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Leading Fisher partition function zeros as indicators of structural transitions in macromolecules

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Abstract

We show that leading zeros, i.e., isolated complex zeros of the canonical partition function near the positive real axis, are robust indicators of conformational transitions in finite macromolecular systems. For a flexible polymer with 250 monomers, we calculate the complex Fisher partition function zeros from a precise estimate of the density of states that was obtained via advanced multicanonical Monte Carlo simulations. Transition temperatures estimated from the leading zeros correspond very well to regions of enhanced thermal activity as signaled by canonical thermodynamic quantities such as the specific heat and fluctuations of the radius of gyration.

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1. Introduction

Phase transitions are exciting natural phenomena and their study has a long tradition. In thermodynamics, first-order phase transitions are characterized by one or more discontinuities in the first derivatives of the appropriate free energy. The most apparent property is the coexistence of phases, which is associated with the latent heat, i.e., the energy necessary to switch from one phase to the other at the transition temperature. In second-order phase transitions, the main feature is the divergence of the correlation length and one or more singularities in the second derivatives of the free energy ("critical behavior") [Landau and Binder (2014)]. Generally, phase transitions can only occur in the thermodynamic limit and their singular features are associated with discontinuities in derivatives of the free energy, which is proportional to the logarithm of the partition function.

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There has also been a growing interest to correlate cooperative behavior in finite systems with properties of phase transitions, although in these cases no singularities in thermodynamic quantities occur. One of the most prominent examples of such systems are polymers. It is well known that even polymers and proteins with a small number of monomers experience structural transitions under certain environmental conditions. This enhanced thermal activity is typically clearly signaled in thermodynamic quantities such as the heat capacity and fluctuations of structural quantities. However, in contrast to thermodynamic phase transitions, these signals do not occur at the same temperature, i.e., the identification of unique transition points in often impossible on this basis [Bachmann (2014)].

Yang and Lee were the first to relate the occurrence of singularities in phase transitions to the approach of complex zeros of the grand canonical partition function in fugacity space to the positive real axis in the thermodynamic limit [Yang and Lee (1952)]. Fisher performed an analytic continuation of the canonical partition function and introduced a complex temperature plane [Fisher (1965)]. Since this approach requires an accurate estimate of the density of states, which can only be obtained numerically for complex systems, it was virtually impossible to apply these methods to interacting systems before the necessary computational capacities and advanced simulation methods such as multicanonical Monte Carlo [Berg and Neuhaus (1992)] and Wang-Landau sampling [Wang and Landau (2001)] became available. Since then, Fisher zeros of the partition function were studied extensively for multiple physical systems, including spin models [Janke and Kenna (2001); Hwang (2009); Fonseca et al. (2012)]), proteins [Alves and Hansmann (2000); Wang and Wang (2003)], and polymers [Taylor et al. (2013); Chen et al. (2013)]. For flexible, elastic polymers, we systematically compared microcanonical inflection-point analysis [Schnabel et al. (2011a)] and the Fisher zeros method for the identification of transition points recently and found that both methods yield similar results [Rocha et al. (2014)].

Here, we investigate Fisher zeros for the specific example of a linear, finite elastic, flexible polymer with 250 monomers in more detail and compare the results with transition signals of conventional thermodynamic quantities.

2. Model and Methods

For our study of the 250-mer, we employ a generic coarse-grained model for linear, elastic, flexible polymers [Schnabel et al. (2009a,b)]. Non-bonded monomers interact pairwise via a truncated and shifted Lennard-Jones (LJ) potential

$$V_{\mathrm{LJ}}^{\mathrm{mod}}(r_{ij}) = V_{\mathrm{LJ}}(\min(r_{ij}, r_c)) - V_{\mathrm{LJ}}(r_c), \tag{1}$$

where r_{ij} denotes the distance between the ith and the jth monomer, r_c is the cutoff distance, and

$$V_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

is the standard LJ potential with parameter values $\epsilon = 1$, $\sigma = 2^{-1/6}r_0$, and $r_c = 2.5\sigma$. The elastic bonds between monomers adjacent along the chain are modeled by the finitely extensible nonlinear elastic (FENE) potential [Bird et al. (1987)]

$$V_{\mathrm{FENE}}(r_{ii+1}) = -\frac{K}{2}R^2 \ln\left[1 - \left(\frac{r_{ii+1} - r_0}{R}\right)^2\right]. \tag{3}$$

This potential possesses a minimum at r_0 and diverges for $r \to r_0 \pm R$. K is a spring constant and we set the parameters to $R = 0.3$, $r_0 = 0.7$, and $K = 40$. For the simulation of this model we employed variants of multicanonical Monte Carlo sampling, the details of which are described elsewhere [Schnabel et al. (2011b); Rocha et al. (2014)].

For the estimation of the partition function zeros, it is necessary to discretize the energy space. A polymer conformation with energy E is assigned the nth bin ($n = 0, 1, \ldots, M-1$), if $E_n \leq E < E_n + \varepsilon$ and $E_n = E_0 + n\varepsilon$, where ε is the energetic bin width and E_0 the ground state energy. By introducing the degeneracy or number of states in the nth bin by g_n and defining $x = e^{-\beta\varepsilon}$ ($\beta = 1/k_{\mathrm{B}}T$, where k_{B} is the Boltzmann constant and T the temperature), the canonical partition function can be written as

$$Z = e^{-\beta E_0}\sum_{n=0}^{M-1} g_n e^{-\beta n\varepsilon} = e^{-\beta E_0}\sum_{n=0}^{M-1} g_n x^n = e^{-\beta E_0}\prod_{m=1}^{M-1}(x - x_m), \tag{4}$$

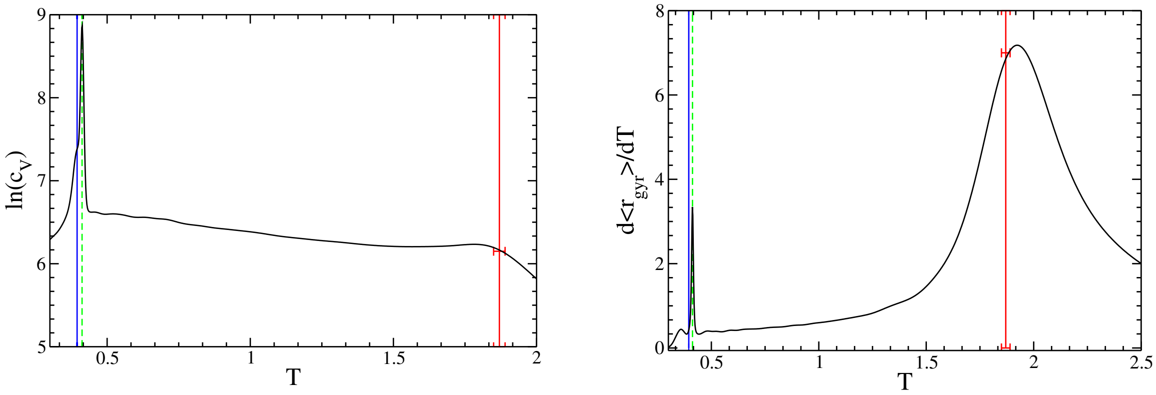

Fig. 1. *Left:* Specific heat c_V and *Right:* Fluctuations of the radius of gyration $d\langle r_{\mathrm{gyr}}\rangle/dT$ as functions of temperature. The vertical lines are located at the transition temperatures obtained by leading Fisher zero analysis.

where in the latter expression the polynomial was decomposed into a product of linear factors, with x_m denoting the mth zero (or root) of the polynomial. The $M-1$ roots are complex, $x_m = a_m + ib_m$, and since $g_n \in \Re$ the complex conjugate $x_{m'} = x_m^* = a_m - ib_m$ is also a root of the polynomial. Because $g_n > 0\ \forall n$, all real-values zeros must be negative.[1] According to the Abel-Ruffini theorem, a polynomial of degree five or higher has no algebraic solution in general, and a numerical zeros finder is needed to estimate the zeros. We have used the methods described in more detail in Rocha et al. (2014). Individual partition function zeros that approach the real axis in the thermodynamic limit or lie closest to it in finite systems are called *leading zeros* x_ℓ. In the thermodynamic limit, these zeros can be associated with the singular behavior of thermodynamic quantities near phase transition points. Since the internal energy is given by $U = -\partial \ln Z/\partial\beta$, the specific heat can be expressed as

$$c_V = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right)_V = \frac{k_{\mathrm{B}} x (\ln x)^2}{N}\sum_{m=1}^{M-1}\frac{-x_m}{(x-x_m)^2} = \frac{k_{\mathrm{B}} x (\ln x)^2}{N}\sum_{m=1}^{M-1}\frac{-a_m(x-a_m)^2 + b_j^2(2x-a_m)}{[(x-a_m)^2+b_m^2]^2}. \tag{5}$$

and diverges if $x \to a_m$ and $b_m \to 0$. For finite systems, the leading zeros dominate the behavior of c_V near the peak position, and the transition temperature can be defined by

$$T_c = \frac{-\varepsilon}{k_{\mathrm{B}} \ln |x_\ell|}. \tag{6}$$

It should be emphasized that the values of the partition function zeros generally depend on the choice of the energy bin width ε (which in this study was chosen to be $\varepsilon = 0.98$). However, it turns out that the leading zeros are much less affected by changes of ε. Therefore, they can be considered safe indicators of transition points in the continuous model.

3. Results and discussion

In conventional canonical analysis of thermodynamic quantities, the most apparent indicators for transition signals of finite systems are peaks and "shoulders" in thermodynamic quantities. For the polymer with 250 monomers that we study here, the specific heat and fluctuations of the radius of gyration are plotted in Figs. 1(left) and 1(right), respectively. Both quantities indicate three transitions, the well-known Θ collapse transition between random-coil conformations and globular structures ("gas-liquid"), the crystallization of globules into solid structures with icosahedral nucleus ("liquid-solid"), and a "solid-solid" transition that only affects the surface layer of the crystalline structure. Although both quantities signal all transitions (which is not always the case for a finite system), it is not simple to locate the transition points. Table 1 lists estimates of transition temperatures obtained by this conventional analysis.

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[1] This can be seen as a trivial solution of the Descartes' rule of signs. In particular, as $g_0 > 0$, zero is not a root of Z either.

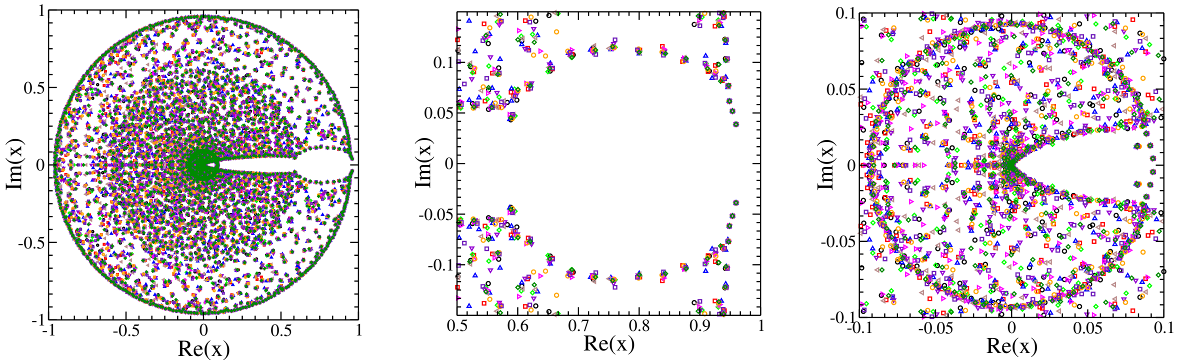

Fig. 2. *Left:* Maps of all Fisher zeros from 10 independent simulations (different symbols), *Center:* Zoom into the rightmost section; the leading zeros near $x = 0.59 \pm 0.05i$ indicate the Θ collapse transition, *Right:* Zoom into the central section of the zeros maps; the strongly first-order-like liquid-solid transition is represented by $x \approx 0.093 \pm 0.004i$, whereas the leading zeros at $x \approx 0.083 \pm 0.012i$ are associated with the solid-solid transition.

Table 1. Comparison of transition temperatures for solid-solid (ss), liquid-solid (ls), and gas-liquid (gl) transitions for the 250-mer as obtained by the partition function zero method (T_Z), compared to peak positions of the heat-capacity curves (T_{cV}) and fluctuations of the radius of gyration ($T_{d\langle r_{\rm gyr}\rangle/dT}$), respectively.

solid-solid			liquid-solid			gas-liquid		
$T_{\rm z}^{\rm ss}$	$T_{\rm cv}^{\rm ss}$	$T_{d\langle r_{\rm gyr}\rangle/dT}^{\rm ss}$	$T_{\rm z}^{\rm ls}$	$T_{\rm cv}^{\rm ls}$	$T_{d\langle r_{\rm gyr}\rangle/dT}^{\rm ls}$	$T_{\rm z}^{\rm gl}$	$T_{\rm cv}^{\rm gl}$	$T_{d\langle r_{\rm gyr}\rangle/dT}^{\rm gl}$
0.40 ± 0.01	0.39 ± 0.01	0.36 ± 0.01	0.41 ± 0.01	0.41 ± 0.01	0.41 ± 0.01	1.87 ± 0.03	1.80 ± 0.05	1.92 ± 0.02

The thus determined transition points of an individual transition are not necessarily very close as the example of the gas-liquid transition shows. This uncertainty is an apparent disadvantage of this kind of analysis.

Since the analysis method based on leading Fisher zeros does not depend on a specific system property but only globally on the most fundamental statistical quantity, the density of states (or, in this context, on the canonical partition function), transition temperatures obtained by this approach can be considered to be unique. Maps of the zeros for the 250-mer, obtained in 10 independent simulations, are shown in Fig. 2(left). Although there is a substantial variation of the location the zeros, which is due to the high sensitivity of the density of states with respect to numerical errors, the region near the cut along the positive real axis is well-shaped and the isolated leading zeros, obtained in the different simulations, coincide very well. This can be seen best in the magnified sections in Figs. 2(center) and Figs. 2(right). Remembering that $x \to 1$ corresponds to $T \to \infty$, and also noting that the density of states was cut in the irrelevant high-energy region for simulation efficiency, the only zeros of interest in Fig. 2(center) are those located near $x = 0.59 \pm 0.05i$. According to Eq. (6), this corresponds to a transition temperature $T_{\rm z}^{\rm gl} \approx 1.87$. The vertical lines in Fig. 1 at this value lie close to the peak positions in the specific heat and the fluctuations of the radius of gyration. Therefore, we can conclude that these leading zeros indicate the gas-liquid (Θ collapse) transition. The transition temperature estimated from the zeros method lies well in between the peak positions of the fluctuating quantities. Comparing the numerical values in Table 1 and taking into account the numerical error, it perfectly interpolates the estimates from the thermodynamic quantities.

Repeating this procedure for the liquid-solid and the solid-solid transition by making use of the leading zeros obtained from the maps shown in Fig. 2(right) and by comparing with the temperatures, where the fluctuations indicate extremal thermal activity (see Table 1), we find, in particular, excellent agreement of all values for the liquid-solid transition. The solid-solid transition is thermodynamically rather ill-defined (the solid phases are not well separated in energetic and structural spaces), both specific heat and fluctuations of global structural quantities such as the radius of gyration are not sufficiently sensitive to indicate this transition very well. On the other hand, the isolated zeros found at $x \approx 0.083 \pm 0.012i$ ($T_{\rm z}^{\rm ss} \approx 0.40$), located clearly separate from the liquid-solid zeros at $x \approx 0.093 \pm 0.004i$ ($T_{\rm z}^{\rm ls} \approx 0.41$), evidently suggest the existence of this additional transition. The reason for the existence of the solid-solid transition and also its weakness for the 250-mer lies in the fact that this polymer crystallizes into a structure with icosahedral core (that in the ground state contains 147 monomers) with an incomplete surface shell. While in the first solid phase that lies between the liquid-solid and the solid-solid transition points, anti-Mackay (or hcp) overlayers dominate, a further optimization toward lower temperatures leads to a Mackay (or fcc) arrangement of surface monomers. It is known that if the chain length were slightly larger than 250, but smaller than 309 (the "magic" length with complete overlayer), the solid-solid transition would be consumed by the liquid-solid transition and the anti-Mackay solid phase pre-empted by the Mackay phase [Schnabel et al. (2009a,b, 2011a); Seaton et al. (2010)].

The liquid-solid transition is a first-order-like transition and the coexistence of states in a certain energetic interval (quantified by the latent heat) results in a circular arrangement of the zeros in this region. This can nicely be seen in Fig. 2(right). This feature is not present in the other cases, which is why we classify those as second-order transitions. Thus, the zero maps are not only very helpful for the location of transitions, but also their classification is possible.

4. Summary

Our analysis of Fisher partition function zeros for a flexible, elastic polymer with 250 monomers and the comparison with the conventional analysis of canonical response quantities has shown that leading Fisher zeros are safe and robust indicators of conformational transitions of a finite polymer. Since in contrast to the conventional approach there are no ambiguities in defining the transition points and, furthermore, a classification of the transitions is possible, this method is an excellent and rather simple alternative to the direct analysis of the microcanonical entropy and the association of transition points with inflection points of the microcanonical temperature [Schnabel et al. (2011a)]. For the 250-mer, we clearly confirm the existence of three conformational transitions: the expected Θ collapse (gas-liquid), crystallization (liquid-solid), and an additional solid-solid transition that is due to monomer re-ordering on the surface layer of the icosahedral solid structures.

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