Multiple Singularities of the Equilibrium Free Energy in a One-Dimensional Model of Soft Rods

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There is a misconception, widely shared among physicists, that the equilibrium free energy of a one-dimensional classical model with strictly finite-ranged interactions, and at nonzero temperatures, cannot show any singularities as a function of the coupling constants. In this Letter, we discuss an instructive counterexample. We consider thin rigid linear rods of equal length 2ℓ whose centers lie on a one-dimensional lattice, of lattice spacing a. The interaction between rods is a soft-core interaction, having a finite energy U per overlap of rods. We show that the equilibrium free energy per rod $\mathcal{F}[(\ell/a),\beta]$, at inverse temperature β, has an infinite number of singularities, as a function of ℓ/a.

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There is a common belief among physicists that in any one-dimensional (1D) classical system, in thermal equilibrium, having strictly finite-ranged pairwise interactions, the thermodynamic potential cannot show a singular dependence on the control parameters [1]. The origin of this folk wisdom is perhaps an unsubstantiated generalization of a rigorous result due to van Hove [2] on the absence of phase transitions in a one-dimensional system of particles with a nonvanishing hard-core length and finite-ranged interparticle interaction. This result was later extended to lattice models [3] and long-ranged interactions having a power-law decay with distance [4–6]. The belief relies on essentially two (correct) arguments: one, about the absence of phase transitions as a function of temperature in 1D models having a finite-dimensional irreducible transfer matrix and second, the Landau argument about the absence of symmetry breaking in 1D systems, when creating a domain wall has a finite energy cost [7]. Several counterexamples of equilibrium phase transitions in 1D models have been known for a long time: DNA unzipping [8,9], interface depinning [10], hidden-state model [11], and condensation in zero-range models [12]. But, the incorrect belief persists. A necessary and sufficient condition for the existence of phase transitions in 1D systems is hard to formulate. This question was discussed in some detail recently by Cuesta and Sanchez [13], who provided a sharper criteria for the absence of phase transitions, based on a generalized Perron-Frobenius-Jentzsch theorem. The general understanding is that singularities in the free energy come from the degeneracy of the largest eigenvalue of the transfer matrix which can occur when the conditions required for the Perron-Frobenius-Jentzsch theorem to hold are not met.

In this Letter, we discuss an example of a 1D system that undergoes an *infinite* number of phase transitions, even though the largest eigenvalue remains nondegenerate. The singularities are robust, geometrical in origin, and come from the singular changes in the Boltzmann weights as a function of the separation between particles (for a similar origin of singularities in pair-correlation function of 2D disks see [14]). This is a simple, instructive example, and it uses a different mechanism of generating singularities in the thermodynamic functions than the earlier models studied. In particular, it gives singular behavior even for finite systems.

In its simplest version, the model consists of soft linear rigid rods of equal length 2ℓ, whose midpoints are fixed at the lattice sites of a 1D lattice of lattice spacing a. The rods are free to rotate in the plane, as illustrated in Fig. 1, where a configuration of N rods is specified by a set of N angles θ_i, with $0 \le \theta_i \le \pi$, for $i = 1$ to N. We assume that there is an interaction between the rods, which depends on their overlap. Each overlap between a pair of nearest neighbor rods costs a constant energy U_1; between a pair of next nearest neighbors the overlap energy is U_2, and so on.

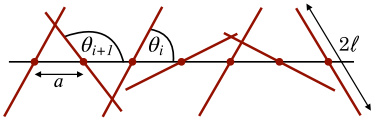

FIG. 1. A configuration of seven rods on a line. Here, a is the spacing between rods. In the displayed configuration, the number of nearest neighbor overlaps $n_1 = 3$ and the number of next nearest overlaps $n_2 = 1$.

Let n_r be the number of pairs of the rth neighbor rods that overlap (see Fig. 1). Clearly, n_r is zero, if $r > (2\ell/a)$. The total energy of the system is

$$\mathcal{H} = \sum_i n_i U_i. \tag{1}$$

This is similar to the hard-rod model that has been studied a lot in the literature, starting with Onsager [15–18]. It differs in two significant ways: the centers of the rods are fixed on a lattice, and we allow U_i to be of any sign (attractive or repulsive). A somewhat similar model of nonspherical molecules whose centers are fixed at equispaced points along a line, but orientations can change, was studied in [16].

Let $\mathcal{F}[(\ell/a) = \kappa, \beta]$ denote the free energy per rod of this system, in equilibrium, at inverse temperature β. We will show that $\mathcal{F}(\kappa, \beta)$ is an analytic function of β, as expected, but has a nonanalytic dependence on κ. In fact, there are infinitely many transitions: as κ is varied, $\mathcal{F}(\kappa, \beta)$ is singular at every positive integer values of κ, for all β. The singularities remain unchanged irrespective of the sign of U_i, whether the interaction is repulsive or attractive. We will show that there are also other singularities at some noninteger values of κ. For example, the probability distribution of orientations changes qualitatively when κ is changed across $1/\sqrt{2}$.

For simplicity of presentation, we begin with the simple case: $U_1 = \infty$. This is the case of hard rods, where no nearest-neighbor overlaps are allowed, thus $n_i = 0$ for all $i \geq 1$. Then, without loss of generality, we may assume $U_i = 0$ for all $i \geq 2$, which corresponds to only nearest neighbor hard-core interactions. In this case, let $\mathcal{F}_1(\kappa)$ denote the free energy per site in the thermodynamic limit (due to hard-core interactions it has no dependence on β and is hence omitted). Then, using the transfer matrix technique, $\mathcal{F}_1(\kappa) = -\log \Lambda(\kappa)$, where $\Lambda(\kappa)$ is the largest eigenvalue of the integral equation

$$\Lambda(\kappa)\psi_\kappa(\theta) = \int_0^\pi \frac{d\theta'}{\pi} T_\kappa(\theta, \theta')\psi_\kappa(\theta'), \tag{2}$$

with $\psi_\kappa(\theta)$ being the associated eigenvector. The transfer matrix $T_\kappa(\theta', \theta)$ has matrix elements 0 or 1 depending on whether a pair of nearest neighbor rods with angles (θ', θ) overlap or not.

We will show below that this system shows three types of singularities: (i) $\mathcal{F}_1''(\kappa)$ is discontinuous at $\kappa = 1/2$, (ii) for κ near 1, say $\kappa = 1 + \varepsilon$, with $|\varepsilon| \ll 1$, $\mathcal{F}_1'(\kappa)$ diverges as $\log(|\varepsilon|)$, and (iii) for $(1/\sqrt{2}) < \kappa < 1$, the probability distribution of orientations $P_\kappa(\theta)$ has square-root singularities as a function of θ, which are not present for lower values of κ.

The numerical verification of these analytical results is shown in Figs. 2–4, obtained by numerically diagonalizing the transfer matrix, using 1000 grid points for the integration range of $\theta = [0, \pi]$. In Fig. 2, $\mathcal{F}_1'(\kappa)$ is exactly zero for $\kappa < 1/2$, and nonzero for $\kappa > 1/2$, initially increasing linearly. Near $\kappa = 1$, it has a sharp peak. In Fig. 3, $\mathcal{F}_1'(\kappa)$ shows a nearly linear dependence on $\log|\kappa - 1|$.

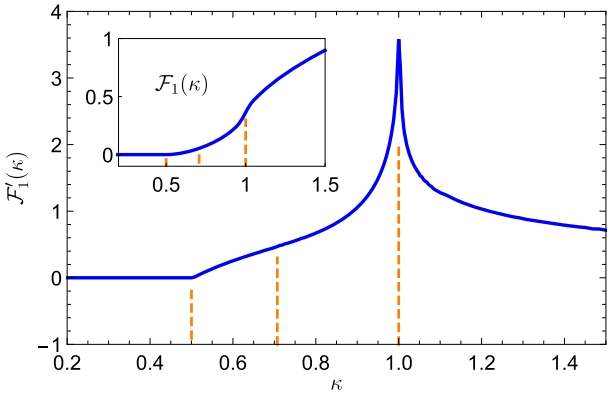

FIG. 2. First derivative of the free energy $\mathcal{F}_1'(\kappa)$ for hard-core nearest neighbor interaction between rods ($U_1 = \infty$). The inset shows the monotonic increase of $\mathcal{F}_1(\kappa)$ as a function of κ.

We determine the probability distribution of orientations $P_\kappa(\theta)$ from the eigenvector $\psi_\kappa(\theta)$ of the transfer matrix. This is plotted in Fig. 4. For $\kappa < 1/2$, all angles are equally likely, and $P_\kappa(\theta)$ takes a constant value π^{-1}. For $1/2 < \kappa < (1/\sqrt{2})$, $P_\kappa(\theta)$ has a nontrivial dependence on θ when $|\cos\theta| > (1/2\kappa)$, but the derivative $P_\kappa'(\theta)$ remains finite. In the range $(1/\sqrt{2}) < \kappa < 1$, $P_\kappa(\theta)$ has a square-root cusp singularity, when $\sin\theta = \kappa$. There is no clear signature of this singularity in the functional dependence of $\mathcal{F}_1(\kappa)$ on κ.

The source of these singularities is geometric in nature, and can be seen most simply in the structure of the transfer matrix. This is illustrated in Fig. 5. Here, the shaded regions in the θ-θ' plane correspond to values of (θ, θ') where the rods intersect, and the matrix element $T_\kappa(\theta, \theta')$ is 0, whereas the plain regions correspond to nonintersecting rods, and the matrix element $T_\kappa(\theta, \theta')$ is 1. The equation of

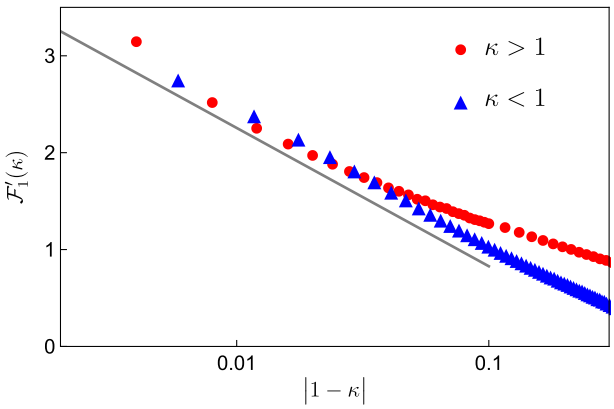

FIG. 3. Logarithmic divergence of the first derivative of the free energy $\mathcal{F}_1'(\kappa)$ near $\kappa = 1$, for $U_1 = \infty$.

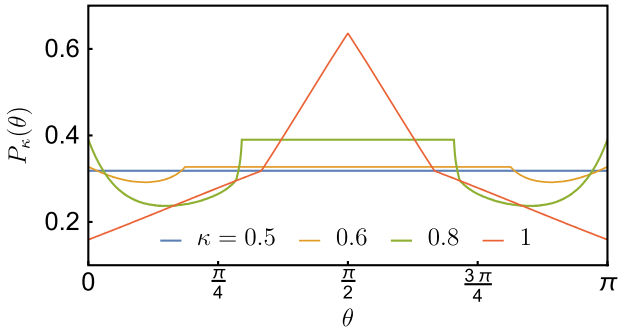

FIG. 4. Probability distribution of the orientation of the rods generated from the eigenvector $\psi_\kappa(\theta)$ associated to the largest eigenvalue of the transfer matrix.

the boundary of the shaded region is easily written down from simple geometry (see Supplemental Material [19] for details). As κ is increased, the shaded regions grow in size, and the eigenvalue of the transfer matrix decreases. For $(1/\sqrt{2}) < \kappa < 1$, the slope of the boundary of the shaded region becomes infinite or zero at some points. When $\kappa = 1$, the boundary becomes a set of straight lines. For $\kappa > 1$, the two shaded patches, which are disjoint when $\kappa < 1$, merge into a single connected shaded region. We will show that precisely these topological changes in the structure of the available phase space lead to the singularities in the free energy function $\mathcal{F}_1(\kappa)$. As noted above, these arguments hold even for finite systems.

Let us first discuss the singularity at $\kappa = 1/2$. For $\kappa < 1/2$, no overlap is possible, and the rods can orient freely without any cost of energy. The associated transfer matrix $T_\kappa(\theta', \theta) = 1$ for all angles, and there are no shaded regions. The largest eigenvalue is $\Lambda(\kappa) = 1$ and the corresponding eigenvector $\psi_\kappa(\theta) =$ constant. As κ is increased beyond $1/2$ the nearest neighbor interaction sets in. If we define $\kappa = (1/2) + \varepsilon$, then it is easily seen that

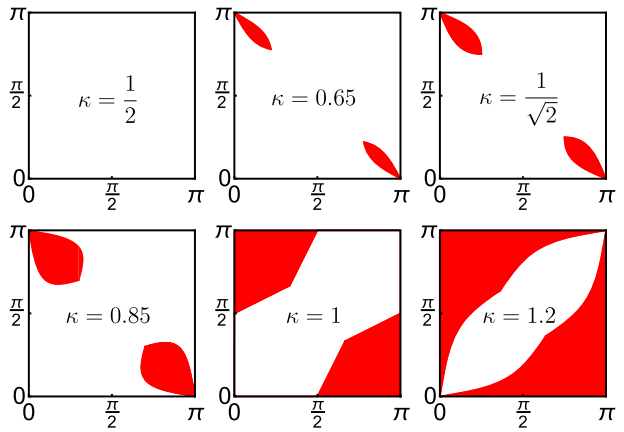

FIG. 5. The transfer matrix $T_\kappa(\theta', \theta)$ on the θ-θ' plane, for different values of κ. The shaded regions denote (θ, θ') values where the rods overlap, and $T_\kappa = 0$. In the plain regions rods do not overlap and $T_\kappa = 1$.

for small $\varepsilon > 0$, the area of the shaded regions in the θ-θ' plane grows as ε^2. Then, treating the shaded regions as perturbation, the first order perturbation theory immediately gives

$$\Lambda(1/2 + \varepsilon) = 1 - C\varepsilon^2 + \text{higher order in } \varepsilon. \quad (3)$$

We find that the constant $C = (32/3\pi^2)$ (details in the Supplemental Material [19]). Thus, at $\kappa = 1/2$, the second derivative of the free energy $\mathcal{F}_1''(\kappa)$ with respect to κ is discontinuous.

We now discuss the singularity at $\kappa = 1$. For this value, the boundary of the excluded region in the θ-θ' plane becomes a set of straight lines (see Fig. 5). Then, the transfer matrix $T_\kappa(\theta', \theta)$ can be exactly diagonalized by converting the integral eigenvalue equation (2) into a second order differential equation (see Supplemental Material [19]). We find that the largest eigenvalue of the transfer matrix for $\kappa = 1$ is given by $\Lambda(1) = [3\sqrt{2}\arcsin(1/3)]^{-1}$. For κ near 1, if we write $\kappa = 1 - \varepsilon$ and define $\Delta T = T_{1-\varepsilon} - T_1$, then, to the first order in ε, the change in the eigenvalue $\Lambda(\kappa)$ equals $\langle\psi_1|\Delta T|\psi_1\rangle$, where $\psi_1(\theta)$ is the eigenvector of the transfer matrix corresponding to the largest eigenvalue at $\kappa = 1$. This change is shown in Fig. 6. The curved boundary of the disallowed region near $(\theta, \theta') \equiv [0, (\pi/2)]$ tends to a hyperbola, and as ε tends to zero, the area of the shaded region in Fig. 6 tends to zero, but only as $\varepsilon \log(1/\varepsilon)$. Moreover, the eigenvector $\psi_1(\theta)$ is positive everywhere, with the ratio between its maximum and minimum values remaining finite. This implies that the change in the matrix element has the same qualitative dependence on ε as the area of the shaded regions. Therefore, we conclude that

$$\Lambda(1 - \varepsilon) = \Lambda(1) + K_1\varepsilon\log\frac{1}{\varepsilon} + K_2\varepsilon + \text{higher order}, \quad (4)$$

where K_1 and K_2 are positive constants. A similar argument holds for negative ε (see Supplemental Material [19]).

We now discuss the singularity at $\kappa = (1/\sqrt{2})$. For this, we consider the range $(1/\sqrt{2}) < \kappa < 1$, and define $\theta_0 = \arcsin\kappa$. Then, as long as the angle of a rod $\theta \in [\theta_0, \pi - \theta_0]$, it can be easily seen, that there is no overlap with its neighbor for any angle θ' of the latter. On the other hand, if

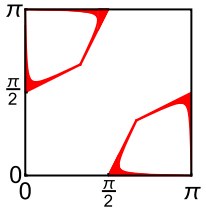

FIG. 6. The picture shows the matrix $\Delta T = T_{1-\varepsilon} - T_1$, for $\varepsilon = 0.02$ on the θ-θ' plane. In the shaded region $\Delta T = 1$, whereas in the plain region it is 0. The area of the shaded region varies as $\varepsilon \log(1/\varepsilon)$, for small ε.

θ is outside this interval, the rods can intersect, if θ' lies in the intervals $[\phi_1, \phi_2]$ and $[\pi - \phi_2, \pi - \phi_1]$, with the expression for ϕ_1 and ϕ_2 given in the Supplemental Material [19]. The important point is that the length of the intervals $|\phi_2 - \phi_1|$ varies as $\sqrt{\theta_0 - \theta}$ for $\theta \to \theta_0$. Then, from the eigenvalue equation (2), we see that

$$\psi_\kappa(\theta) = K_3 - K_4 \int_{\phi_1(\theta)}^{\phi_2(\theta)} \psi_\kappa(\theta') d\theta', \tag{5}$$

where K_3 and K_4 are functions of κ only. Using this fact that $\psi_\kappa(\theta')$ is bounded by nonzero constants, both from above and below, we see that, for θ approaching θ_0 from below

$$\psi_\kappa(\theta) \approx K_3 - K_5 \sqrt{\theta_0 - \theta}, \tag{6}$$

where K_5 depends only on κ. This shows that $\psi_\kappa(\theta)$ has a cusp singularity at $\theta = \theta_0$. As the probability density $P_\kappa(\theta)$ is proportional to $\psi_\kappa(\theta)^2$, it also has a cusp singularity at θ_0.

Our above arguments can be readily generalized to the case of soft rods ($U_1 \neq +\infty$), but keeping $U_i = 0$ for $i > 1$. The matrix ΔT only gets multiplied by a factor $(1 - e^{-\beta U_1})$. In fact, one can even determine the exact eigenvalues of the transfer matrix at $\kappa = 1$, for an arbitrary pair-potential U_1. This is given by (see Supplemental Material [19])

$$\Lambda(1) = \frac{(1 - e^{-\beta U_1})}{3\sqrt{2}} \left(\arctan \frac{(1 - e^{-\beta U_1})}{\sqrt{2}(2 + e^{-\beta U_1})} \right)^{-1}. \tag{7}$$

For soft pairwise interactions, overlaps between pairs of rods beyond the nearest neighbors are allowed. In the case, where such overlaps cost a nonzero amount of energy, i.e., $U_i \neq 0$ for $i > 1$, one can treat these pair interactions U_i, as perturbations to the problem with only nonzero U_1. Noting that the overlap region in the (θ_j, θ_{j+i}) plane, for $i > 1$, again has a similar hyperbolic shape, we see that at all integer values of $\kappa = i$ the largest eigenvalue $\Lambda(\kappa)$ has singularities of the form $U_i(i - \kappa) \log |[1/(\kappa - i)]|$.

In Fig. 7, we present evidence of these additional transitions from Monte Carlo simulations. We took $U_i = 1$ for all i. Clearly, $\langle \theta \rangle = (\pi/2)$, for all κ. A signature of the transitions can be seen in the variance of the angle defined by $\langle M^2 \rangle = (1/N) \langle \{ \sum_i [\theta_i - (\pi/2)] \}^2 \rangle$. The variance clearly shows a singularity at all integer values of κ. Also, the positions of the singularities do not depend on the value of β, as long as it remains nonzero.

It is clear that the conditions for applicability of the van Hove theorem are not met. As the theorem demands, the matrix elements are analytic functions of β; however, in our case they are nonanalytic (in fact discontinuous) functions of the control parameter κ. This nonanalyticity is generic to all hard-core (or soft-core) models, and is at the root of the singular behavior found in the problem discussed here.

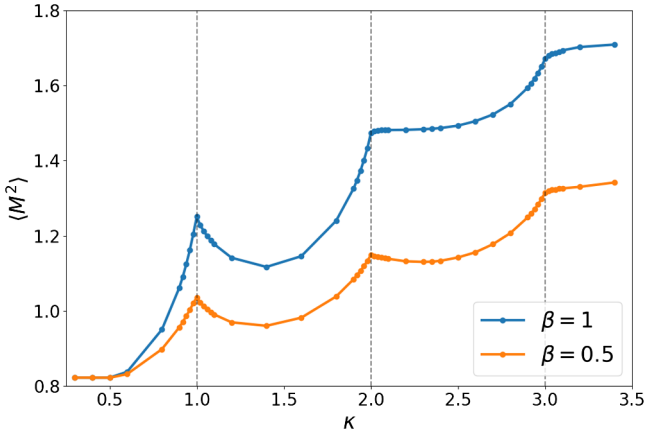

FIG. 7. Variance of the angular distribution of rods generated from Monte Carlo simulations of a system of 100 rods and averaged over 10^6 sample configurations.

The free energy $F(\kappa, \beta)$ is a nonconvex function of κ (see inset of Fig. 2). Here, κ is a parameter that specifies the number of rods per unit length, and convexity of the free energy as a function of density is a fundamental property, which is essential for thermodynamic stability. In our model, the spacing between particles is fixed and cannot be changed. Hence a convex envelope construction, in the manner of Maxwell, is not possible, and convexity is not assured. In fact, if the spacing between rods is allowed to vary, then the free energy has no singularities, in agreement with all the previous studies of this model [16–18].

Additionally, for all finite κ, the correlation length remains finite, as the largest eigenvector remains nondegenerate. Moreover, the behavior of the free energy is different from the familiar first order phase transitions. Here, the first derivative of the free energy *diverges* near the transition points, but the correlation length remains finite.

It is easy to construct other models which show similar behavior. For example, consider a chain of Ising spins σ_i, placed on a lattice of uniform spacing a. The Hamiltonian of the system is $H = -\sum_{(i,j)} J(r_{ij}) \sigma_i \sigma_j$, where $J(r)$ is a distance-dependent exchange interaction $J(r)$, and r_{ij} is the distance between the sites i and j. If we choose, $J(r) = 1 - r$, for $0 < r < 1$, and zero for $r > 1$, there is no long-range order in the problem. However, as the lattice spacing a is varied, the free energy becomes a nonanalytic function of a, at all integer values of $1/a$, following the same reasoning as in our model.

Varying lattice spacing is not merely a theoretical possibility. In molecular solids [20] thermal expansion can change the lattice spacing, in a polymer chain [21] they can be stretched using optical tweezers. In cold atoms lattice spacing can be directly controlled [22]. We hope that the transitions discussed here can be experimentally realized, in systems with large elastic constants, which suppresses local fluctuations in atom spacings, or in experiments in optical lattices, especially as it occurs also in finite systems.

In summary, we have discussed a mechanism of phase transitions, which is simple, but has not been sufficiently emphasized in the past. We have illustrated this mechanism with the example of a model of soft rods on a lattice in 1D with short range interactions, which shows an infinite number of phase transitions. One would expect similar behavior to occur for objects of different shapes and even in higher dimensions. These will be reported in a future publication [23].

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