The 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 transitions 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, the nuclear liquid-gas transition observed by multifragmentation in heavy ion reactions, and the solid-liquid phase transition of sodium clusters, have gained increasing interest over the last few years. Among others Gross et al. have suggested a micro-canonical treatment, where phase transitions of different order are distinguished by the curvature of the entropy $S = k_B \ln \Omega(E)$. 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.

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

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

(1)

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

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

(2)

It has been shown that phase transitions can be classified by a set of three parameters $(\alpha, \gamma, \tau_1)$, 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 $\alpha$ 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. For finite systems $\tau_1$ 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 and the first order nature of the nuclear multifragmentation phase transition. The differences between both schemes can be revealed within a simple statistical model for atomic clusters. The 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

$$Z(\beta) = \sum_{i=1}^{2} \sigma_i \exp(-\beta E_i) \prod_{j=1}^{3N-6} \frac{2\pi}{\beta \omega_{ij}}$$

(3)

$$= \beta^{-(3N-6)} \left(\rho_1 \exp(-\beta E_1) + \rho_2 \exp(-\beta E_2)\right),$$

where the $\omega_{ij}$ are the normal modes of isomer $i$ and the $\sigma_i$ are the permutational degeneracies of the isomers and $\rho_1 = \sigma_1 \prod_{j=1}^{3N-6} 2\omega_{ij}$. The zeros of $Z$

$$B_k = \left(\ln(\rho_2/\rho_1) + i(2k+1)\pi\right)/\Delta E,$$

(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 Figure 1). It is important to note, that with increasing system size the energy difference between the isomers will also increase, thus
FIG. 1: Logarithm of the canonical potential energy difference expectation value \( \log(\langle \Delta E \rangle) \) in the complex temperature plane for (a) \( \rho_2/\rho_1 = 50000 \), (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.

\( \beta [1/\Delta E] \) 

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 \( \rho_2/\rho_1 = 50000 \) 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 \( \rho_2/\rho_1 \).

\( \tau_1 \) approaches zero. The microcanonical caloric curve \( T(E) = 1/\beta k_B \ln(\Omega(E)) \) for this model can be calculated via the inverse Laplace transform \( \Omega(E) = \mathcal{L}^{-1}\{Z(\beta)\} \). Fig. 2 shows that the back-bending arrogated in the Gross scheme for a first order phase transition can be tuned in an 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 micro-canonical 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 Pettini et al. 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 which can be handled independently. Within the micro-canonical ensemble structural phase transition might be washed out or hidden by the kinetic energy contributions to the entropy.

FIG. 3: Canonical specific heat reduced by the kinetic contribution for the same values of \( \rho_2/\rho_1 \) as in Figure 1. For values with \( \rho_2/\rho_1 \) 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 gravieling transition exhibits at positive temperature a very weak hump in the specific heat (the graph is amplified by a factor of 25).

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). Fig.3 and Fig.4 show i) that the zeros in the complex temperature plane sensitively detect phase transitions and ii) it is very important to use $\beta$ 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. 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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