

STRUCTURE FORMING PROCESSES IN
MESOSCOPIC POLYMER SYSTEMS

by

TOMAS KOCI

(Under the direction of Michael Bachmann)

ABSTRACT

This is going to be the best abstract ever :)

INDEX WORDS: Polymer Aggregation, Monte Carlo Simulations, Parallel Tempering,
Multicanonical Sampling, Canonical Analysis, Microcanonical
Inflection-Point Analysis, Flexible Polymer, Structural Transitions,
Finite Systems, Finite-Size Effects

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TOMAS KOCI

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Approved:

Major Professor: Michael Bachmann

Committee: Steven P. Lewis
Heinz-Bernd Schuttler

Electronic Version Approved:

Alan Dorsey
Dean of the Graduate School
The University of Georgia
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Chapter 1

Introduction

Kickass intro...

Chapter 2

Elements of Statistical Mechanics

Statistical mechanics aims at explaining the microscopic origins of macroscopic properties of systems with large numbers of degrees of freedom. The exact solution for a single phase space trajectory of a complex system requires enormous computational efforts and in most cases provides only a limited insight. In contrast to the chaotic nature of most phase space trajectories, collective system properties such as entropy, pressure, or temperature, for the most part exhibit relatively simple behavior. The formalism of statistical mechanics allows us to study these properties by considering the average behavior of a large number of identically prepared systems, i.e. the statistical ensemble. It is well established that in the thermodynamic limit all ensembles become equivalent. However this is emphatically not true in the case of intrinsically finite systems for which the choice of an ensemble is non-trivial. Therefore, I shall briefly discuss several prominent statistical ensembles starting with the most fundamental one, the *microcanonical ensemble*.

2.1 The microcanonical ensemble

Let us consider a mechanically and adiabatically isolated system with a constant number of particles (N), volume (V), and energy (E). At any given moment, the system is to be found in a particular microstate μ , which is represented by a point in a $6N$ dimensional phase-space. At a fixed energy E , the accessible microstates are constrained to the surface of constant energy $\mathcal{H}(\mu) = E$, where \mathcal{H} is the Hamiltonian of the system. The total number of microstates corresponding to a macrostate with a fixed energy E is obtained by calculating the density of states^{1,2}

$$g(E) = \int \mathcal{D}\mathcal{P}\mathcal{D}\mathcal{Q} \delta(E - \mathcal{H}(\mathcal{P}, \mathcal{Q})), \quad (2.1)$$

where

$$\mathcal{D}\mathcal{P}\mathcal{D}\mathcal{X} = \prod_{n=1}^N \frac{d^3 p_n d^3 x_n}{(2\pi\hbar)^3} \quad (2.2)$$

is the Lebesgue measure over phase space. Assuming that no additional quantities are conserved, i.e. the system is ergodic, all accessible microstates have equal a priori probabilities. The microcanonical equilibrium probability distribution is given by

$$p(\mu)_E = \begin{cases} 1/g(E), & \text{if } \mathcal{H}(\mu) = E \\ 0, & \text{if } \mathcal{H}(\mu) \neq E, \end{cases} \quad (2.3)$$

and the expectation value of an observable O at a fixed energy E is found by averaging over the surface of constant energy

$$\langle O \rangle_E = \int \mathcal{D}\mathcal{P}\mathcal{D}\mathcal{Q} O(\mathcal{P}, \mathcal{Q}) \delta(E - \mathcal{H}(\mathcal{P}, \mathcal{Q})). \quad (2.4)$$

¹In the context of computer simulations, the energy space becomes by necessity discretized and the density of states is determined by counting the number of microstates within some finite energy range $[E, E + \Delta E]$.

²Please refer to section 2.3 for detailed discussion of alternative definitions of the density of states.

The density of states of a typical mesoscopic system can easily span several thousands of orders of magnitude. It is therefore convenient to define the microcanonical equilibrium entropy

$$S(E) = k_B \ln g(E), \quad (2.5)$$

as an *extensive* quantity with dimensions of energy over temperature.³

2.1.1 Microcanonical temperature

Temperature is one of the fundamental concepts of statistical mechanics and has been traditionally defined in terms of the average kinetic energies of particles in a system. Here we motivate a more fundamental definition of temperature as an intrinsic system property, which can be obtained directly from the microcanonical density of states $g(E)$. For this purpose, let us consider an adiabatically isolated system composed of two weakly interacting subsystems, S_1 and S_2 . The energy of the combined system is fixed and can be written as the sum of the energies of the two subsystems $E = E_1 + E_2$. The probability density for a given pair of subsystem energies (E_1, E_2) is

$$\rho(E_1, E_2) = \frac{g_1(E_1)g_2(E - E_1)}{g(E)}, \quad (2.6)$$

where the density of states of the combined system is expressed as a convolution

$$g(E) = \int dE_1 g_1(E_1)g_2(E - E_1). \quad (2.7)$$

In systems with many degrees of freedom, the probability density $\rho(E_1, E_2)$ is a sharply peaked distribution around the equilibrium energies (\bar{E}_1, \bar{E}_2) ⁴. These can be found by setting

³If temperature is measured in the more natural units of energy, entropy becomes a unitless quantity and the Boltzmann constant equals to unity.

⁴The energy fluctuations per particle around the equilibrium energy \bar{E}_1 scale as $N^{-1/2}$.

the energy derivative of the probability density to zero, from which we obtain

$$\frac{1}{g_1} \frac{dg_1}{dE_1} \Big|_{\bar{E}_1} = \frac{1}{g_2} \frac{dg_2}{dE_2} \Big|_{E-\bar{E}_1}, \quad (2.8)$$

or alternatively in terms of the microcanonical entropy

$$\frac{dS_1}{dE_1} \Big|_{\bar{E}_1} = \frac{dS_2}{dE_2} \Big|_{E-\bar{E}_1}. \quad (2.9)$$

Motivated by the familiar observation that interacting systems at thermal equilibrium have equal temperatures, we define the microcanonical temperature as

$$T(E) = \left(\frac{dS(E)}{dE} \right)^{-1}. \quad (2.10)$$

Frequently, it is more convenient to consider the inverse microcanonical temperature defined as

$$\beta(E) = \frac{dS(E)}{dE}. \quad (2.11)$$

In the following section, we discuss the central role of inverse microcanonical temperature and its energy derivatives in the classification of structural phase transitions.

2.1.2 Microcanonical analysis of phase transitions

A macrostate of a system is specified by a set of macroscopic variables and possesses the characteristics of the predominant microstates. Macrostates are said to belong to the same thermodynamic phase, if in a given range of some external control parameters⁵ all of the system's thermodynamic observables are analytic, i.e. have convergent Taylor expansions. Singularities in the observables signify the presence of phase transitions between distinct

⁵Some common examples of external control parameters are the canonical temperature, pressure, or the chemical potential.

phases, typically marked by abrupt changes in macroscopic properties in response to minute variations of external control parameters. Phase transitions can be roughly divided into two categories. *Abrupt* transitions are characterized by the coexistence of two distinct phases and discontinuities in most physical properties. *Continuous* transitions, although less common in nature, have been the object of most intense research. They are marked by diverging correlation lengths, large fluctuations, and scale invariance.

Divergences and singularities in thermodynamic observables and their derivatives are only found in systems which satisfy the thermodynamic limit. In mesoscopic systems⁶, due to finite size effects, divergences are replaced by peaks and discontinuities are smoothed over. For clarity, we designate the term *pseudophase transition* to represent significant conformational changes in finite systems. Likewise, thermodynamic phases in finite systems shall be referred to as *pseudophases*. In the following, we present a powerful formalism for the analysis of pseudophase transitions in the microcanonical ensemble; the microcanonical inflection point analysis.

Microcanonical inflection-point analysis

Unlike its canonical counterpart – the heat-bath temperature – the microcanonical inverse temperature is an inherent property of the system, derived directly from the fundamental microcanonical quantities $S(E)$ and E . We assert that all essential information about energetically and entropically driven thermodynamic processes is contained in its curvature. Hence the microcanonical inverse temperature is an ideal starting point for a comprehensive analysis of pseudophase transitions.

In analogy to the principle of minimal sensitivity [1], structural transitions between pseu-

⁶Typical length scales in mesoscopic systems are of the order of $\sim 10^3$ nanometers. In this regime, exact quantum many-body interactions can be replaced by effective classical potentials, and cooperative effects dominate structure formation processes. Mesoscopic systems are distinct from macroscopic systems due to the presence of significant finite-size effects, which disallow the simplifying assumptions of the thermodynamic limit.

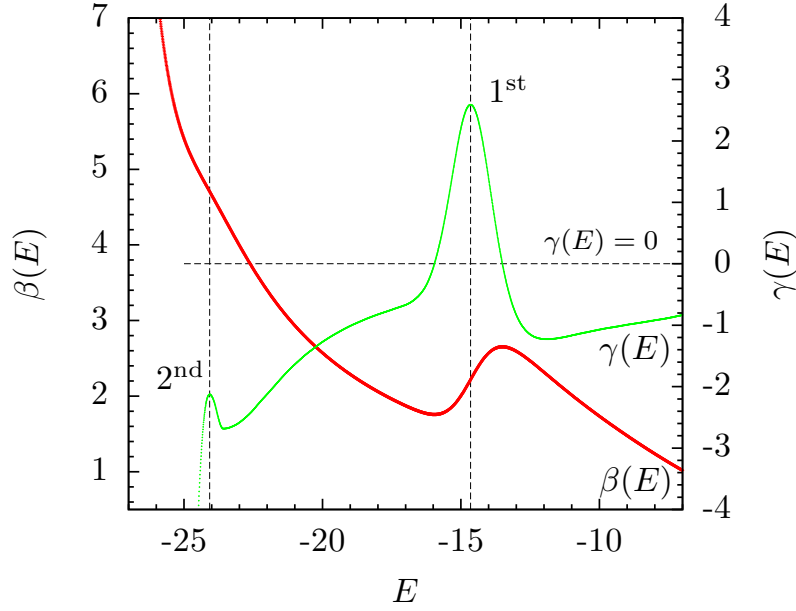


Figure 2.1: Microcanonical inflection-point analysis of the inverse microcanonical temperature $\beta(E)$. The prominent back-bending region in $\beta(E)$, together with the positive-valued peak in its energy derivative $\gamma(E)$ at $E \approx -15$, indicates a *first-order* transition. The negative-valued peak at $E \approx -24$ corresponds to a *second-order* transition.

dophases occur when $\beta(E)$, or one of its energy derivatives, responds least sensitively to variations in energy. In particular, *first-order* transitions are associated with inflection points in $\beta(E)$ that have a positive slope, accompanied by positive-valued peaks in the energy derivative $\gamma(E) = d\beta(E)/dE$. Similarly, a *second-order* transition occurs when $\beta(E)$ exhibits an inflection point with a negative slope and $\gamma(E)$ attains a negative-valued peak. Examples of microcanonical *first-* and *second-order* transition signals are shown in Fig. 2.1. The formalism can be naturally extended to higher-order transitions. Inflection point in the $(2n)$ th-derivative of entropy, accompanied by a positive-valued valley in the $(2n + 1)$ th-derivative, indicates a $(2n + 1)$ th-order transition. Similarly, a $(2n)$ th-order transition is marked by an inflection point in the $(2n - 1)$ th-derivative of entropy and a negative-valued peak in the $(2n)$ th-order derivative.

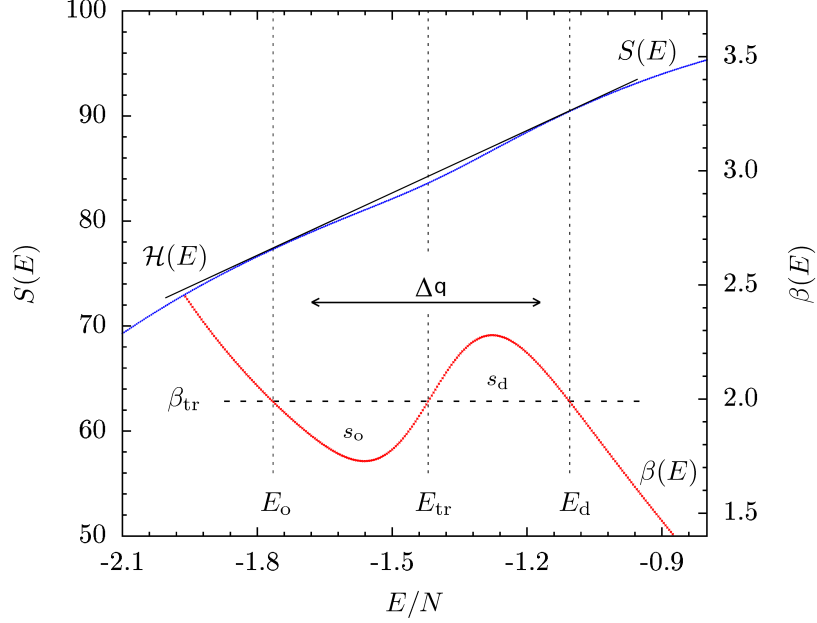


Figure 2.2: The convex region of the microcanonical entropy $S(E)$ and the back-bending of the microcanonical inverse temperature $\beta(E)$ are prominent indicators of *first-order* transitions. The slope of the double-tangent Gibbs hull $\mathcal{H}(E)$ defines the transition temperature β_{tr} . The Maxwell construction, defined by equal areas of s_o and s_d , is itself positioned at β_{tr} . The transition energy E_{tr} indicates the location of the largest separation between $\mathcal{H}(E)$ and $S(E)$, which signifies maximal entropic suppression of the transition states. The latent heat ΔQ corresponds to the width of the transition region between E_d and E_o .

Alternatively, for *first-order* transitions the transition temperature β_{tr} can be obtained by the means of the Maxwell construction, which was originally introduced to repair the unphysical back-bending in the pressure versus volume phase diagram for the van der Waals gas. However, in mesoscopic systems, finite-size effects lead to entropic suppression of the transition states, which is manifested in the backbending of $\beta(E)$ and the convex intruder in $S(E)$. Figure 2.2 shows an example of a Maxwell construction. Its position is determined by the equality of the areas s_o and s_d . Often referred to as *surface entropies*, s_o and s_d are

defined in terms of the integrals

$$s_o = \int_{E_o}^{E_{tr}} dE (\beta_{tr} - \beta(E)), \quad (2.12)$$

$$s_d = \int_{E_{tr}}^{E_d} dE (\beta(E) - \beta_{tr}). \quad (2.13)$$

There are three intersections between the Maxwell line and the inverse temperature at energies E_o , E_{tr} , and E_d . The separation between the boundary energies of the ordered pseudophase E_o and the disordered pseudophase E_d , corresponds to the latent heat $\Delta Q = E_d - E_o$. The transition energy E_{tr} indicates the location where the intermediate states experience maximal entropic suppression. The slope of the double-tangent Gibbs construction, also shown in Figure 2.2, provides yet another definition of β_{tr} . As a function of energy, the Gibbs hull is defined as

$$\mathcal{H}(E) = S(E_o) + \beta_{tr}[E - E_o], \quad (2.14)$$

where β_{tr} can be expressed in terms of the energy and entropy differences between the ordered and disordered pseudophases as

$$\beta_{tr} = \frac{S_d - S_o}{E_d - E_o} = \frac{\Delta S}{\Delta Q}. \quad (2.15)$$

With the exception of composite multi-step transitions, characterized by additional oscillations in the back-bending region of $\beta(E)$, the transition temperatures obtained by the means of the Maxwell and Gibbs constructions are identical.

The formalism of the microcanonical inflection-point analysis makes no reference to the thermodynamic limit. In fact, it is equally suitable for analysis of macroscopic and mesoscopic systems alike. This is in stark contrast to the more traditional canonical analysis which is defined under the assumption of the thermodynamic limit and has to be modified for the treatment of finite systems.

2.2 The canonical ensemble

The canonical ensemble describes the behavior of a closed system in thermal equilibrium with a large external heat bath at a fixed temperature T . In analogy to the density of states in the microcanonical ensemble, the partition function $Z(T)$ contains all the essential information about the thermodynamic properties of the system under consideration. It can be defined directly as a Laplace transform⁷ of the microcanonical density of states $g(E)$

$$Z(T) = \sum g(E) e^{-\frac{E}{k_B T}}, \quad (2.16)$$

where T is the canonical heat bath temperature and k_B is the Boltzmann constant. While the condition of thermal equilibrium prohibits any net average energy transfer between the system and the heat bath, the system can gain or lose energy through constant fluctuations and dissipations. This leads to the well known temperature dependent Boltzmann distribution, where the probability for a given microstate μ is given by

$$p(\mu) = \frac{1}{Z(T)} e^{-\frac{\mathcal{H}(\mu)}{k_B T}}, \quad (2.17)$$

and \mathcal{H} is the Hamiltonian of the system. The appropriate thermodynamic potential in the canonical ensemble is the Helmholtz free energy

$$F(T) = -k_B T \ln Z. \quad (2.18)$$

This quantity represents the energy available to perform work and can be used to obtain all other thermodynamic quantities by differentiation. The temperature derivative of the free

⁷Here we assume that the system under investigation has discrete energy levels, which is always true in the context of computational studies. In the case of a continuous energy spectrum, the discrete sum is replaced by the integral $Z(T) = \int dE g(E) e^{-\frac{E}{k_B T}}$.

energy defines the canonical entropy

$$S(T) = -\frac{\partial}{\partial T} F(T) \Big|_{N,V}, \quad (2.19)$$

which measures the amount of disorder in the system. The internal energy U is defined as a sum over all microstate energies weighted by the Boltzmann distribution

$$U(T) = \frac{\sum_{\mu} \mathcal{H}(\mu) e^{-\frac{\mathcal{H}(\mu)}{k_B T}}}{Z(T)} = \frac{\sum_E E g(E) e^{-\frac{E}{k_B T}}}{Z(T)} \quad (2.20)$$

and represents the average energy of the system. Alternatively, the internal energy can be obtained by differentiating the free energy

$$U(T) = k_B T^2 \frac{\partial}{\partial T} \ln Z \Big|_{N,V} = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \Big|_{N,V}. \quad (2.21)$$

The amount of energy needed to increase the temperature of the system by one unit is given by the specific heat C_V , defined as a temperature derivative of the internal energy

$$C_V(T) = \frac{\partial}{\partial T} U(T) \Big|_{N,V} = -T \frac{\partial^2}{\partial T^2} F(T) \Big|_{N,V}, \quad (2.22)$$

or differentiating the third term in equation 2.20 we get

$$\begin{aligned} C_V(T) &= \frac{\partial}{\partial T} \frac{\sum_E E g(E) e^{-\frac{E}{k_B T}}}{Z(T)} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \frac{\sum_E E g(E) e^{-\beta E}}{\sum_E g(E) e^{-\beta E}} \\ &= \frac{1}{k_B T^2} \left[\left(\frac{\sum_E E^2 g(E) e^{-\beta E}}{Z(T)} \right) - \left(\frac{\sum_E E g(E) e^{-\beta E}}{Z(T)} \right)^2 \right] \\ &= \frac{1}{k_B T^2} \left(\langle E^2 \rangle - \langle E \rangle^2 \right), \end{aligned} \quad (2.23)$$

where the last expression corresponds to the variance of the Boltzmann distribution. This result is of a profound physical importance, establishing the connection between the macroscopic response quantity C_V , and microscopic fluctuations.

2.2.1 Canonical analysis of phase transitions

Sudden dramatic changes in macroscopic properties, as a response to small variations of an external control parameter, indicate that the system under investigation is undergoing a phase transition. Here we consider temperature-driven transitions and apply a classification scheme similar to Ehrenfest's.

In the thermodynamic limit, it is generally possible to identify some property of the system which is non-zero in the ordered phase and zero in the disordered phase, i.e. the order parameter. A standard example is the magnetization m in a ferromagnetic system, where $m = 1$ in the ordered ferromagnetic phase and $m = 0$ in the disordered paramagnetic phase. The derivative of the order parameter with respect to its conjugate variable defines a response quantity⁸ which is discontinuous at the transition point. Order parameters also play a central role in the formulation of the Landau theory, where they are used as a basis for the expansion of the free energy around the transition point.

First order transitions are characterized by a jump discontinuity in the entropy, also expressible as the negative of the first temperature derivative of the free energy. This results in the coexistence of two distinct phases⁹ at the transition temperature, whose energetic separation corresponds to the latent heat

$$\Delta Q = T_{\text{trans}} \Delta S, \tag{2.24}$$

⁸In the case of the magnetization m , the appropriate conjugate thermodynamic variable is the external field H , and the corresponding response quantity is the magnetic susceptibility χ .

⁹As a familiar example, consider the coexistence of gas bubbles and liquid at the boiling point of water.

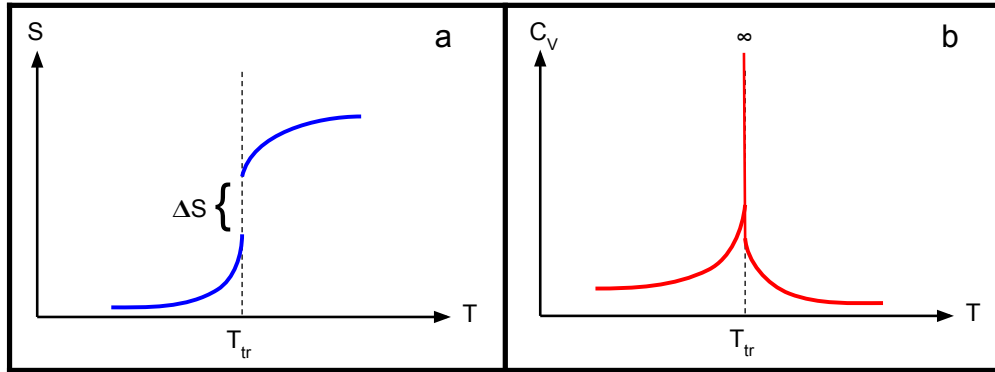


Figure 2.3: (Aa) The jump discontinuity in the canonical entropy S , and (b) the delta peak in the specific heat C_V , are characteristic of a first order phase transition.

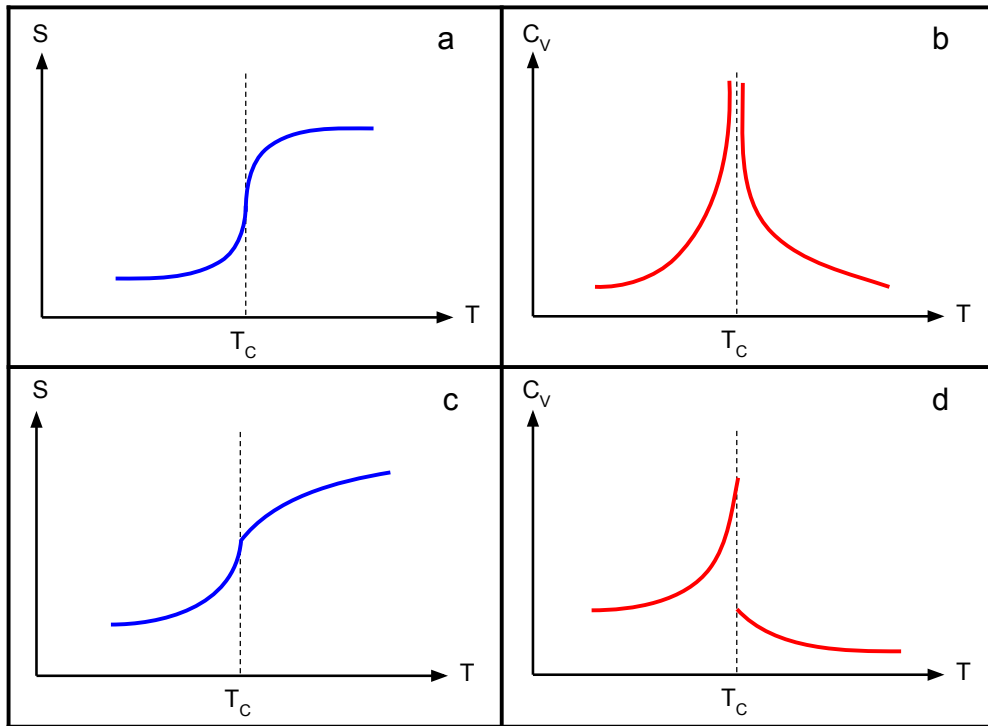


Figure 2.4: Second order transitions are characterized by discontinuities in response quantities, such as the specific heat. (a,b) In the case of a **critical** second order transition, the entropy S attains an infinite slope at T_c accompanied by a divergence in the specific heat C_V . (c,d) So called *lambda* transitions, do not exhibit criticality and are characterized by a jump discontinuity in C_V and a cusp singularity in entropy.

where ΔS is the height of the discontinuity. The specific heat C_V has a delta peak at the transition temperature, as shown in Fig. 2.3.

Second order transitions do not possess discontinuities in entropy, and for that reason are often called *continuous* transitions. Instead, discontinuities are found in the second derivative of the free energy with respect to temperature. It is customary to make use of the relationship shown in Eq. 2.22, and consider the specific heat C_V which also has the same discontinuities. In the vicinity of the transition point T_c , the specific heat exhibits a power law behavior $C_V(\tau) \propto |\tau|^{-\alpha}$, where $\tau = (T - T_c)/T_c$ and α is the associated critical exponent. Examples of common types of discontinuities of C_V are shown in Fig. 2.4. Other important quantities such as the magnetic susceptibility χ and the correlation length ξ also exhibit a power law behavior near the transition point, governed by the critical exponents γ and ν respectively.

Canonical analysis in mesoscopic systems

The description of phase transitions in the terms of discontinuities and divergences is valid only in the thermodynamic limit. In situations where the thermodynamic behavior of a system is affected by finite size effects, this idealized description no longer applies. Nevertheless, the numerous examples of abrupt changes of macroscopic properties in finite systems necessitate the generalization of the theory. In order to avoid possible confusion, we shall refer to significant conformational changes in finite systems as *pseudophase transitions*. Similarly, sets of macrostates with sufficiently similar macroscopic properties will be denoted *pseudophases*.

In the generalized formalism, peaks in the specific heat and other response quantities indicate regions of increased thermodynamic activity, i.e. pseudophase transitions. The order of the transition is determined from the shape of the canonical energy distribution in the transition region. Bimodal distributions reveal the coexistence of two pseudophases

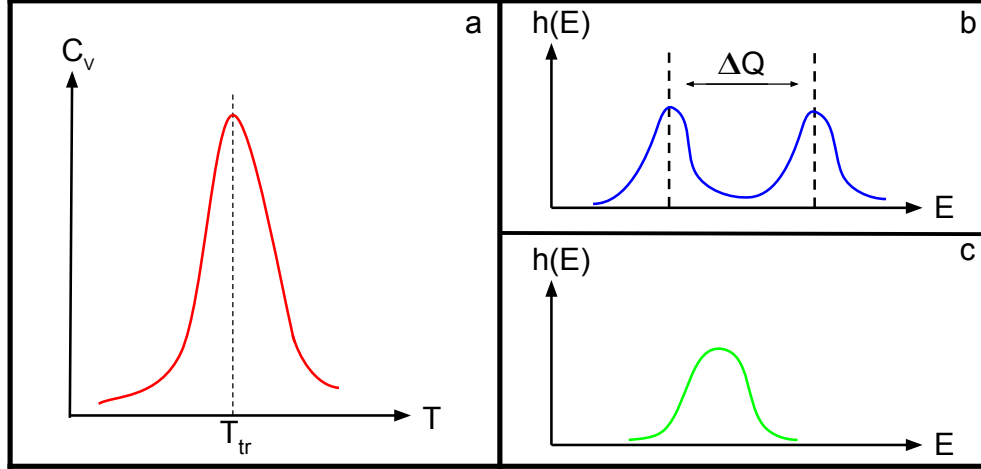


Figure 2.5: (a) The peak in the specific heat C_V indicates a region of heightened thermodynamic activity. (b) The two peaks in the bimodal canonical energy distribution correspond to the ordered and disordered pseudophases, energetically separated by the latent heat ΔQ . Pseudophase coexistence and latent heat are reliable indicators of a first-order pseudophase transition. (c) Second-order transitions are marked by wide unimodal energy distributions at the transition point.

and indicate a first-order transition, where the latent heat of the transition is given by the energetic separation of the two peaks in the distribution. Second-order transitions correspond to unimodal energy distributions. The power law behavior of response quantities contains significant finite-size corrections and in some cases is altogether not applicable. An example of canonical analysis, applied to first- and second-order pseudophase transitions, is illustrated in Fig. 2.5.

Here it should be mentioned that second-order pseudophase transitions do not always produce peaks in the specific heat. Therefore, it is necessary to investigate the behavior of several response quantities in order to obtain an accurate picture of the transition properties of the system under investigation. However, due to finite size effects, the signals obtained from different quantities will in general not coincide at a single transition temperature. This

fact further fortifies the argument that the microcanonical inflection-point analysis¹⁰, which defines a unique transition temperature in mesoscopic and macroscopic systems alike, is the natural formalism for the analysis of finite systems.

2.3 Configurational density of states

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¹⁰Introduced in Sec. 2.1.2

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Summary and Outlook

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Figure 8.1: Example of a figure.

Table 8.1: Example of a table.
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