Analytic Model of the Schottky Anomaly and Phase Transition

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The Schottky anomaly is a peak in the specific heat at low temperatures without divergence, in contrast to a phase transition which is characterized by a singularity of a physical quantity. A model with the analytic form of a density function, where both the phase transition and the Schottky anomaly appear depending on the limit of the model parameters, is presented. The model allows a unified analytic treatment of the phase transition and the Schottky anomaly.

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I. INTRODUCTION

The Schottky anomaly is a peak in the specific heat that appears at low temperature in systems with a finite number of discrete energy levels [1]. In contrast to the peak originating from a phase transition, which becomes singular in the thermodynamic limit, the Schottky anomaly is characterized by a finite peak. Because the Schottky anomaly contains information on the low-lying energy levels of the system, it has been a research topic of much interest [2–25].

All the information on the thermodynamic properties, including the phase transitions and the Schottky anomaly, is contained in the density of states, the number of microstates for a given energy value, because all the physical quantities can be computed from the density of states. For most physical systems, the density of states is an increasing function of energy, and this leads to the dominance of the energy effect and the entropy effect at low and high temperatures, respectively. This temperature-dependent conflict between the energy and the entropy effect, is a necessary condition and the direct cause of the phase transition if it exists. On the other hand, the Schottky anomaly arises due to the energy gap between the ground state and the first excited state, as well as the finite number of energy levels. Because the peak of the specific heat of the Schottky anomaly and the phase transition have distinct properties and physical origins, to have a simple toy model that provides a simple and clear picture of the physics underlying these phenomena would be interesting.

In this work, a simple analytic model for the density of states, where the energy levels are discrete with uniform spacing, and the number of microstates either increases or decreases exponentially with energy, is presented. Both the Schottky anomaly and the phase transition are shown to appear depending on the limits of the model parameters. In consideration of the fact that most previous theoretical studies, especially those on phase transitions, have been based on numerical studies of model Hamiltonians, an analytic solution is expected to provide much of the intuition that is lacking in numerical studies. Also, the current analytic model leads to a unified analytic treatment of both the Schottky anomaly and the phase transition and provides insight into their origins.

II. MODEL

For most physical systems, the densities of states are increasing functions of energy, leading to positive values of the microcanonical temperature. Also, this leads to the dominance of the energy and entropy effects at low and high temperatures, respectively, which is the direct cause of the phase transition when one exists. On the other hand, the Schottky anomaly appears for a system with discrete energy levels. Even for a system with an infinite number of energy levels, if there are discrete low-lying energy levels well separated from higher levels, the number of energy levels becomes effectively finite at low temperature, leading to a Schottky peak in the low-temperature region [2–25].

Therefore, in this work, a model with discrete energy levels, with the number of microstates being given as an exponential of the energy values, is considered. A finite number of energy levels, which will be denoted as \( N \), will be assumed to exist. That is, the energy levels and...
the density of states

\[ E = j\epsilon \quad (j = 0, \ldots, N), \]
\[ \Omega_j = Q^j \quad (j = 0, \ldots, N), \] (1)

where \( \Omega_j \) is the number of microstates with \( E = j\epsilon \) for \( \epsilon > 0 \), will be considered. The model is well defined for any positive real value of \( Q \). The microcanonical entropy is then defined as \( S_1 = k_B \log \Omega_j \), where \( k_B \) is the Boltzmann constant. Obviously, \( S_j \) is an increasing function of energy only for \( Q > 1 \), but the case for \( Q \leq 1 \) will also be considered.

An example of a microscopic Hamiltonian that gives rise to the energy levels in Eq. (1) with \( Q > 1 \) is a model of the sequential folding of a protein. A protein of size \( N + 1 \) with a spin-like variable \( \psi_i = 0, \ldots, Q \) at each bond \( i \) (\( i = 1, \ldots, N \)) is considered. The protein is then modelled by using the Hamiltonian

\[ H = \sum_{i=1}^{N} f(\psi_i), \] (2)

where \( f(0) \equiv 0 \) and \( f(x \neq 0) \equiv 1 \). For each bond, \( \psi_i = 0 \) is interpreted as a folded state and \( \psi_i > 0 \) as unfolded states with degeneracy \( Q \). The inequality \( \psi_i \leq \psi_j \) for \( i < j \) is assumed to be always true, that is, folding and unfolding can occur only in sequential order. Then, a partially folded state with energy \( E = j\epsilon \) has the form \( (\psi_1, \psi_2, \ldots, \psi_N) = (0, 0, \ldots, 0, \psi_{N-j+1}, \ldots, \psi_N) \), where \( j \) unfolded bonds \( \psi_{N-j+1}, \ldots, \psi_N \) can take any values among \( 1, \ldots, Q \), leading to the degeneracy of \( Q^j \).

The Hamiltonian in Eq. (2) is similar to a previous model that describes the sequential folding of a protein where \( Q = 1 \) was used [26] and to the \( \beta \)-hairpin of Muñoz-Eaton model where \( \Omega_j = (Q - 1)Q^{j-1} \) for \( j > 1 \), which approaches Eq. (1) when \( Q \gg 1 \) [27].

This work will not focus on any particular microscopic origin of Eq. (1), but simply take Eq. (1) as the starting point for the analysis, which is well defined for any real value of \( Q \). If various physical quantities are to be computed for a canonical ensemble, the partition function has to be introduced first, which is easily obtained from Eq. (1) as

\[ Z(\beta) = \sum_j e^{-\beta j\epsilon} \Omega_j = \sum_{j=0}^{N} e^{-\beta j\epsilon} Q^j \]
\[ = (1 - Q^{N+1} e^{-(N+1)\beta \epsilon})/(1 - Q e^{-\beta \epsilon}), \] (3)

where \( \beta \equiv 1/k_B T \), with \( T \) being the heat bath temperature.

### III. AVERAGE ENERGY AND SPECIFIC HEAT

Because the partition function is given in analytic form in Eq. (3), the specific heat can also be computed in analytic form. First, taking the log of the partition function, we get

\[ \ln Z = \ln(1 - Q^{N+1} e^{-(N+1)\beta \epsilon}) - \ln(1 - Q e^{-\beta \epsilon}). \] (4)

We then obtain the average energy and the specific heat by taking derivatives:

\[ \langle E \rangle = -\frac{d \ln Z}{d \beta} = \frac{(N+1)\epsilon Q^{N+1} e^{-(N+1)\beta \epsilon}}{1 - Q^{N+1} e^{-(N+1)\beta \epsilon}} + \frac{\epsilon Q e^{-\beta \epsilon}}{1 - Q e^{-\beta \epsilon}}, \]

\[ C = \frac{\partial \langle E \rangle}{\partial T} = k_B \beta^2 \frac{d^2 \ln Z}{d \beta^2} = k_B \beta^2 \epsilon^2 \left[ \frac{(N+1)^2 Q^{N+1} e^{-(N+1)\beta \epsilon}}{(1 - Q^{N+1} e^{-(N+1)\beta \epsilon})^2} + \frac{Q e^{-\beta \epsilon}}{(1 - Q e^{-\beta \epsilon})^2} \right]. \] (5)

In these expressions, the first and the second terms are separately divergent at \( k_B T = 1/\ln Q \), but cancel each other to give finite values of \( \langle E \rangle \) and \( C \) for all values of \( T \). The dimensionless quantities \( \langle E \rangle/\epsilon \) and \( C/k_B \) are plotted as functions of \( k_B T/\epsilon \) in Figures 1, 2, and 3 for \( Q = 2.0, 1.0 \) and 0.5, respectively.

1. Schottky anomaly

For a system with a finite number of discrete energy levels, a universal peak appears in the specific heat, called the Schottky anomaly [1]. This can be seen as follows: As \( T \rightarrow 0 \), \( \langle E \rangle \) approaches the ground-state energy \( E_0 \) because a gap exists between the ground state and the first excited state; therefore, only the ground state is populated in this limit. On the other hand, as \( T \rightarrow \infty \), all the microstates are occupied with equal probability, and because the number of energy levels is finite, \( \langle E \rangle \) approaches a finite value, which is an energy averaged over all microstates with equal weights and is clearly larger than \( E_0 \). Therefore, the specific heat vanishes both for \( T \rightarrow 0 \) and \( T \rightarrow \infty \), with a peak in the intermediate range of temperatures where \( \langle E \rangle \) increases.

Because our model system consists of a finite number of discrete energy levels, the condition is satisfied and,