0=E_0^L-E_0^R \ll \Gamma(E_0),$$

this asymmetric system may resemble a symmetric one, with the characteristic, kinklike energy levels split (see Fig. 4)

$$\Delta E_0^{\pm} \approx \frac{1}{2}[(\delta E_0)\pm\Gamma(E_0)\sqrt{\nu_1\nu_2}].$$

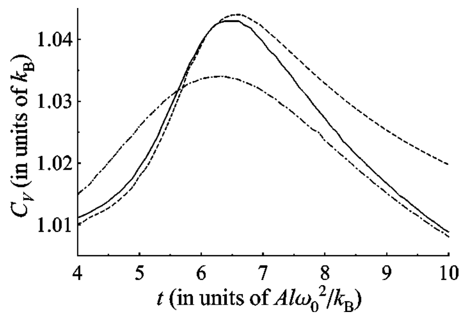

FIG. 4. Specific heat for $B=0.1$, $C=-0.01$ — exact results (solid line) and RTCT approximation (dashed line); $C=0$ (symmetric DM) — dashed-dotted line.

The numerical analysis confirms this prediction: during the temperature evolution the PDF (Fig. 5), originally localized in the deeper right well, gradually leaks to the left well, achieving the two peak structure characteristic for the symmetric double well potential.

(2) Large asymmetry. Growing asymmetry between the left and right wells can lead to the level crossing phenomena. In the case of a symmetric potential, the energy levels in separated wells, $\Gamma=0$, are degenerated; this degeneration is removed when they are getting closer, $\Gamma>0$. In the WKB interpretation this is referred to as an effect of tunnelling; the RTCT method extends this interpretation on the case of an asymmetric potential [11].

For the double well potential composed of two *different* Morse potentials where the lower, right well is much narrower than the upper, left well, the levels in the wells evolve in a different manner. The ground level in the right well moves up with temperature (inverse effective mass) quicker than the ground level in the left well. As a result they would cross before the true ground level of the system would reach the top of potential barrier (see Fig. 6). In the thermodynamic context the interchange in the stability of oscillations in the narrow and in the wide well takes place: at low remperatures oscillations in the lower well correspond to the lower value of the free energy; when the temperature increases then, due to their larger entropy, oscillations in the shallower but wider well are getting more stable. The transition between these two regimes corresponds to the "avoided level crossing." This interpretation is qualitatively confirmed within the RTCT: when the right ground level is still well below the left ground level,

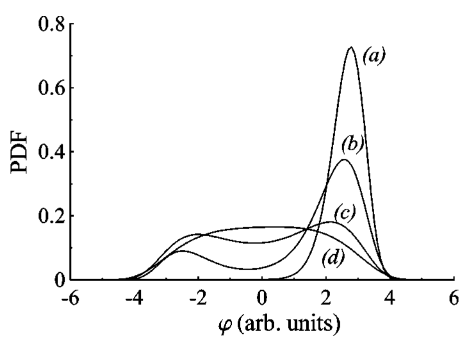

FIG. 5. PDF for $B=0.1$, $C=-0.01$: $t=4.02$ (a), 6.7 (b), 9.5 (c), 15.0 (d).

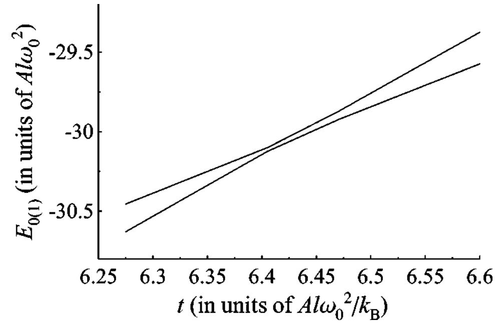

FIG. 6. The avoided level crossing — the ground and first excited level for large asymmetry.

$$E_0^R-V_0\ll E_0^L-V_0,$$

the true ground level is

$$E_0\approx E_0^R+\Delta E_0,$$

where

$$\Delta E_0=-\frac{1}{4}\Gamma^2(E_0)\tan[W_2(E_0)]\nu_1. \tag{10}$$

This split is exponentially small, with the energy of the bell shape in the exponent [see Eq. (6)]; therefore, this regime may be called a "bell-shape regime." As the temperature increases, the left and right ground levels approach

$$\delta E_0\ll E_0^L-V_0,$$

which corresponds to the nearly singular behavior of the split. In fact, the ground level split in the level crossing region, $\delta E_0\ll\Gamma(E_0)$, takes the form

$$\Delta E_0^{\pm}\approx\frac{1}{2}[(\delta E_0)\pm\Gamma(E_0)\sqrt{\nu_1\nu_2}],$$

and this regime may be referred to as a "kink regime." At higher temperatures, when the left ground level gets lower than the right ground level, the ground state wave function is localized in the left well; further temperature increase gives rise to the scenario when the wave function gradually develops the central peak. The peculiar character of that sort of behavior is reflected in the temperature dependence of the specific heat (see Fig. 7). This function should exhibit an extremely sharp maximum for wide and/or high, nontransparent barriers. In fact, the systems with a large barrier appear to consist of two nearly independent phases: the low-temperature one, corresponding to the deeper and narrower right well, and the high-temperature one, corresponding to the shallower well. Transition between these two phases takes place within the temperature interval where the relation $\delta E_0\approx\Gamma(E_0)$ holds that might be extremely narrow for nearly nontransparent barriers (small values of Γ).

In conclusion, let us make a few important remarks. The thermodynamic properties of the systems with an asymmetric potential appear to be quite rich and nontrivial. The common feature for all of these systems is a local maximum in

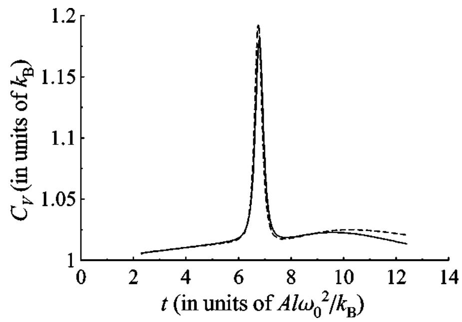

FIG. 7. Specific heat for large asymmetry: exact results (solid line) and RTCT approximation (dashed line).

the specific heat function, similar to its counterpart in kink-bearing systems. In systems with large, particular asymmetry, such that the lower well is narrower than the upper, wider well, the specific heat may develop another, extremely high and narrow peak. Two regimes, the "bell shape" and "kink" regime, are identified in that case. Let us notice that a similar behavior of the specific heat was observed in photoinduced phase transitions [16] and was attributed to the entropy difference between the low and high spin phases, which coincides with our interpretation. The above analysis leads to the conclusion that the appearance of the sharp maximum in the specific heat is a manifestation of a "level crossing," or phase transformation from the stable to the metastable phase driven by entropy increase. Hence, this phenomenon should be the indicative factor for such a phase change in a large class of photoinduced systems. The thermodynamic scenario of spin crossover compounds [16] and other photoinduced systems is much wider and richer. In fact, Gütlich *et al.* observed two peaks in the specific heat that might be interpreted as a result of antiferromagnetic interactions. A thorough discussion of that and related estions, a detailed analysis and identification of different contributions to the thermodynamic functions in continuous and discrete [14] systems will be the subject of our subsequent papers.

In fact, Gütlich *et al*. [16] observed two peaks in the specific heat that might be naively interpreted as a result of two subsequent changes in two subsystems. A thorough discussion of this and related questions, the phenomenological interpretation, and identification of different contributions to the thermodynamic functions in continuous and *discrete* [14] systems with an asymmetric double well will be the subject of a separate paper.

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