Classification of Phase Transitions in Small Systems

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We present a classification scheme for phase transitions in finite systems like atomic and molecular clusters based on the Lee-Yang zeros in the complex temperature plane. In the limit of infinite particle numbers the scheme reduces to the Ehrenfest definition of phase transitions and gives the right critical indices. We apply this classification scheme to Bose-Einstein condensates in a harmonic trap as an example of a higher order phase transition in a finite system and to small Ar clusters.

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Small systems do not exhibit phase transitions. Following Ehrenfest's definition this statement is true for almost all small systems. Instead of exhibiting a sharp peak or a discontinuity in the specific heat at some well-defined critical temperature the specific heat shows a more or less smooth hump extending over some finite temperature range. For example, for the melting of atomic clusters this is commonly interpreted as a temperature region where solid and liquid clusters coexist [1,2] and as a finite-system analog of a first order phase transition. Proykova and Berry [3] interpret a structural transition in TeF_6 clusters as a second order phase transition. A common way to investigate if a transition in a finite system is a precursor of a phase transition in the corresponding infinite system is to study the particle number dependence of the appropriate thermodynamic potential [4]. However, this approach will fail for all system types where the nature of the phase transition changes with increasing particle number which seems to be the case, e.g., for sodium clusters [5] or ferrofluid clusters [6]. For this reason a definition of phase transitions for systems with a fixed and finite particle number seems to be desirable. The only recommended feature is that this definition should reduce to the Ehrenfest definition when applied to infinite systems for systems where such limits exist. An approach in this direction has been made by studying the topological structure of the n-body phase space and *a hypothetical definition* based on the inspection of the shape of the caloric curve [7]. A mathematical more rigid investigation giving the sufficient and necessary conditions for the existence of van der Waals–type loops has been given by Wales and Doye [8].

Our ansatz presented in this Letter is based on earlier works of Lee and Yang [9] and Grossmann *et al.* [10] who gave a description of phase transitions by analyzing the distributions of zeros (DOZ's) of the grand canonical $\Xi(\beta)$ and the canonical partition function $Z(\beta)$ in the complex temperature plane. For macroscopic systems this analysis merely contributes a sophisticated view of the thermodynamic behavior of the investigated system. We will show that for small systems the DOZ's are able to reveal the thermodynamic secrets of small systems in a distinct manner. In the following we restrict our discussion to the canonical ensemble and denote complex temperatures by $\mathcal{B} = \beta + i\tau$ where β is as usual $1/k_B T$ [11].

In the case of finite systems one must not deal with special considerations regarding the thermodynamic limit. We write the canonical partition function $Z(\mathcal{B}) = \int dE \times \Omega(E) \exp(-\mathcal{B}E)$, with the density of states $\Omega(E)$, as a product $Z(\mathcal{B}) = Z_1(\mathcal{B}) Z_i(\mathcal{B})$ where $Z_1(\mathcal{B})$ describes the limiting behavior of $Z(\mathcal{B})$ for $T \to \infty$ imposing $\lim_{\mathcal{B}\to 0} Z_i(\mathcal{B}) = 1$. In general, $Z_1(\mathcal{B})$ will not depend on the interaction between the particles or the particle statistics but it will depend on the external potential imposed. For example, for N particles in a d-dimensional harmonic trap we have $Z_1(\mathcal{B}) \approx \mathcal{B}^{-dN}$ and for a d-dimensional gas $Z_1(\mathcal{B}) \approx \mathcal{B}^{-dN/2}$. In the following we will assume that $Z_1(\mathcal{B})$ has no zeros except at $\mathcal{B} = \infty$. Then the zeros of $Z(\mathcal{B})$ are the same as those of $Z_i(\mathcal{B})$. Applying the product theorem of Weierstrass [12] the canonical partition function can be written as a function of the zeros of $Z_i(\mathcal{B})$ in the complex temperature plane. Because $Z(\mathcal{B})$ is an integral function its zeros $\mathcal{B}_k = \mathcal{B}_{-k}^* = \beta_k + i\tau_k$ ($k \in \mathbb{N}$) are complex conjugated

$$Z(\mathcal{B}) = Z_1(\beta) Z_i(0) \exp[\mathcal{B}\,\partial_{\mathcal{B}} \ln Z_i(0)] \times \prod_{k\in\mathbb{N}} \left(1 - \frac{\mathcal{B}}{\mathcal{B}_k}\right)\left(1 - \frac{\mathcal{B}}{\mathcal{B}_k^*}\right) \exp\left(\frac{\mathcal{B}}{\mathcal{B}_k} + \frac{\mathcal{B}}{\mathcal{B}_k^*}\right). \tag{1}$$

The free energy $F(\mathcal{B}) = -\frac{1}{\mathcal{B}} \ln[Z(\mathcal{B})]$ is analytic, i.e., it has a derivative at every point, everywhere in the complex temperature plane except at the zeros of $Z(\mathcal{B})$. If the zeros are dense on lines in the complex plane, different phases are represented by different regions of holomorphy of $F(\mathcal{B})$ and are separated by these lines in the complex temperature plane. The DOZ contains the complete thermodynamic information about the system and all desired thermodynamic functions are derivable from it. The calculation of the specific heat $C_V(\mathcal{B})$ by standard differentiation yields

$$C_V(\mathcal{B}) = C_1(\mathcal{B}) - \sum_{k\in\mathbb{N}} \left[\frac{k_B \mathcal{B}^2}{(\mathcal{B}_k - \mathcal{B})^2} + \frac{k_B \mathcal{B}^2}{(\mathcal{B}_k^* - \mathcal{B})^2} \right]. \tag{2}$$

Zeros of $Z(\mathcal{B})$ are poles of $F(\mathcal{B})$ and $C_V(\mathcal{B})$. As can be seen from Eq. (2) the major contributions to the specific heat come from zeros close to the real axis, and a zero approaching the real axis infinitely close causes a divergence in the specific heat.

In the following we will give a discretized version of the classification scheme of Grossmann *et al.* [10]. To characterize the DOZ close to the real axis let us assume that the zeros lie approximately on a straight line. The crossing angle of this line with the imaginary axis (see Fig. 1) is then $\nu = \tan\gamma$ with $\gamma = (\beta_2 - \beta_1)/(\tau_2 - \tau_1)$. The crossing point of this line with the real axis is given by $\beta_{\mathrm{cut}} = \beta_1 - \gamma\tau_1$. We define the discrete line density ϕ as a function of τ_k as the average of the inverse distances between $\mathcal{B}_k$ and its neighboring zeros

$$\phi(\tau_k) = \frac{1}{2}\left(\frac{1}{|\mathcal{B}_k - \mathcal{B}_{k-1}|} + \frac{1}{|\mathcal{B}_{k+1} - \mathcal{B}_k|}\right), \quad (3)$$

with $k = 2, 3, 4, \ldots$. Guidelined by the fact that the importance of the contribution of a zero to the specific heat decreases with increasing τ we approximate $\phi(\tau)$ in the region of small τ by a simple power law $\phi(\tau) \sim \tau^{\alpha}$. A rough estimate of α considering only the first two zeros yields

$$\alpha = \frac{\ln\phi(\tau_3) - \ln\phi(\tau_2)}{\ln\tau_3 - \ln\tau_2}. \quad (4)$$

Together with τ_1, the imaginary part of the zero closest to the real axis, the parameters γ and α classify the DOZ. As will be shown below, the parameter τ_1 is the essential parameter to classify phase transitions in small systems. For a *true* phase transition in the Ehrenfest sense we have $\tau_1 \to 0$. For this case it has been shown [10] that a phase transition is completely classified by α and γ. In the case $\alpha = 0$ and $\gamma = 0$ the specific heat $C_V(\beta)$ exhibits a δ peak corresponding to a phase transition of first order. For $0 < \alpha < 1$ and $\gamma = 0$ (or $\gamma \neq 0$) the transition is of second order. A higher order transition occurs for $1 < \alpha$ and arbitrary γ. This implies that the classification of phase transitions in finite systems by γ, α, and τ_1, which reflects the finite size effects, is a straightforward extension of the Ehrenfest scheme.

The imaginary parts τ_i of the zeros have a simple straightforward interpretation in the quantum mechanical case. By going from real temperatures $\beta = 1/(k_{\mathrm{B}}T)$ to complex temperatures $\beta + i\tau/\hbar$ the quantum mechanical partition function can be written as

$$Z(\beta + i\tau/\hbar) = \mathrm{Tr}[\exp(-i\tau H/\hbar)\exp(-\beta H)], \quad (5)$$

$$= \langle\Psi_{\mathrm{can}}|\exp(-i\tau H/\hbar)|\Psi_{\mathrm{can}}\rangle \quad (6)$$

$$= \langle\Psi_{\mathrm{can}}(t=0)\,|\,\Psi_{\mathrm{can}}(t=\tau)\rangle,$$

introducing a *canonical state*, which is the sum of all eigenstates of the system appropriately weighted by the Boltzmann factor, $|\Psi_{\mathrm{can}}\rangle = \sum_i \exp(-\beta\epsilon_i/2)\,|\phi_i\rangle$. Within this picture a zero of the partition function occurs at times τ_i where the overlap of a time evoluted canonical state and the initial state vanishes. This resembles a correlation time, but some care is in order here. The time τ_i is not connected to a single system, but to an ensemble of infinitely many identical systems in a heat bath, with a Boltzmann distribution of initial states. Thus, the times τ_i are those times after which the whole ensemble loses its memory.

Equation (5) is nothing but the canonical ensemble average of the time evolution operator $\exp(-i\tau H/\hbar)$. Following Boltzmann the ensemble average equals the long time average which was proven quantum mechanically by Tasaki [13]. Therefore τ_i indeed resembles times for which the long time average of the time evolution operator vanishes.

The observation of Bose-Einstein condensation in dilute gases of finite number ($\sim 10^3$–10^7) of alkali atoms in harmonic traps [14] has renewed the interest in this phenomenon which has already been predicted by Einstein [15] in 1925. The number of condensed atoms in these traps is far away from the thermodynamic limit, raising the interesting question how the order of the phase transition changes with an increasing number of atoms in the condensate. For this reason we treat the Bose-Einstein condensation in a three-dimensional isotropic harmonic trap ($\hbar = \omega = k_{\mathrm{B}} = m = 1$) as an example for the application of the classification scheme given above.

For noninteracting bosons the occupation numbers of an eigenstate $|i\rangle$ and $N + 1$ particles can be evaluated by a simple recursion [16]

$$\eta_i(N+1, \mathcal{B}) = \frac{Z_N(\mathcal{B})}{Z_{N+1}(\mathcal{B})}\exp(-\mathcal{B}\epsilon_i)[\eta_i(N, \mathcal{B}) + 1]. \quad (7)$$

Since the particle number is a conserved quantity in the canonical ensemble the direct calculation of the normalization factor can be omitted by using the relation

$$\frac{Z_N(\mathcal{B})}{Z_{N+1}(\mathcal{B})} = \frac{N+1}{\sum_{i=0}^{\infty}\exp(-\mathcal{B}\epsilon_i)[\eta_i(N, \mathcal{B}) + 1]}. \quad (8)$$

Since $Z_N(\mathcal{B})$ is an exponentially decreasing function in β it is a difficult numerical task to calculate its zeros directly. Zeros of the partition function are reflected by poles of the ground state occupation number

$$\eta_0(N, \mathcal{B}) = -\frac{1}{\mathcal{B}}\frac{\partial_{\epsilon_0} Z_N(\mathcal{B})}{Z_N(\mathcal{B})} \quad (9)$$

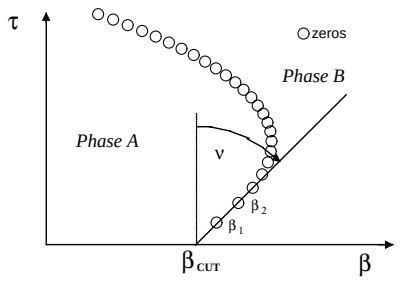

FIG. 1. Schematic plot of the DOZ illustrating the definition of the classification parameters given in the text.

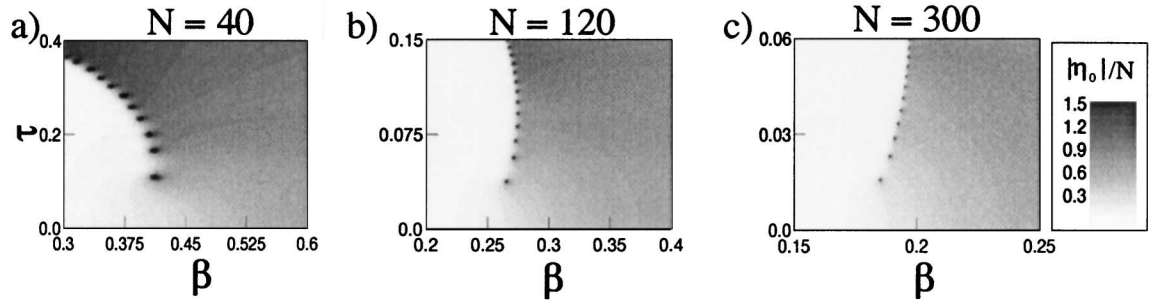

FIG. 2. Contour plots of the ground state occupation number $|\eta_0|/N$ in the complex temperature plane for 40, 120, and 300 particles in a three-dimensional isotropic trap. The black spots indicate the locations of zeros of the partition function.

evaluated at complex temperatures. Figure 2 displays contour plots of $|\eta_0(N,\mathcal{B})|/N$ for 40, 120, and 300 particles. The locations of the zeros of $Z(\mathcal{B})$ [poles of $\eta_0(N,\mathcal{B})$] are indicated by the white spots. The separation of the condensed (dark) and the normal (bright) phase is conspicuous. The zeros act like *boundary posts* between both phases. The boundary line between both phases gets more and more pronounced as the number of particles increases and the distance between neighboring zeros decreases. Figure 2 virtually displays how the phase transition approaches its thermodynamic limit. We have determined the classification parameters for the phase transition by a numerical analysis of the DOZ for up to 400 particles. The results are given in Fig. 3. The parameter α is constant at about 1.25. The small fluctuations are due to numerical errors in the determination of the location of the zeros. This value of α indicates a third order phase transition in the three-dimensional harmonic trap. Results for the two-dimensional systems and other trap geometries, which will be published elsewhere in detail, indicate that the order of the phase transition depends strongly on the trap geometry. The parameter γ and the noninteger fraction of α are related to the critical indices of the phase transition, e.g., $\gamma = 0$ indicates equal critical indices for approaching the critical temperature from the left and from the right. Regarding the finite size effects τ_1 is of major importance. As can be seen in Fig. 3(b) τ_1 is approximately proportional to $1/N$ so that the systems of bosons in a three-dimensional harmonic trap approach a true higher order phase transition linearly with increasing particle number N.

It appears that the DOZ for Bose-Einstein condensates is rather smooth. As an example for a little more complicated situation we calculated the DOZ for small Ar clusters, which have been extensively studied in the past [17]. Their thermodynamic behavior is governed by a *hopping process* between different isomers and *melting* [18]. Many indicators of *phase transitions* in Ar clusters have been investigated, e.g., the specific heat [19], the rms bond length fluctuation [20], and the onset of a $1/f$-noise behavior of the potential energy in time dependent molecular dynamics simulations [21]. However, for a good reason, all these attempts lack a definite classification of the transitions taking place in these clusters. Without going into the details of our numerical method which is based on a determination of the interaction density of states by extensive Monte Carlo simulations along with an optimized data analysis [22] we give here the results for Ar_6 and Ar_{30}. Figure 4 displays contour plots of the absolute value of the specific heat $c_V(\mathcal{B})$ in the complex temperature plane. For Ar_6 the poles lie on a straight line at $T \simeq 15$ K and are equally spaced with resulting classification parameters $\alpha = 0$, $\gamma = 0$, and $\tau_1\hbar = 0.05$ ps. From earlier works [23] it is well known that at this temperature a hopping transition between the octahedral and the bicapped tetrahedral isomer occurs. Our classification scheme now indicates that this isomer hopping can be identified as a first order phase transition. Ar_{30} already has a tremendous number of different isomers, and a much more complicated form of the DOZ arises [see Fig. 4(b)]. The DOZ cuts the complex temperature plane into three regions with two transition lines approaching the real axis. Comparing with the literature the region below 31 K can be identified as the

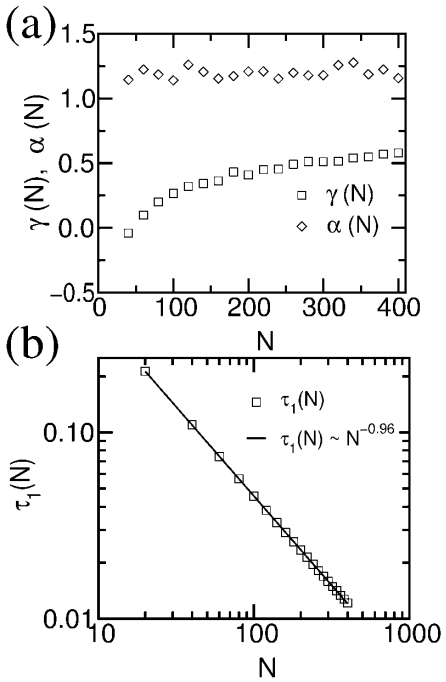

FIG. 3. Plots of the classification parameters α, γ, and τ_1 versus the number of particles for a three-dimensional harmonic trap.

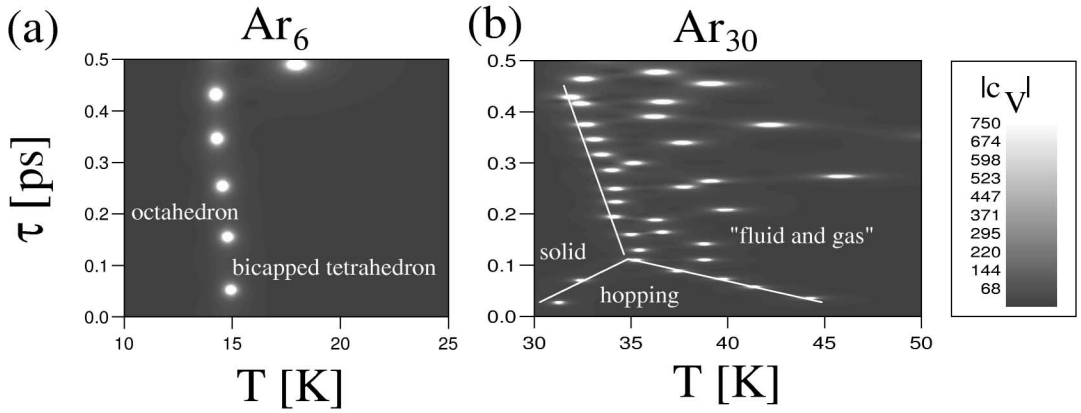

FIG. 4. Contour plots of the specific heat $|c_V|$ for Ar_6 and Ar_{30} clusters.

solid phase and the region above 45 K as a fluid phase. Because our Monte Carlo simulations are performed at zero pressure at this temperature, also the evaporation of atoms from the cluster starts which corresponds to the onset of the gas phase. The phase between these two transition lines is commonly interpreted as the melting, isomer hopping, or coexistance region. The analysis of the order of the phase transitions is quite difficult in this case and will be investigated in a more systematic study. Nevertheless the DOZ displays in a distinct manner the phase separation for Ar_{30} and can be viewed as a unique fingerprint.

In conclusion we have found that the DOZ of the canonical partition function can be used to classify phase transitions in finite systems. The DOZ of a specific system acts like a unique fingerprint. The classification scheme given above is equivalent to that given by Grossmann *et al.* but extended to the region of finite particle numbers. We have found that the zeros of the partition function act like boundary posts between different phases in the complex temperature plane. The finite size effects for the Bose-Einstein condensation are reflected by a $1/N$ dependence of the parameter τ_1 and only a slight change of the parameter α which indicates the order of the phase transition. For Ar clusters the DOZ leads to enlightening pictures of the complex process of melting or isomer hopping, identifying in a distinct manner two critical temperatures supporting an old assumption of Berry *et al.* [17]. This classification scheme developed for the canonical ensemble should also hold for other ensembles, i.e., different experimental conditions should not influence the *nature* of the systems although, e.g., the shape of the caloric curve may significantly differ.

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