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Origins of phase transitions in small systems

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The identification and classification of phases in small systems, e.g., nuclei, social and financial networks, clusters, and biological systems, where the traditional definitions of phase transitions are not applicable, is important to obtain a deeper understanding of the phenomena observed in such systems. Within a simple statistical model, we investigate the validity and applicability of different classification schemes for phase transtions in small systems. We show that the whole complex temperature plane contains necessary information in order to give a distinct classification.

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The thermodynamics of small systems, e.g., Bose-Einstein condensates in magneto-optical traps [1–3], the nuclear liquid-gas transition observed by multifragmentation in heavy ion reactions [4–6], and the solid-liquid phase transition of sodium clusters [7–9], have gained increasing interest over the last few years. Because these systems are far away from the thermodynamic limit, the standard tools for the description of phase transitions are not applicable and other concepts are needed. Within the last few years several classification schemes for phase transitions in finite systems have been proposed [10]. In this report, we compare these classification schemes by means of a simple statistical model for atomic clusters and show that graveling transitions occurring in these models can only be completely understood by considering the whole complex temperature plane.

Among others, Gross and Votyakov and Gross *et al.*, have suggested a microcanonical treatment [10–12], where phase transitions of different order are distinguished by the curvature of the entropy $S=k_{\rm B}\ln\Omega(E)$. According to their scheme, a *back bending* in the microcanonical caloric curve $T(E)=1/\partial_E \ln[\Omega(E)]$, i.e., the appearance of negative heat capacities, is a mandatory criterion for a first-order transition. Caloric curves without back bending, where the associated specific heat shows a hump, are classified as higher-order transitions.

From classical statistical mechanics, it is clear that the back-bending feature is forbidden in the thermodynamic limit by the van Hove theorem [13]. Since the canonical and the microcanoncical caloric curves must give the same results in this limit and the canonical caloric curve is proportional to the mean-squared energy fluctuations the microcanonical caloric curve cannot exhibit a back bending. However, in small systems necessary and sufficient conditions for this type of microcanonical caloric curves have been derived by Wales and Berry and Wales and Doye [14,15]. An analysis of thermodynamic stability has gained that a loop in the microcanonical caloric curve with turning points $T_m > T_f$ occurs if the entropy S is bimodal for canonical temperatures in this range. As an equivalent condition, the authors showed that neglecting phase-space regions corresponding to intermediate compositions, i.e., solidlike and liquidlike forms, also result in a back bending.

We have proposed a classification scheme based on the distribution of zeros of the canonical partition function in the complex temperature plane [16]. The classical partition function

$$Z(\beta)=\left(\frac{1}{2\pi\beta}\right)^{3N/2}\int \mathrm{d}x^{3N}\exp[-\beta V(x)] \qquad (1)$$

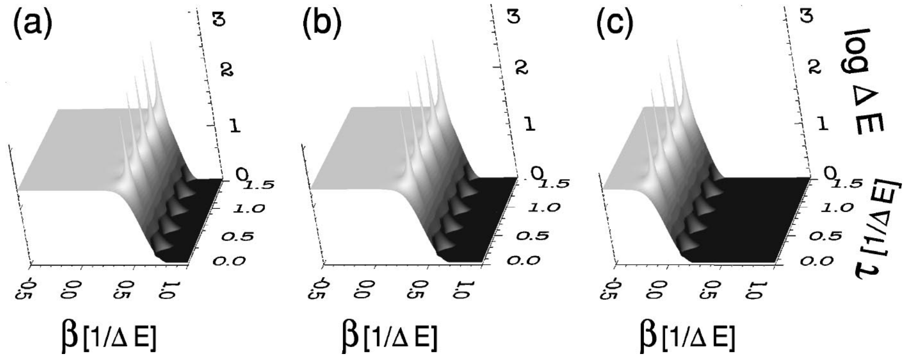

FIG. 1. Logarithm of the canonical potential-energy difference expectation value $\log(\langle\Delta E\rangle)$ in the complex temperature plane for (a) $\rho_2/\rho_1=50\,000$, (b) $\rho_2/\rho_1=5000$, and (c) $\rho_2/\rho_1=0.5$. The location of the zeros of the partition function are signaled by the sharp needles. In all cases, the distributions of zeros indicate first order phase transitions.

can be factored into a product of the kinetic part and a product depending on the zeros $\mathcal{B}_k = \beta_k + i\tau_k$, with $\mathcal{B}_{-k} = \mathcal{B}_k^*$ of this integral function in the complex temperature plane,

$$Z(\beta) = \left(\frac{1}{2\pi\beta}\right)^{3N/2} \prod_{k=-M}^{M} \left(1 - \frac{\beta}{\mathcal{B}_k}\right) \exp\left(\frac{\beta}{\mathcal{B}_k}\right). \tag{2}$$

Phase transitions then can be classified by a set of three parameters (α, γ, τ_1), describing the distribution of zeros close to the real axis, where $\gamma = \tan \nu$ is the crossing angle between the real axis and the line of zeros, and α is determined from the approximated density of zeros $\phi(\tau) \sim \tau^\alpha$ on this line. For infinite systems, it has been exactly shown that $\alpha = 0$, $\gamma = 0$, and $\tau_1 = 0$ corresponds to a first-order phase transition, while $\alpha > 0$ corresponds to a higher-order phase transition [17]. For finite systems, τ_1 is always greater than zero reflecting the size of the system. The classification scheme can be extended to values of $\alpha < 0$ also being interpreted as first-order phase transitions. This scheme sensitively reproduces the space dimension and particle-number dependence of the transition order in Bose-Einstein condensates [18] and the first-order nature of the nuclear multifragmentation phase transition [19].

The differences between both schemes can be revealed within a simple statistical model for atomic clusters. A harmonic superposition of different vibriational densities of states is well established in the cluster literature [20–23]. This multiple normal-modes model describes structural transitions within small noble gas clusters by considering several isomers and the vibrational eigenfrequencies of the isomers. For a two-isomer system, the partition function can be written as

$$\begin{aligned} Z(\beta) &= \sum_{i=1}^{2} \sigma_i \exp(-\beta E_i) \prod_{j=1}^{3N-6} \frac{2\pi}{\beta\omega_{ij}} \\ &= \beta^{-(3N-6)}[\rho_1 \exp(-\beta E_1) + \rho_2 \exp(-\beta E_2)], \end{aligned} \tag{3}$$

where the ω_{ij} are the normal modes of isomer i and the σ_i are the permutational degeneracies of the isomers and $\rho_i = \sigma_i \Pi_{j=1}^{3N-6}(2\pi/\omega_{ij})$. The zeros of Z

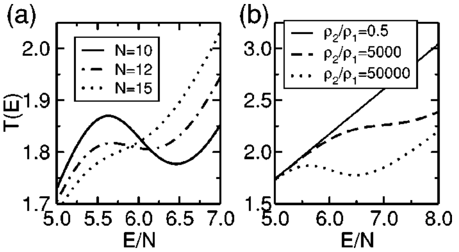

FIG. 2. Microcanonical caloric curves for the multiple normal-modes model with energy difference between the isomers $\Delta E = 20$. For (a) $N = 10$, 12, and 15 and constant $\rho_2/\rho_1 = 50\,000$ the back bending is manifest for $N = 10$, can be tuned out by increasing the particle number, and disappears for N as low as $N = 15$. In (b) for constant $N = 10$, the back bending can be tuned out by decreasing the ratio ρ_2/ρ_1.

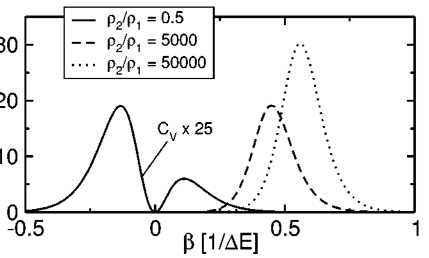

FIG. 3. Canonical specific heat reduced by the kinetic contribution for the same values of ρ_2/ρ_1 as in Fig 1. For values with ρ_2/ρ_1 larger than 1, the expected signals of a first-order phase transition are seen. The value $\rho_2/\rho_1 = 0.5$ corresponds formally to a first-order phase transition at negative temperature. This *graveling* transition exhibits at positive temperature a very weak10 hump in the specific heat (the graph is amplified by a factor of 25).

$$\mathcal{B}_k = [\ln(\rho_2/\rho_1) + i(2k+1)\pi]/\Delta E, \tag{4}$$

lie on a straight line and are equally spaced yielding $\alpha = \gamma = 0$, thus implying a first-order phase transition in any case $(\Delta E = E_2 - E_1)$ (see Fig. 1). It is important to note, that with increasing system size, the energy difference between the isomers will also increase, thus, τ_1 approaches zero. The microcanonical caloric curve $T(E) = 1/\partial_E \ln[\Omega(E)]$ for this model can be calculated via the inverse Laplace transform $\Omega(E) = \mathcal{L}^{-1}\{Z(\beta)\}$. Figure 2 shows that the back bending advocated in the Gross scheme for a first-order phase transition can be tuned in and out by variation of the model parameters.

The kinetic part of the partition function $\beta^{-(3N-6)}$ plays the crucial role. If this is taken into account the microcanonical caloric curves change dramatically, whereas this part has no effect on the distribution of zeros (the particle number dependence of the canonical partition function is not only reflected by the kinetic part itself but also implicitly by the ground-state energies). The change in the topology of the configuration space or equivalently configurations space regions with significantly changing vibrational entropies seems to be a necessary condition for phase transitions in small systems. Similar results have been pointed out by Franzosi *et al.* [24,25]. Equivalent findings are those of Wales and

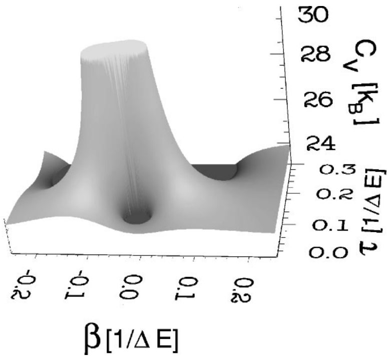

FIG. 4. Specific heat in the complex temperature plane for $\rho_2/\rho_1 = 0.5$. The figure displays how the interplay of the zero and the pole of the specific heat influences the behavior of the specific heat curve at positive temperatures.

Berry, and Wales and Doye *et al.* [14,15]. Utilizing also the harmonic superposition of vibriational densities of states and assuming ''coexistence'' of liquidlike and solidlike phases, the loop in the microcanonical caloric curve is also tunable by variations of system-inherent parameters. Especially, the mean difference in the potential energy of both phases correspond to variations of ρ_2/ρ_1 in our model.

Within classical statistical mechanics, the kinetic part of canonical partition function is separable and the partition function splits up into a kinetic and a potential part that can be handled independently. Within the microcanonical ensemble structural phase transition might be *washed* out or hidden by the kinetic-energy contributions to the entropy. Equivalent effects of the kinetic- and potential-energy contributions have been previously found [15].

A very interesting feature of the multiple normal-modes model occurs in the case where the isomer with the lower ground-state energy has a larger vibrational entropy [see Fig. 1(c)]. In this case, formally a first-order phase transition at negative temperatures occurs. The structural transition between the isomers, which occurs when the temperature is increased, is accompanied by a drop in the vibrational entropy. This is a *graveling* transition with a significantly smaller signal in the specific heat than that of the *normal* transition (see Fig. 3). Figures 3 and 4 show (i) that the zeros in the complex temperature plane sensitively detect phase transitions and (ii) it is very important to use β as the natural variable since only this yields continuous pictures of thermodynamic properties.

In conclusion, we have found that the classification of phase transitions in small systems based on the curvature of the microcanonical caloric curves seems to be not rigorous enough to make distinct statements about the order. In the *zero*-classification scheme, the potential-energy surface characterizes the phase behavior of the system, while in the scheme of Gross, the density of states is the characterizing quantity. We have shown that the investigation of the whole complex temperature plane adds a valuable amount of information in order to classify phase transitions in small systems.

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