

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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MESOSCOPIC POLYMER SYSTEMS

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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 the time evolution of every particle in a single complex system requires enormous computational efforts, and in most cases provides little insight. In contrast to the stochastic motion of microscopic particles in a thermal environment, 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 for very large systems near 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 [1]. Therefore, we shall briefly introduce several prominent statistical ensembles, starting with arguably 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 states¹

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

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 [2]. In computational studies, the energy space is by necessity discretized into intervals of width ΔE , and the density of states $g(E_i)$ is obtained by counting the microstates within a thin shell of width ΔE . Formally, $g(E_i)$ is a discrete function defined as

$$g(E_i) = \int_{E_i - \Delta E/2}^{E_i + \Delta E/2} g(E) dE, \quad (2.3)$$

where $g(E)$ in the integrand is the continuous density of states [1].

Assuming that no additional quantities are conserved, i.e. the system is ergodic, all accessible microstates have equal a priori probabilities [3]. The microcanonical equilibrium probability distribution is given by

$$p(\mu)_E = \begin{cases} 1/g(E), & \text{if } \mathcal{H}(\mu) = E \\ 0, & \text{if } \mathcal{H}(\mu) \neq E, \end{cases} \quad (2.4)$$

¹Please refer to section 2.3 for detailed discussion of alternative definitions of the density of states.

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

$$\langle O \rangle_E = \int \mathcal{D}\mathcal{P} \mathcal{D}\mathcal{Q} \ O(\mathcal{P}, \mathcal{Q}) \ \delta(E - \mathcal{H}(\mathcal{P}, \mathcal{Q})). \quad (2.5)$$

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

$$S(E) = k_B \ln g(E), \quad (2.6)$$

as an *extensive* quantity with dimensions of energy over temperature.²

2.1.1 Microcanonical temperature

Temperature is one of the most fundamental concepts of statistical mechanics. Traditionally, it has been defined in terms of average kinetic energies of particles in a system [4]. In the following, we wish to motivate a more fundamental definition and introduce temperature as an intrinsic system property which can be obtained directly from the microcanonical density of states. 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 constant and can be written as the sum of the energies of the two subsystems $E = E_1 + E_2$. At a fixed system energy E , the probability density for subsystem S_1 to contain energy E_1 is written as

$$\rho(E_1)_E = \frac{g_1(E_1)g_2(E - E_1)}{g(E)}. \quad (2.7)$$

²If temperature is measured in the more natural units of energy, entropy becomes a unitless quantity and the Boltzmann constant equals to unity.

The density of states of the combined system is given by the convolution of the subsystem densities

$$g(E) = \int dE_1 g_1(E_1) g_2(E - E_1). \quad (2.8)$$

In systems with many degrees of freedom, the probability density $\rho(E_1)_E$ is a sharply peaked distribution around the equilibrium energy \bar{E}_1 ³. Hence the convolution in Eq. 2.8 can be well approximated by the maximum value of the integrand [5]. The maximum is found when the derivative of the integrand with respect to E_1 is set to zero. It follows that

$$\left. \frac{1}{g_1} \frac{dg_1}{dE_1} \right|_{\bar{E}_1} = \left. \frac{1}{g_2} \frac{dg_2}{dE_2} \right|_{E-\bar{E}_1}, \quad (2.9)$$

or alternatively in terms of the microcanonical entropy

$$\left. \frac{dS_1}{dE_1} \right|_{\bar{E}_1} = \left. \frac{dS_2}{dE_2} \right|_{E-\bar{E}_1}. \quad (2.10)$$

In analogy to the familiar observation that interacting systems at thermal equilibrium have equal temperatures, we define the microcanonical temperature as

$$T(E) = \left(\frac{dS(E)}{dE} \right)^{-1}. \quad (2.11)$$

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

$$\beta(E) = \frac{dS(E)}{dE}. \quad (2.12)$$

³The energy fluctuations per particle around the equilibrium energy \bar{E}_1 scale as $N^{-1/2}$ [5].

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 parameters⁴ 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 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 [5].

Divergences and singularities in thermodynamic observables and their derivatives are only found in systems which satisfy the thermodynamic limit. In mesoscopic systems⁵, due to finite size effects, divergences are replaced by peaks and discontinuities are smoothed over [1]. 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.

⁴Some common examples of external control parameters are the canonical temperature, pressure, or the chemical potential.

⁵Typical 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.

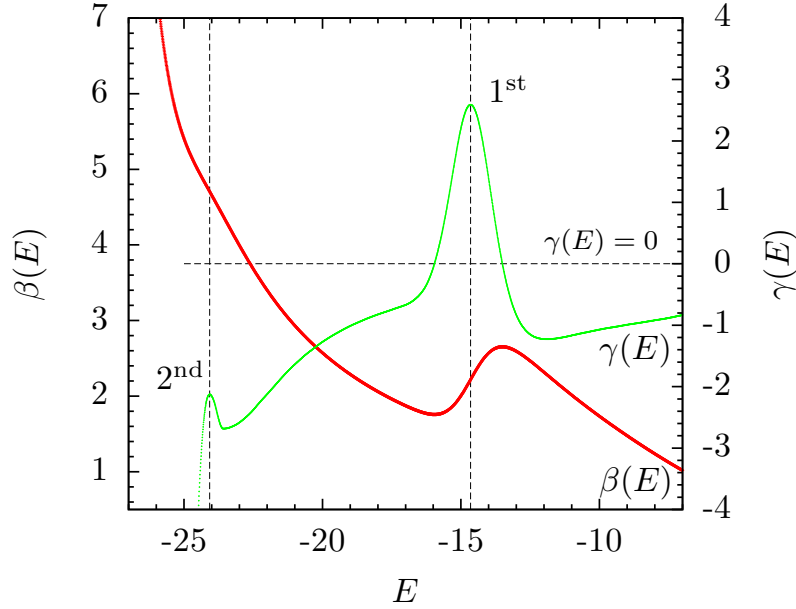


Figure 2.1: Microcanonical inflection-point analysis of the inverse microcanonical temperature $\beta(E)$. The prominent back-bending region in $\beta(E)$, together with the positive-valued peak in its energy derivative $\gamma(E)$ at $E \approx -15$, indicates a first-order transition. The negative-valued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

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 [6].

In analogy to the principle of minimal sensitivity [7], structural transitions between pseudophases occur when $\beta(E)$, or one of its energy derivatives, respond least sensitively to variations in energy [8]. In particular, first-order transitions are associated with inflection

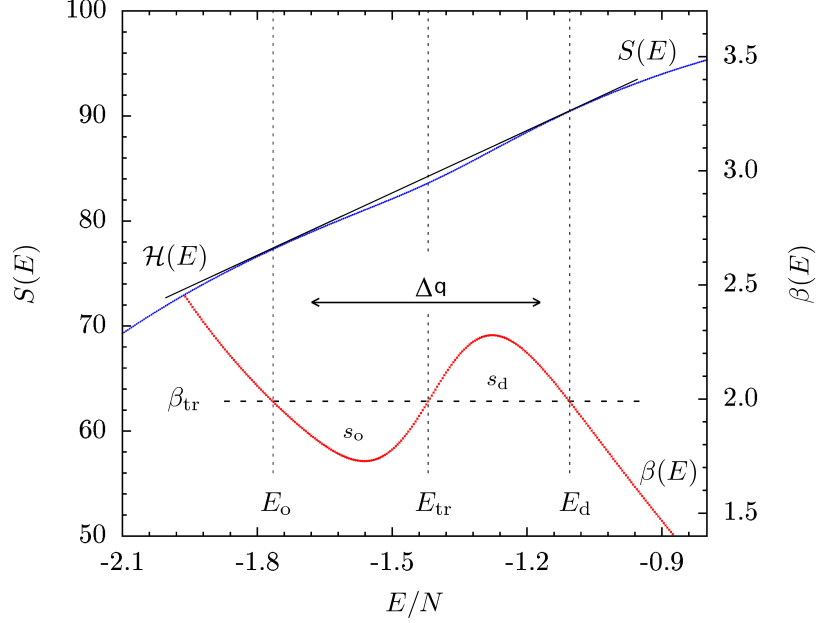


Figure 2.2: The convex region of the microcanonical entropy $S(E)$ and the back-bending of the microcanonical inverse temperature $\beta(E)$ are prominent indicators of *first-order* transitions. The slope of the double-tangent Gibbs hull $\mathcal{H}(E)$ defines the transition temperature β_{tr} . The 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 .

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 pseudophase 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.

Alternatively, in the case of 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 isotherms for the van der Waals gas. In mesoscopic systems, the finite-size effects lead to the entropic suppression of transition states, which is manifested in the backbending of $\beta(E)$ and the convex intruder in $S(E)$. The position of the Maxwell construction is determined by the equality of the areas s_o and s_d [Fig.2.2]. Commonly referred to as *surface entropies*, s_o and s_d are defined as the integrals

$$s_o = \int_{E_o}^{E_{\text{tr}}} dE (\beta_{\text{tr}} - \beta(E)), \quad (2.13)$$

$$s_d = \int_{E_{\text{tr}}}^{E_d} dE (\beta(E) - \beta_{\text{tr}}). \quad (2.14)$$

The Maxwell line intersects the inverse temperature at the energies E_o , E_{tr} , and E_d . The latent heat $\Delta Q = E_d - E_o$ corresponds to the energetic separation between the ordered and the disordered pseudophases. The transition energy E_{tr} indicates the location where intermediate states experience the maximal entropic suppression [1].

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

$$\mathcal{H}(E) = S(E_o) + \beta_{\text{tr}}[E - E_o], \quad (2.15)$$

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

$$\beta_{\text{tr}} = \frac{S_d - S_o}{E_d - E_o} = \frac{\Delta S}{\Delta Q}. \quad (2.16)$$

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 which is 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 [9]. It can be defined directly as a Laplace transform⁶ of the microcanonical density of states $g(E)$

$$Z(T) = \sum_i g(E_i) e^{-\frac{E_i}{k_B T}}, \quad (2.17)$$

where T is the canonical temperature and k_B is the Boltzmann constant. The condition of thermal equilibrium prohibits any net average energy transfer between the system and the heat bath. However, the system can temporarily gain or lose energy through constant fluctuations and dissipations. The probability for a given microstate μ at a temperature T

⁶Here 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 $Z(T) = \int dE g(E) e^{-\frac{E}{k_B T}}$.

is given by the Boltzmann distribution

$$p(\mu) = \frac{1}{Z(T)} e^{-\frac{\mathcal{H}(\mu)}{k_B T}}, \quad (2.18)$$

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

$$F(T) = -k_B T \ln Z(T). \quad (2.19)$$

This quantity represents the energy available to perform work and can be used to obtain all other thermodynamic quantities by differentiation [4, 5]. The temperature derivative of the free energy defines the canonical entropy

$$S(T) = -\frac{\partial}{\partial T} F(T) \Big|_{N,V}, \quad (2.20)$$

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

$$U(T) = \frac{\sum_{\mu} \mathcal{H}(\mu) e^{-\frac{\mathcal{H}(\mu)}{k_B T}}}{Z(T)} = \frac{\sum_E E g(E) e^{-\frac{E}{k_B T}}}{Z(T)}, \quad (2.21)$$

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

$$U(T) = k_B T^2 \frac{\partial}{\partial T} \ln Z(T) \Big|_{N,V} = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \Big|_{N,V}. \quad (2.22)$$

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

$$C_V(T) = \left. \frac{\partial}{\partial T} U(T) \right|_{N,V} = -T \left. \frac{\partial^2}{\partial T^2} F(T) \right|_{N,V}. \quad (2.23)$$

On the other hand, starting with the third term in equation 2.21 we obtain the following expression

$$\begin{aligned} C_V(T) &= \frac{\partial}{\partial T} \frac{\sum_E E g(E) e^{-\frac{E}{k_B T}}}{Z(T)} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \frac{\sum_E E g(E) e^{-\beta E}}{\sum_E g(E) e^{-\beta E}} \\ &= \frac{1}{k_B T^2} \left[\left(\frac{\sum_E E^2 g(E) e^{-\beta E}}{Z(T)} \right) - \left(\frac{\sum_E E g(E) e^{-\beta E}}{Z(T)} \right)^2 \right] \\ &= \frac{1}{k_B T^2} (\langle E^2 \rangle - \langle E \rangle^2), \end{aligned} \quad (2.24)$$

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 of macroscopic properties, in 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 describe 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 [1, 9]. 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

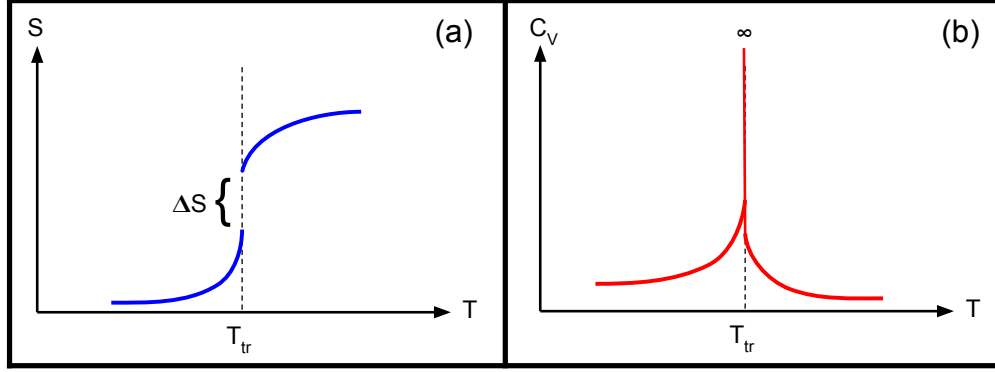


Figure 2.3: (a) The jump discontinuity in the canonical entropy S , (b) and the delta peak in the specific heat C_V , are characteristic of a first order phase transition.

paramagnetic phase. The derivative of the order parameter with respect to its conjugate variable defines a response quantity⁷ which is discontinuous at the transition point. Order parameters also play a central role in the formulation of the Landau theory, where they serve as a basis for the expansion of the free energy around the transition point [10].

First order transitions are characterized by a jump discontinuity ΔS in entropy and the coexistence of two distinct phases⁸ at the transition temperature. The energetic separation between the two phases corresponds to the latent heat

$$\Delta Q = T_{\text{trans}} \Delta S, \quad (2.25)$$

where ΔS is the height of the discontinuity and T_{trans} is the transition temperature. The specific heat C_V exhibits a delta peak at T_{trans} , as shown in Fig. 2.3 (b).

⁷In 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 .

⁸As a familiar example, consider the coexistence of gas bubbles and liquid at the boiling point of water.

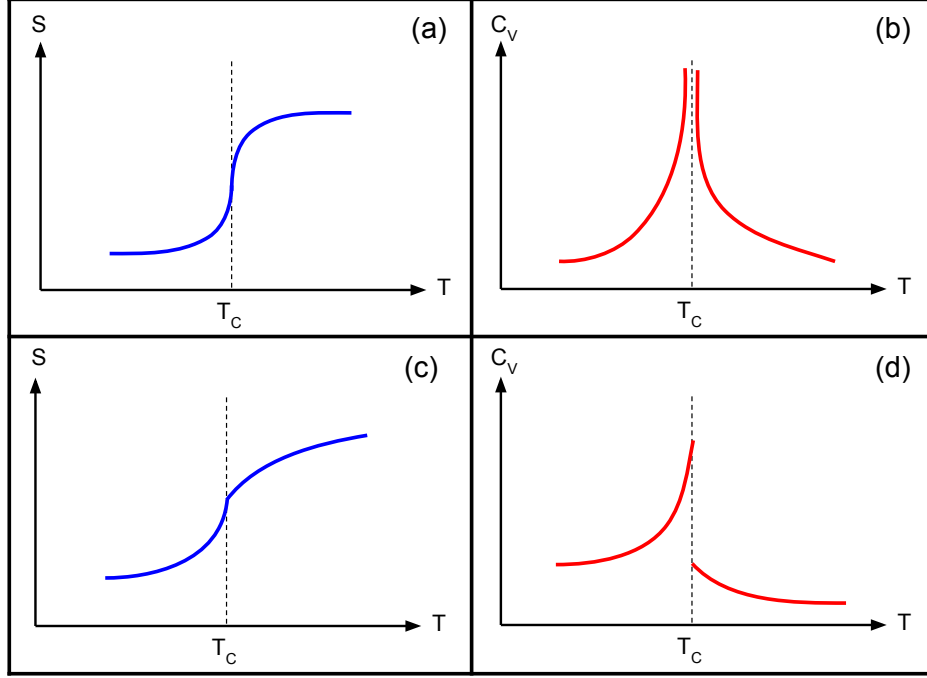


Figure 2.4: Second order transitions are characterized by discontinuities in response quantities, such as the specific heat. (a,b) In the case of a **critical** second order transition, the entropy S attains an infinite slope at T_c accompanied by a divergence in the specific heat C_V . (c,d) So called *lambda* transitions are characterized by a jump discontinuity in C_V and a cusp singularity in entropy.

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 derivatives of the free energy with respect to temperature. It is customary to make use of equation 2.23, and consider the specific heat C_V which also contains 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.

The striking observation, that in the vicinity of the critical temperature T_c , the behavior of physical systems with diverse microscopic properties can be described in terms of the same critical exponents, is formalized in the theory of Universality [10].

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 and indicate a first-order transition [11]. The associated latent heat of the transition is given by the energetic separation between 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 [9]. An example of canonical analysis, applied to first- and second-order pseudophase transitions, is illustrated in Fig. 2.5.

It should be mentioned that second-order pseudophase transitions do not always produce peaks in the specific heat. In general, it is necessary to investigate the behavior of several response quantities in order to obtain an accurate picture of the transition properties of

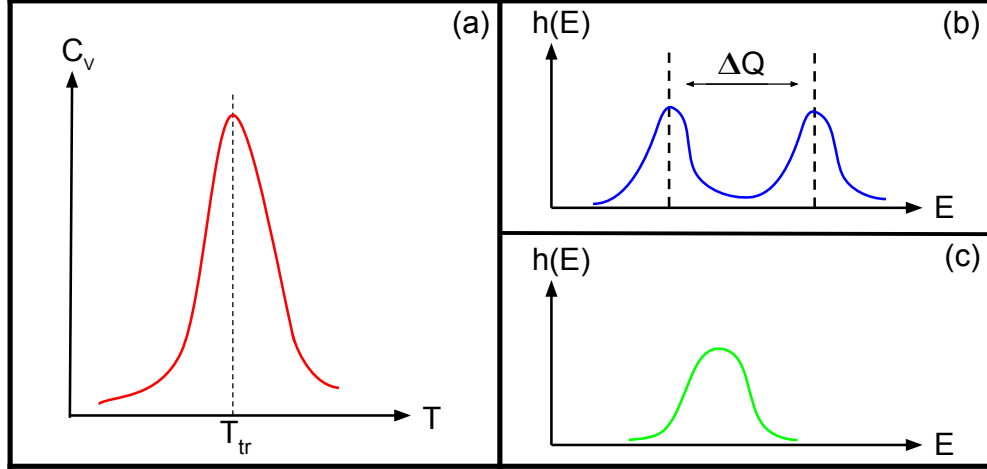


Figure 2.5: (a) The peak in the specific heat C_V indicates a region of heightened thermodynamic activity. (b) The two peaks in the bimodal canonical energy distribution correspond to the ordered and disordered pseudophases, energetically separated by the latent heat ΔQ . Pseudophase coexistence and 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.

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 reality further fortifies the argument that the microcanonical inflection-point analysis⁹, which defines a unique transition temperature in mesoscopic and macroscopic systems alike, is the preferred formalism for the analysis of finite systems.

⁹Introduced in Sec. 2.1.2

2.3 Alternative definitions of the density of states

In section 2.1 we have defined the microcanonical density of states $g(E)$ as an integral over the surface of constant energy in the $6N$ -dimensional phase space. We have argued that $g(E)$ contains all the essential information about the thermodynamic properties of the system under consideration, and introduced the formalism of the microcanonical inflection-point analysis which uses the logarithm of $g(E)$ as its starting point. In section 2.2 we have shown that the canonical partition function $Z(T)$ can be obtained by performing a Laplace transform of $g(E)$. Clearly, the microcanonical density of states plays a fundamental role in equilibrium statistical mechanics, and as such needs to be carefully defined.

Two distinct definitions of the density of states arise from certain ambiguity in the exact meaning of the microcanonical ensemble in computational studies. The density of states can be defined in the context of the conformational microcanonical ensemble (N, V, E_p) as a function of the potential energy only

$$g_c(E_p) = \int \mathcal{D}\mathcal{Q} \, \delta(E_p - \mathcal{H}(\mathcal{Q})) \quad (2.26)$$

This definition is commonly used in Monte Carlo simulations of magnetic systems where the kinetic energy contributions have little physical significance and the sampling can be restricted to the conformational space. However, in systems where the transfer between potential and kinetic energy has important physical interpretation, the sampling of the full phase space becomes necessary. The standard definition of the microcanonical ensemble (N, V, E) is applied and the measured density of states becomes a function of the total system energy, which can be written as the sum of the potential and kinetic energies

$$E = E_p + E_k. \quad (2.27)$$

In order to distinguish between the two definitions, we shall use the symbol $\Gamma(E)$ to represent the latter definition of the density of states. The connection between the conformational density of states and $\Gamma(E)$ is expressed as a convolution [12]

$$\Gamma(E) = \int dE_k g_c(E - E_k) g_k(E_k), \quad (2.28)$$

where

$$g_k(E_k) = \int \mathcal{DP} \delta(E_k - \mathcal{H}(\mathcal{P})) \quad (2.29)$$

is the kinetic density of states obtained by integrating over the momentum space.

We shall now turn our attention to the consequence of choosing either the conformational or the full density of states as the starting point for a systematic analysis of the thermodynamic properties of a system under consideration. In the following we will discuss the impact of ignoring the momentum degrees of freedom on the results of both the canonical and microcanonical analysis. As an illustration, we will provide results from Monte Carlo simulations of two short flexible homopolymers.

2.3.1 Consequences for canonical analysis

The canonical partition function $Z(T)$ and the microcanonical density of states are connected via a Laplace transform. We begin with the full density of states $\Gamma(E)$ and using the definition from Eq. 2.28 write

$$Z(T) = \mathcal{L}\{\Gamma(E)\} = \mathcal{L}\{g_c * g_k\} = \mathcal{L}\{g_c\}\mathcal{L}\{g_k\}, \quad (2.30)$$

where the last step follows from the convolution theorem [13].

The partition function of the system can hence be conveniently written as a product of two independent partition functions

$$Z(T) = Z_c(T)Z_k(T), \quad (2.31)$$

which depend on the potential and kinetic energies respectively. It follows that the average ensemble energy can be expressed as the sum of the average potential and kinetic energies

$$\begin{aligned} U(T) &= k_B T^2 \frac{\partial}{\partial T} \ln Z \Big|_{N,V} \\ &= k_B T^2 \frac{\partial}{\partial T} \ln Z_c \Big|_{N,V} + k_B T^2 \frac{\partial}{\partial T} \ln Z_k \Big|_{N,V} \\ &= \langle E_c \rangle + \langle E_k \rangle. \end{aligned} \quad (2.32)$$

With the exception of systems with rigid constraints, the average kinetic energy is given by the equipartition theorem

$$\langle E_k \rangle = \frac{3Nk_B T}{2}, \quad (2.33)$$

where N is the number of particles in the system. It follows that the specific heat C_V obtains only a trivial additive constant from the kinetic energy term

$$\begin{aligned} C_V(T) &= \frac{\partial}{\partial T} U(T) \Big|_{N,V} \\ &= \frac{\partial}{\partial T} \langle E_c \rangle \Big|_{N,V} + \frac{\partial}{\partial T} \frac{3Nk_B T}{2} \\ &= C_{V,\text{conf.}} + \frac{3Nk_B}{2}. \end{aligned} \quad (2.34)$$

In conclusion, the locations and shapes of signals for pseudophase transitions are not affected by the inclusion of the momentum space into a sampling scheme. To substantiate this assertion, in Fig. 2.6 we present the results from a Monte Carlo study of a short

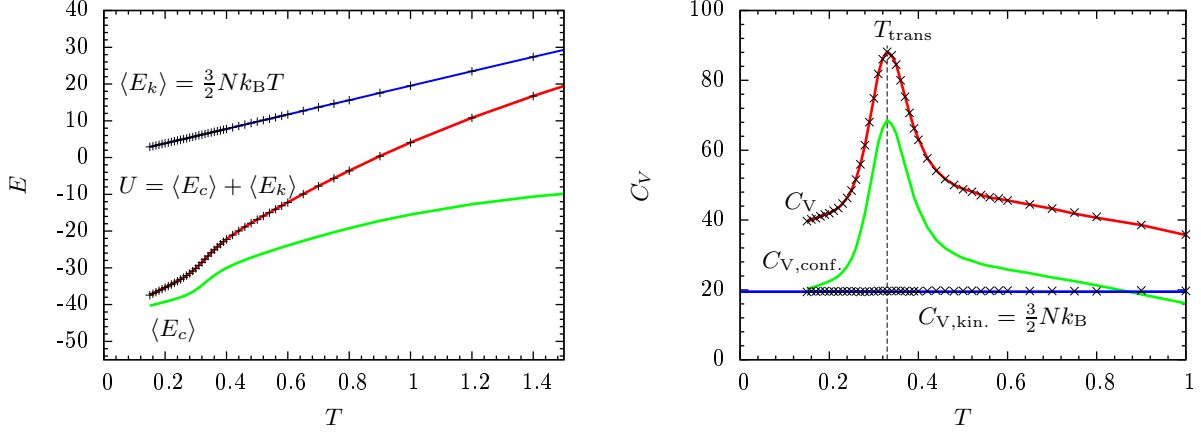


Figure 2.6: Results of a Monte Carlo simulation of a short flexible homopolymer of length $N = 13$. The average kinetic energy $\langle E_k \rangle$ and the kinetic contributions $C_{V,\text{kin.}}$ towards the specific heat are plotted as points on top of their respective theoretical curves (blue). The average potential energy $\langle E_c \rangle$ and the configurational specific heat $C_{V,\text{conf.}}$ (green) were obtained by sampling of the configurational space. Sampling of the full phase space was performed to obtain the total average energy U and the combined specific heat C_V (red). As expected, the combined specific heat is identical to $C_{V,\text{conf.}}$, except for a trivial additive constant.

flexible homopolymer. The average kinetic energy $\langle E_k \rangle$ and the kinetic contributions $C_{V,\text{kin.}}$ towards the specific heat are plotted as points on top of their respective theoretical curves (blue), showing good agreement with the predicted values. The average potential energy $\langle E_c \rangle$ and the configurational specific heat $C_{V,\text{conf.}}$ (green) were obtained by the sampling of the configurational space only. Sampling of the full phase space was performed to obtain the total average energy U and the combined specific heat C_V (red). As expected, the combined specific heat is identical to $C_{V,\text{conf.}}$, except for a trivial additive constant. The estimate of the transition temperature is independent of the choice of either definition of the density of states.

2.3.2 Consequences for microcanonical analysis

The application of the Laplace transform to the total density of states $\Gamma(E)$, allowed us to conveniently disentangle the convolution in Eq. 2.28 into separate kinetic and conformational contributions [Eq. 2.30]. Unfortunately, in the microcanonical ensemble no such simplification is readily available. Let us however consider a class of physical systems whose momenta and positional degrees of freedom are independent. Explicit integration over the momentum space yields a simple expression for the kinetic density of states

$$g_k(E_k) = \int \mathcal{DP} \delta(E_k - \mathcal{H}(\mathcal{P})) = E_k^{\frac{3N-2}{2}}. \quad (2.35)$$

Combining the result with Eq. 2.28 we obtain

$$\Gamma(E) = \int dE_k g_c(E - E_k) E_k^{\frac{3N-2}{2}}. \quad (2.36)$$

Next, taking a derivative with respect to the total energy E and dividing both sides by $\Gamma(E)$ we get two equivalent expressions for the microcanonical inverse temperature

$$\beta(E) = \int dE_k \frac{3N-2}{2E_k} \left[\frac{g_c(E - E_k) E_k^{\frac{3N-2}{2}}}{\Gamma(E)} \right] \quad (2.37)$$

$$= \int dE_p \beta_c(E_p) \left[\frac{g_c(E_p) (E - E_p)^{\frac{3N-2}{2}}}{\Gamma(E)} \right]. \quad (2.38)$$

Recognizing the two terms enclosed in square brackets as the microcanonical probability densities for the kinetic and potential energies, we can rewrite equations 2.37 and 2.38 as

$$\beta(E) = \int dE_k \frac{3N-2}{2E_k} \rho(E_k)_E = \frac{3N-2}{2} \left\langle \frac{1}{E_k} \right\rangle, \quad (2.39)$$

and

$$\beta(E) = \int dE_p \beta_c(E_p) \rho(E_p)_E = \langle \beta_c \rangle. \quad (2.40)$$

The microcanonical inverse temperature, obtained by the differentiation of the total density of states, can therefore be interpreted as an average of the conformational and kinetic analogs weighted by their respective microcanonical probability distributions.

When the number of particles in the system is large, the probability densities $\rho(E_k)_E$ and $\rho(E_p)_E$ are expected to be sharply peaked around the most probable kinetic \bar{E}_k and potential \bar{E}_p energies respectively. We can therefore apply the saddle point approximation to the integrals in equations [2.39, 2.40] and obtain the following first order approximations for the inverse temperature

$$\beta(E) \approx \beta_c(\bar{E}_p), \quad (2.41)$$

and

$$\beta(E) \approx \frac{3N-2}{2} \left(\frac{1}{\bar{E}_k} \right). \quad (2.42)$$

The first expression suggests that it is possible to reconstruct $\beta(E)$ from the conformational inverse temperature β_c , and that the two quantities contain essentially the same information. We test the validity of this hypothesis by comparing the microcanonical results of Monte Carlo simulations of a flexible elastic 55-mer, which were carried out in both the conformational space and the full phase space.

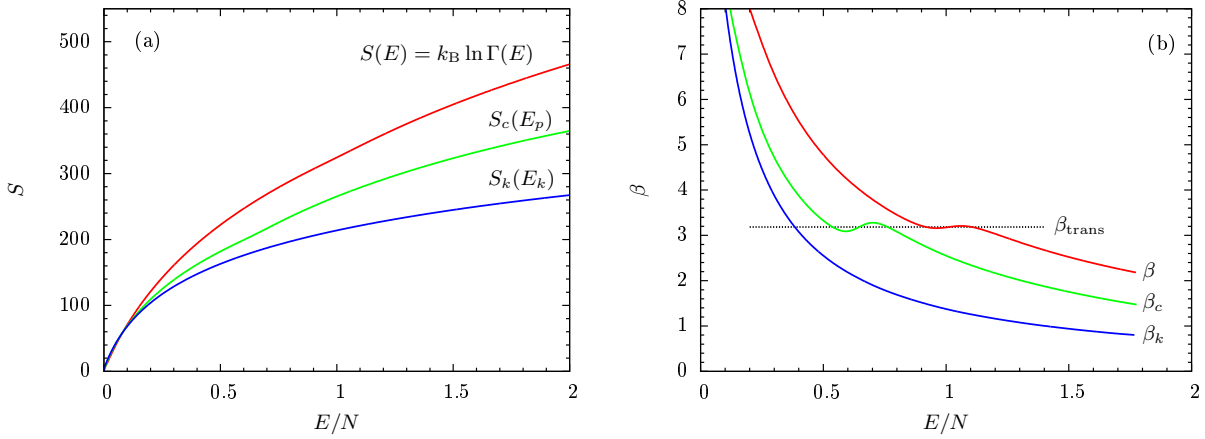


Figure 2.7: Comparison of microcanonical results from a Monte Carlo simulation of a flexible homopolymer of length $N = 55$. (a) The combined S , conformational S_c , and kinetic S_k entropy curves. (b) The kinetic inverse temperature β_k is a strictly convex function and the application of the inflection-point analysis reveals no transition signals. The conformational inverse temperature β_c clearly differs from $\beta(E)$, however both indicate a first-order pseudophase transition at virtually the same temperature.

The kinetic entropy in Fig. 2.7 is a strictly concave function and the application of the inflection-point analysis to the corresponding inverse temperature β_k reveals no transition signals. The conformational inverse temperature clearly differs from $\beta(E)$, however both indicate a first-order pseudophase transition at virtually the same temperature. In Fig. 2.8 we show the comparison between the true $\beta(E)$ and the reconstruction obtained from the conformational inverse temperature according to equations 2.41 and 2.42. It is evident that the approximation is valid, except in the back-bending region of the first-order transition due to the bimodality of the probability densities $\rho(E_k)_E$ and $\rho(E_p)_E$.

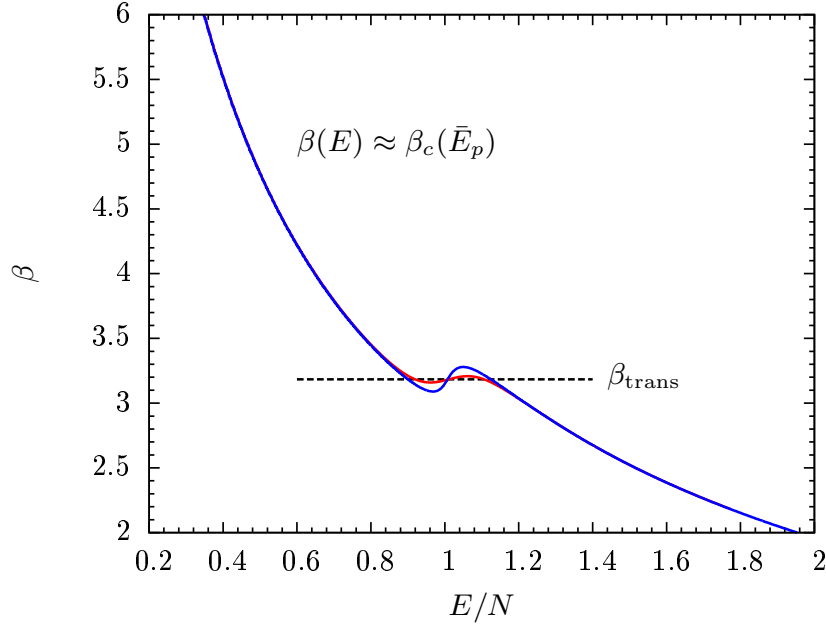


Figure 2.8: Comparison of the inverse microcanonical temperature $\beta(E)$ (red) and the conformational inverse temperature $\beta_c(\bar{E}_p)$ (blue) evaluated at the most probable potential energy \bar{E}_p . The approximation introduced in equation 2.41 holds except in the back-bending region of the first-order pseudophase transition. The inverse transition temperature β_{trans} obtained from the two quantities is virtually identical.

The expression in equation 2.42 can be rewritten as

$$k_{\text{B}}T(E) \approx \frac{2}{3N-2} \left(\frac{1}{\bar{E}_k} \right)^{-1}, \quad (2.43)$$

which clearly resembles the well known relationship between the canonical temperature and the average kinetic energy. In the thermodynamic limit, this approximation becomes exact and the equivalency of the microcanonical and canonical ensembles is restored.

Chapter 3

Computational Methods

Computational algorithms are powerful tools that enable the investigation of many-body physical systems under thermal conditions, that are far too complex to be solved analytically. In fact, only a handful of systems with large number of degrees of freedom are exactly solvable¹, and even the simplest solutions often require bewildering mathematical gymnastics. Consequently, computational studies are the main source of advances in the fundamental understanding of complex microscopic and mesoscopic systems such as biopolymers and proteins [1].

Two complementary classes of computational algorithms have been particularly successful in unravelling the thermodynamic properties of physical systems. *Molecular dynamics* simulations generate a single phase space trajectory by updating the positions and momenta of every particle in a system according to Hamilton's equations [14, 15]. Alternatively, carrying out a stochastic sampling of the phase space, *Monte Carlo* simulations estimate the equilibrium properties without an explicit consideration of the system's dynamics [1, 9]. In this chapter, we shall focus our attention to Markov chain Monte Carlo methods. We will briefly discuss the essential theory and introduce the well established Metropolis and Paral-

¹The most prominent examples of exactly solvable systems with large number of degrees of freedom are the ideal gas and the two dimensional Ising model.

lel Tempering algorithms as well as the lesser known Multiple Gaussian modified ensemble method.

3.1 Markov chain Monte Carlo

The aim of all Monte Carlo methods is to extract the equilibrium thermodynamic properties of physical systems by performing an efficient stochastic sampling of the phase space. For this purpose, a set of random microstates $\{\mu_1, \mu_2, \dots, \mu_M\}$ is generated according to some previously known probability distribution $p(\mu_i)$, and the expectation value for any observable $O(\mu)$ is estimated by calculating the average

$$\bar{O} = \frac{1}{M} \sum_{i=1}^M O(\mu_i). \quad (3.1)$$

In most Monte Carlo methods, the set of random microstates is generated according to a discrete-time Markov chain (DTMC) [16]. Markov chains are sequences of random states, generated according to the time-independent transition probabilities $T(\mu \rightarrow \nu)$ which satisfy the Markov property. In simple terms, the probability of moving to state ν from state μ depends only on the present state, and is independent of the history of the process. In order to achieve the correct statistical sampling of an equilibrium thermodynamic ensemble, the following conditions must also be satisfied.

The process must be **ergodic**, i.e., there must be a path of non-zero probability between any pair of states. More formally, the state space \mathcal{S} of the Markov chain must consist of a single aperiodic recurrence class. When ergodicity is satisfied, the ensemble average $\langle O \rangle$ can be approximated by the measured expectation value \bar{O} [Eq. 3.1]

$$\bar{O} = \frac{1}{M} \sum_{i=1}^M O(\mu_i) \approx \langle O \rangle = \int \mathcal{D}\mathcal{P} \mathcal{D}\mathcal{Q} O(\mathcal{P}, \mathcal{Q}) p(\mathcal{P}, \mathcal{Q}), \quad (3.2)$$

where M is the length of the Markov chain. According to the ergodic hypothesis [15], the approximation becomes exact in the limit of an infinitely long Markov chain

$$\lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M O(\mu_i) = \int \mathcal{D}\mathcal{P} \mathcal{D}\mathcal{Q} \, O(\mathcal{P}, \mathcal{Q}) p(\mathcal{P}, \mathcal{Q}). \quad (3.3)$$

The time evolution of a discrete-time Markov process is described by the master equation

$$\frac{\Delta p(\mu)}{\Delta t} = \sum_{\nu} p(\nu) T(\nu \rightarrow \mu) - p(\mu) T(\mu \rightarrow \nu). \quad (3.4)$$

The equilibrium condition requires that the probability distribution $p(\mu)$ is stationary. In other words, the probability currents into and out of the state μ must be always equal

$$\sum_{\nu} p(\nu) T(\nu \rightarrow \mu) = \sum_{\nu} p(\mu) T(\mu \rightarrow \nu). \quad (3.5)$$

Also known as the **balance** condition, equation 3.5 sometimes allows for solutions that are not permitted in the equilibrium ensemble [9]. The stricter condition of **detailed balance** requires that the probability of a transfer between any two states must be equal to the probability of the reverse process. Embodied in the expression

$$p(\mu) T(\mu \rightarrow \nu) = p(\nu) T(\nu \rightarrow \mu), \quad (3.6)$$

this condition is sufficient to prevent any non-physical solutions as well as to ensure that the process is invariant under time reversal.

Having introduced the conditions of ergodicity and detailed balance, we can now derive the expression for transition probabilities which will ensure correct stochastic sampling according to an equilibrium distribution $p(\mu)$. For convenience, we will separate the transition probabilities into two separate terms and write

$$T(\mu \rightarrow \nu) = s(\mu \rightarrow \nu) a(\mu \rightarrow \nu). \quad (3.7)$$

Assuming the current state μ , the probability of generating a new state ν is given by the selection probability $s(\mu \rightarrow \nu)$, while the probability of accepting the proposed update is controlled by the *acceptance* probability $a(\mu \rightarrow \nu)$. Combining equations 3.6 and 3.7, we express the ratio of the transition probabilities as

$$\frac{T(\mu \rightarrow \nu)}{T(\nu \rightarrow \mu)} = \frac{s(\mu \rightarrow \nu) a(\mu \rightarrow \nu)}{s(\nu \rightarrow \mu) a(\nu \rightarrow \mu)} = \frac{p(\nu)}{p(\mu)}. \quad (3.8)$$

The ratio of the forward and backward selection probabilities $\sigma(\mu, \nu) = s(\mu \rightarrow \nu) / s(\nu \rightarrow \mu)$ depends on the choice of the particular update scheme. In the remainder of this thesis, we shall assume that the forward and backward selection probabilities are equal and the ratio equals to unity, which is valid for most local Monte Carlo updates. This simplifying assumption allows us to rewrite equation 3.8 without making explicit references to the selection probabilities

$$\frac{a(\mu \rightarrow \nu)}{a(\nu \rightarrow \mu)} = \frac{p(\nu)}{p(\mu)}. \quad (3.9)$$

3.1.1 Metropolis sampling

Any set of acceptance probabilities which satisfies equation 3.9 is allowable, however the standard choice is to set the higher of the two probabilities to unity. This yields the well known Metropolis acceptance criterion [9, 17]:

$$a(\mu \rightarrow \nu) = \min \left(1, \frac{p(\nu)}{p(\mu)} \right). \quad (3.10)$$

Under most circumstances, Metropolis sampling is carried out according to the canonical microstate probability distribution $p(\mu) \propto e^{-\beta E(\mu)}$, where β is the inverse canonical temper-

ature. Hence the acceptance probability is governed by the energy difference between the proposed and the current states

$$a(\mu \rightarrow \nu) = \min \left(1, \frac{e^{-\beta E(\nu)}}{e^{-\beta E(\mu)}} \right) = \min(1, e^{-\beta \Delta E}). \quad (3.11)$$

The average of the observable $O(\mu)$, measured over the length of a finite Metropolis run, serves as an estimate for the canonical expectation value $\langle O \rangle$ [Eq. 3.2]. In the limit of an infinite run, this approximation becomes exact [Eq. 3.3]. However, since all simulations are of finite length, it is imperative to account for the statistical errors introduced due to the finiteness of the measured data sets. The standard bias corrected error estimator for the calculated average \bar{O} , obtained from a finite set of M uncorrelated measurements, is written as

$$\text{err}(\bar{O}) = \pm \sqrt{\frac{1}{M(M-1)} \sum_m (O_m - \bar{O})^2}. \quad (3.12)$$

In reality, most measurements obtained from Monte Carlo simulations are correlated. Hence it is necessary to introduce the modified error estimator

$$\text{err}(\bar{O}) = \pm \sqrt{\frac{1}{M(M_{\text{eff}} - 1)} \sum_m (O_m - \bar{O})^2}, \quad (3.13)$$

where M_{eff} is the number of uncorrelated measurements².

The Metropolis method provides the means for an efficient sampling of microstates which are dominant at a given temperature. However, the microstates which are found in the tails of the canonical energy distribution are rarely visited. Further shortcomings of the Metropolis algorithm, such as the propensity for getting trapped in low-energy configurations and the notorious reduction in sampling efficiency near pseudophase transitions, motivate the introduction of more efficient sampling methods.

²For detailed description of the more practical *binning* and *jackknife* error estimation methods, please refer to chapter 4 in [1].

3.1.2 Parallel tempering

In situations where the Metropolis method fails to produce data of reasonable quality, the standard way of increasing sampling efficiency is to perform the simulation in a conveniently chosen *generalized ensemble*³. In parallel tempering [18–21], multiple canonical ensembles with different inverse temperatures $\{\beta_1 < \beta_2 < \dots < \beta_N\}$ are simulated in parallel according to the standard Metropolis scheme. In this context, the generalized ensemble is defined as the direct product of N canonical ensembles, and the partition function is given by

$$Z_{\text{PT}}(\beta_1, \beta_2, \dots, \beta_N) = \prod_{i=1}^N Z_{\text{can}}(\beta_i). \quad (3.14)$$

At judiciously chosen intervals, an exchange of conformations between adjacent temperature threads i and j is proposed. The combined probability for states (μ, ν) at respective temperatures (β_i, β_j) is given by

$$p_{\mu\nu} = \frac{e^{-\beta_i E(\mu)}}{Z_{\text{can}}(\beta_i)} \frac{e^{-\beta_j E(\nu)}}{Z_{\text{can}}(\beta_j)}, \quad (3.15)$$

and the acceptance probability for the exchange of conformations is obtained from Eq. 3.10

$$\begin{aligned} a(\mu \leftrightarrow \nu; \beta_i, \beta_j) &= \min \left(1, \frac{e^{-\beta_i E(\nu)} e^{-\beta_j E(\mu)}}{e^{-\beta_i E(\mu)} e^{-\beta_j E(\nu)}} \right) \\ &= \min \left(1, e^{[\beta_j - \beta_i][E(\nu) - E(\mu)]} \right). \end{aligned} \quad (3.16)$$

The exchange rates are governed by the overlap of canonical energy distributions of the adjacent ensembles, hence the efficiency of the method depends sensitively on the choice of an appropriate temperature set. As a general rule, the density of temperatures must be increased in ordered phases and in the vicinity of pseudophase transitions.

³The microstate probability distribution of a generalized ensemble can be arbitrary and does not have to bear any resemblance to the Boltzmann distribution.

In principle, each replica is allowed to traverse the entire simulated temperature range which leads to the decrease of the autocorrelation time and reduces the likelihood of getting trapped in local energy minima at low temperatures. However, the performance of this method rapidly decreases near first-order transitions, where the joint effects of the entropic suppression of intermediate states and the energetic separation between the ordered and disordered pseudophases, virtually prevent the exchange of configurations between adjacent ensembles.

3.1.3 Multiple Gaussian modified ensemble

An alternative generalized ensemble method that offers improved performance is based on the combination of parallel tempering with the Gaussian modified ensemble (GME) method [22]. The idea behind GME is to modify the canonical Boltzmann distribution by multiplying it by a Gaussian function, in order to promote sampling in selected energy regions. The mean energy E_G and the variance ΔE_G^2 of the Gaussian form controls the location and the width of the region of enhanced sampling. The modified microstate probability at the inverse temperature β is given by

$$P_{\text{GME}}(\mu) \propto e^{-\beta E_\mu - (E_\mu - E_G)^2 / \Delta E_G^2}. \quad (3.17)$$

The measurements obtained from simulations in a modified ensemble must be reweighted in order to obtain the expectation values in the original canonical ensemble. In the context of the modified Gaussian ensemble this is done by calculating

$$\langle O \rangle_{\text{can}, \beta} = \frac{\sum_{i=1}^M O_i e^{\beta(E_i - E_G)^2 / \Delta E_G^2}}{\sum_{i=1}^M e^{\beta(E_i - E_G)^2 / \Delta E_G^2}}. \quad (3.18)$$

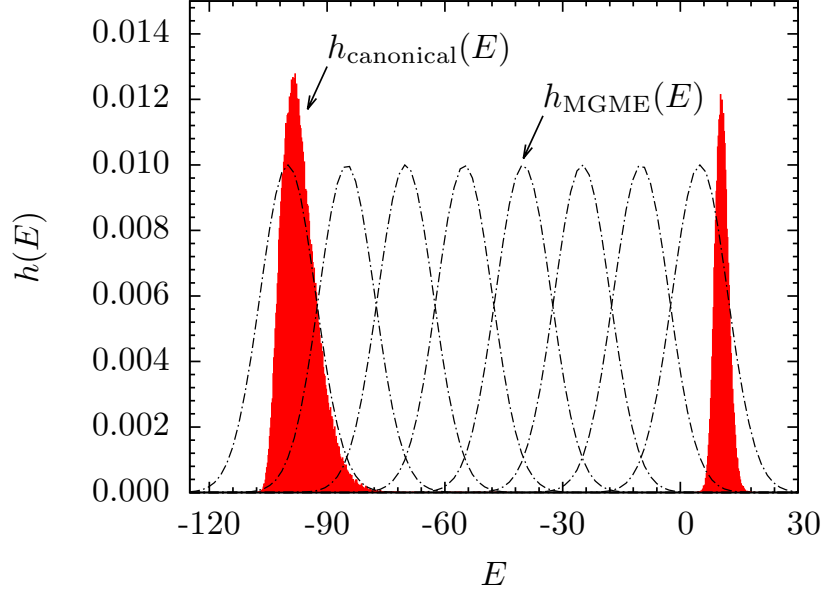


Figure 3.1: Canonical and GME energy histograms at a first-order pseudophase transition. The bimodal canonical energy histogram indicates the coexistence of ordered and disordered pseudophases, separated by an entropically suppressed energy region. Each GME ensemble enhances the sampling of suppressed states over a limited energy range.

Strong first-order transitions with bimodal energy distributions typically require several overlapping GME ensembles to cover the relevant energy range, as illustrated in Fig. 3.1. The acceptance probability for the exchange of conformations (μ, ν) between neighboring GME ensembles with mean energies $(E_{G,i}, E_{G,j})$ at a constant inverse temperature β is

$$a(\mu \leftrightarrow \nu) = \min(1, e^{\Delta G}), \quad (3.19)$$

where

$$\Delta G = \frac{(E_\mu - E_{G,j})^2 - (E_\nu - E_{G,j})^2}{\Delta E_{G,j}^2} - \frac{(E_\nu - E_{G,i})^2 - (E_\mu - E_{G,i})^2}{\Delta E_{G,i}^2}. \quad (3.20)$$

The direct product of GME ensembles defines the multiple Gaussian modified ensemble (MGME). With a proper choice of ensemble parameters $(E_G, \Delta E_G)$ it is possible to achieve a significantly enhanced sampling of previously inaccessible states. This can be further improved by allowing for exchanges between GME ensembles at different temperatures. However, previous knowledge of the system under consideration is usually needed to make a reasonable estimate for the ensemble parameters. Therefore other more systematic methods, such as the multicanonical [23–28] and Wang-Landau sampling [29–31], are often used.

3.2 Histogram reweighting methods

In chapter 2, we have introduced the microcanonical inflection point analysis as the means for the systematic study of pseudophase transitions in the microcanonical ensemble. Application of this method however presumes the precise knowledge of the microcanonical density of states $g(E)$ [Eq 2.3]. Previously introduced sampling methods do not directly measure $g(E)$ but rather generate canonical energy histograms $h(E, \beta_i)$. Hence, it is necessary to introduce a general method for estimating the density of states from energy histograms.

3.2.1 Multiple-histogram reweighting

Canonical histogram $h(E, \beta_i)$ provides an approximation for the Boltzmann distribution $p_{\text{can}}(E, \beta_i)$, which is itself proportional to the microcanonical density of states

$$h(E, \beta_i) \approx p_{\text{can}}(E, \beta_i) \propto g(E) e^{-\beta_i E} \quad (3.21)$$

Therefore each histogram yields an estimate of the density of states

$$\bar{g}_i(E) = h(E, \beta_i) e^{\beta_i E} \quad (3.22)$$

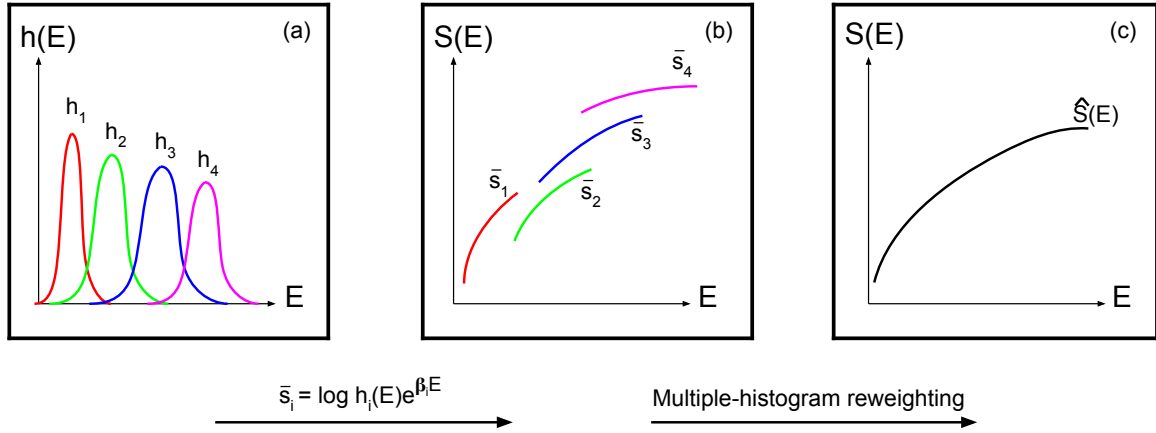


Figure 3.2: (a) Illustration of the canonical energy histograms $h(E, \beta_i)$, (b) the individual estimates of the logarithm of the density of states $\bar{S}_i(E)$, (c) and the combined estimate of the logarithm of the density of states $\hat{S}(E)$ obtained by reweighting.

Individual estimates $\bar{g}_i(E)$ are only reliable for energies in the vicinity of the peak of the canonical histogram obtained at the temperature β_i . Therefore a sufficient overlap between the histograms of adjacent replicas is necessary to ensure that an accurate estimate of the density of states can be obtained for the entire energetic range.

The task is now to combine the individual estimates $\bar{g}_i(E)$ and obtain an improved estimate $\hat{g}(E)$. Unfortunately, general Monte Carlo methods do not yield absolute estimates for the partition function $Z(\beta)$ and the estimates $\bar{g}_i(E)$ cannot be directly related if obtained at different temperatures. However, it is possible to introduce a reference partition function

$$\hat{Z}_i = \sum_E \hat{g}(E) e^{-\beta_i E}, \quad (3.23)$$

which serves as the appropriate weight in the estimator for the density of states

$$\hat{g}(E) = \frac{\sum_{i=1}^R h(E, \beta_i)}{\sum_{i=1}^R M_i \hat{Z}_i^{-1} e^{-\beta_i E}}. \quad (3.24)$$

The equations 3.23 and 3.24 must be solved iteratively until $\hat{g}(E)$ has converged. The relationship between the energy histograms, the individual estimates $\bar{g}_i(E)$, and the final estimate $\hat{g}(E)$ of the density of states is illustrated in Fig. 3.2. For detailed derivation and a further discussion of the multiple-histogram reweighting method please refer to [32, 33].

3.2.2 Beziere smoothing

The estimator for the density of states, obtained either by multiple-histogram reweighting or directly by multicanonical sampling, is not a smooth function but rather a discrete set of stochastic values. The formalism of the microcanonical inflection point analysis requires the accurate knowledge of its energy derivatives. These have to be computed by numerical differentiation which is prone to enhancing the random statistical fluctuations of the original data set. It is therefore desirable to approximate the density of states by a smooth analytic function, which can be done very effectively with Beziér curves [1, 34].

Beziér curve of order n is a parametric curve defined by a set of $(n + 1)$ control points $\{P_0, P_1, \dots, P_n\}$ and the formula

$$B(t) = \sum_{i=0}^n \mathcal{B}_i^{(n)}(t) P_i, \quad (3.25)$$

where $B_i^{(n)}$ are the Bernstein basis polynomials [35] of degree n

$$B_i^{(n)}(t) = \binom{n}{i} (1-t)^{n-i} t^i. \quad (3.26)$$

The discrete values of the estimated density of states $g(E_i)$ serve as control points for the approximating Beziér curve. Assuming that the set of $(n + 1)$ control points $\{g(E_0), g(E_1), \dots, g(E_n)\}$ is equally spaced in the energy space over the interval $[E_{\min}, E_{\max}]$,

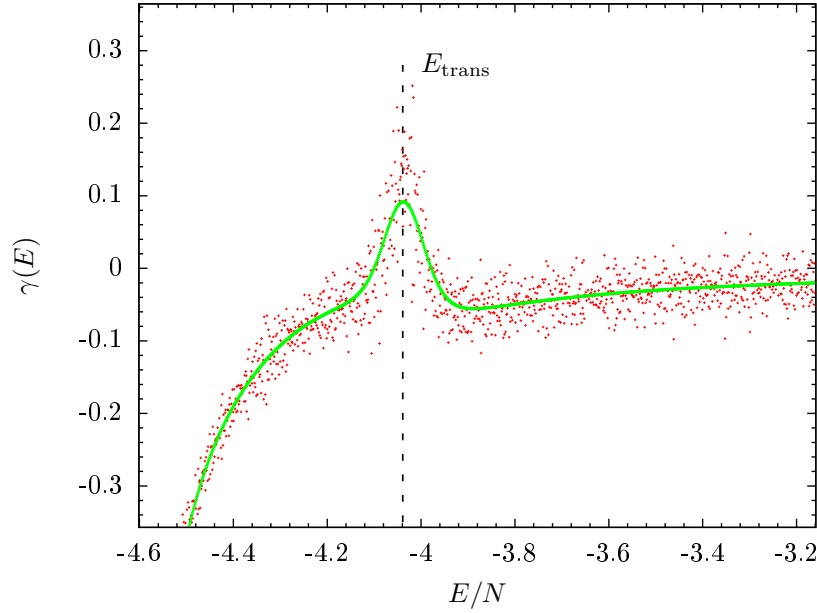


Figure 3.3: Comparison between the noisy derivative of the microcanonical inverse temperature $\gamma(E) = d\beta/dE$ and the Beziér approximation $\gamma_{\text{bez}}(E)$. The systematic error in the Beziér approximation is visible near E_{trans} , where the curvature of $\gamma(E)$ changes abruptly.

the approximating Beziér function can be directly calculated from

$$g_{\text{bez}}(E) = \sum_{i=0}^n \binom{n}{i} \left(\frac{E_{\text{max}} - E}{E_{\text{max}} - E_{\text{min}}} \right)^{n-i} \left(\frac{E - E_{\text{min}}}{E_{\text{max}} - E_{\text{min}}} \right)^i g(E_i). \quad (3.27)$$

The numerical error introduced by the approximation scheme is typically much smaller than the random statistical fluctuations in the original noisy data set [1]. However it should be mentioned that Beziér smoothing may introduce systematic errors to the derivatives of $g(E)$ in areas of abrupt changes in curvature. This is illustrated in Fig. 3.3 where we compare the noisy derivative of the microcanonical inverse temperature $\gamma(E) = d\beta/dE$ and the Beziér approximation $\gamma_{\text{bez}}(E)$ in the region of a first-order pseudophase transition.

3.3 Simple Monte Carlo updates

The efficiency of Monte Carlo simulations depends in equal measure on the choice of the sampling algorithm and on the selection of appropriate conformational updates. All update sets must be ergodic, i.e., it must be in principle possible to connect any two arbitrary states through a finite number of updates. Additionally, all updates must preserve the constraints of the model, such as volume exclusion and boundary conditions. The efficiency of individual updates depends strongly on the model to which they are being applied. Hence, there is no general set of updates that guarantees good performance across different physical models. In the following, we shall briefly discuss conformational updates which are suitable for simulations of off-lattice polymers and proteins.

3.3.1 Single displacement update

The single displacement update is easy to implement, satisfies ergodicity, and has equal forward and backward selection probabilities. The original conformation of a polymer chain $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ is updated by a random⁴ displacement $\Delta\mathbf{r}_i$ of a randomly selected i -th monomer. The displacement vector is defined in the Cartesian coordinates as $\Delta\mathbf{r}_i = (\Delta x_i, \Delta y_i, \Delta z_i)$, where each component is selected with uniform probability from some interval $[-l, l]$. In general, longer displacement updates lead to larger energy differences between the old and the new states $\Delta E = E_{\text{new}} - E_{\text{old}}$. In Monte Carlo simulations, large positive values of the ratio $\Delta E/T$ result in an exponential suppression of the acceptance rates [Eq. 3.11]. In order to achieve acceptance rates within the optimal range of $\sim 30\% - 70\%$, the set of temperature dependent displacement parameters $l(T_i)$ must be determined. Unfortunately, for most off-lattice polymer models, only very short displace-

⁴Monte Carlo simulations make extensive use of pseudo-random numbers. The popular Mersenne Twister pseudo-random number generator [36] is used throughout this thesis. For more information on the ‘art’ of random number generation please refer to [9].

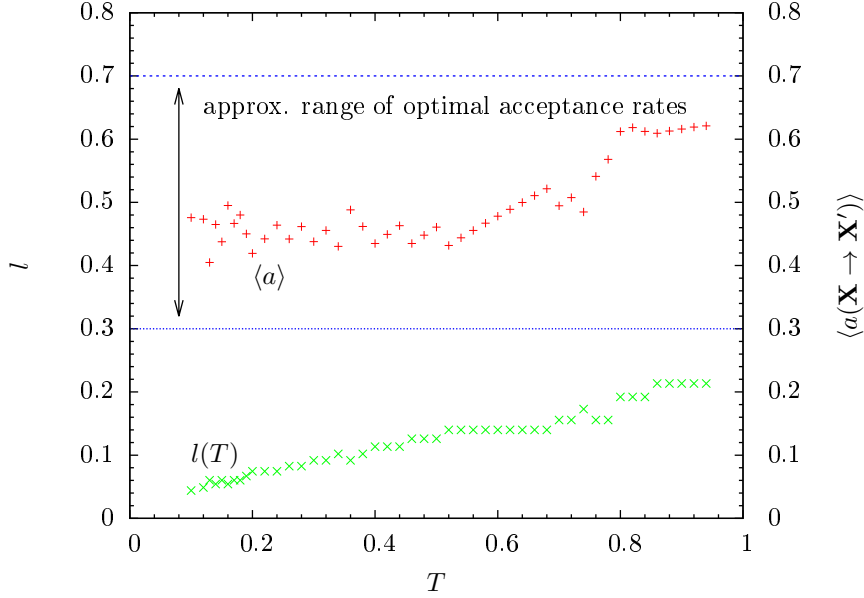


Figure 3.4: Example of a distribution of the temperature dependent displacement parameter $l(T)$, used in a parallel tempering simulation of a flexible elastic 55-mer. The values of $l(T)$ were selected to keep the average acceptance rates $\langle a \rangle$ within the optimal range of $\sim 30\% - 70\%$.

ment updates are allowed at low temperatures and the generated sequence of states becomes strongly correlated. An example of the temperature dependence of $l(T_i)$, obtained from a simulation of a flexible elastic 55-mer, is shown in Fig. 3.4. Polymer models which contain stiff bonds cannot be sampled using displacement updates and require more sophisticated rotational updates [1].

3.3.2 Pivot update

The pivot update consists of rotating a portion of the polymer chain over a randomly chosen rotation axis. This allows for a global change in the polymer conformation and decreases the correlation between the sampled states. In practice, first a random monomer is selected to serve as the pivot and the direction of the rotation axis is defined by a random vector

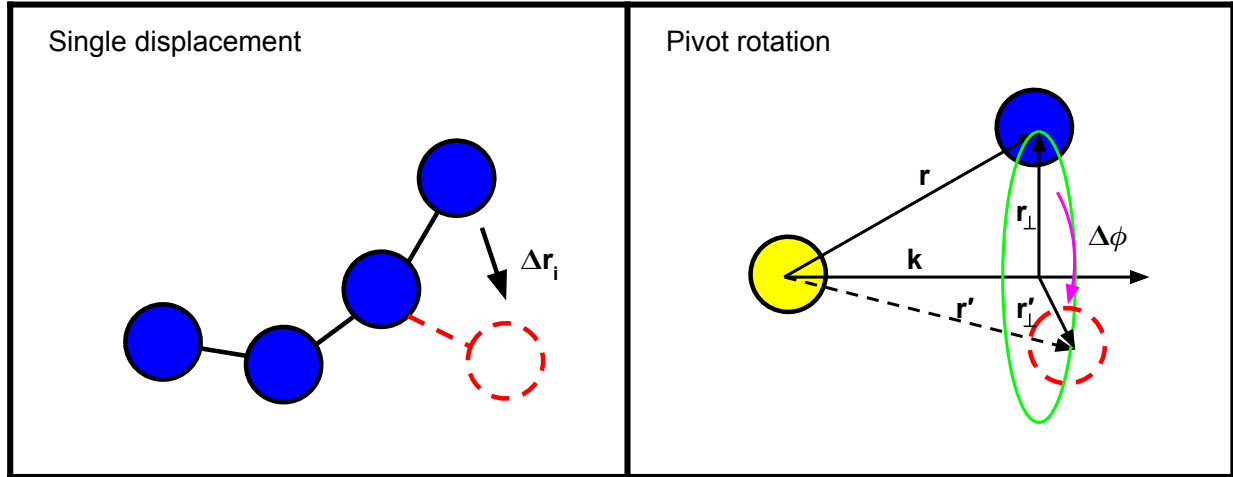


Figure 3.5: Schematic depiction of the single-displacement and the rotational pivot updates. In a displacement update, a randomly selected monomer is moved according to a randomly generated displacement vector $\Delta \mathbf{r}_i$. The pivot update consists of rotating a portion of the polymer chain over a randomly chosen axis \mathbf{k} by a random angle $\Delta \phi$.

k. With equal probability, either terminus of the chain is selected for rotation. The vector which connects the pivot to any monomer which is to be rotated is denoted as \mathbf{r} . The random rotation angle $\Delta \phi$ is selected with uniform probability from some interval $[-\lambda, \lambda]$. Finally, the projection \mathbf{r}_\perp of the vector \mathbf{r} into the plane perpendicular to \mathbf{k} is rotated by $\Delta \phi$ and the resultant vector connecting the pivot and the rotated monomer is given by \mathbf{r}' . A schematic depiction of the single-displacement and the pivot updates is provided in Fig. 3.5. It should be mentioned, that when used in simulations of polymer models with elastic bonds, the pivot update is not ergodic since it preserves bond length [1]. Therefore it is recommended to combine rotational updates with single displacement updates whenever applicable.

Chapter 4

Off-Lattice Polymer Models

It is hardly possible to overestimate the importance of defining an appropriate model to represent a real physical system in a computational study. What constitutes an ‘appropriate’ model depends largely on the system under investigation and on the level of detail which is needed to correctly capture the properties of a given physical phenomena. For example, the study of chemical reaction kinetics, ground-state geometries of molecules, or the optical and electronic properties of semiconductors, requires detailed knowledge of the electronic structure and interactions. In such cases, Density functional theory (DFT) [37] or other quantum mechanical modelling methods need to be employed. On the other hand, a wide range of interesting physical phenomena, such as protein folding, polymer collapse, adsorption, and aggregation, are driven by cooperative structure forming processes and as such are not expected to depend sensitively on the precise electronic or even atomic structures. In principle, it is possible to gain insight into these processes by the means of simplified models with a reduced number of effective parameters [1, 38]. In this chapter we shall briefly discuss the concept of *coarse-graining* and introduce the model for the flexible elastic homopolymer together with a set of structural order parameters which are particularly effective at characterizing the conformational geometries of polymers in the solid pseudophase.

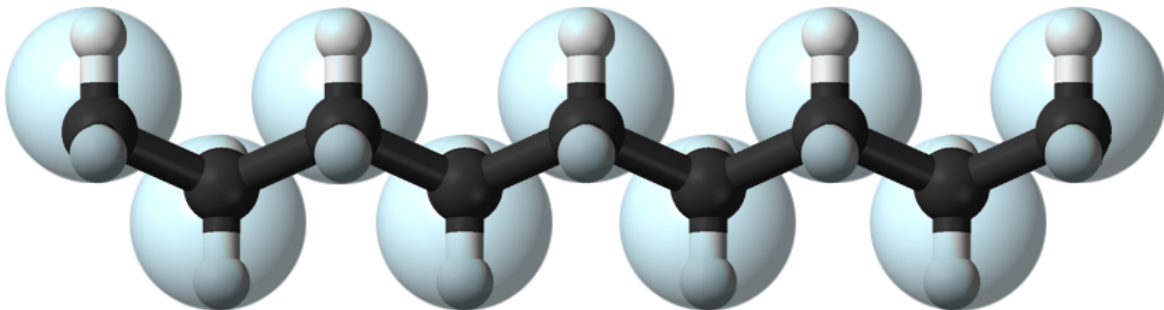


Figure 4.1: An example of a coarse-grained model of polyethylene. Methylene groups (CH_2) are replaced by coarse-grained interaction sites which are depicted as transparent spheres. The interactions between the sites are described in terms of effective potentials.

4.1 Coarse-grained models

The general idea behind coarse-graining is the observation that for a wide range of physical phenomena the individual degrees of freedom of a system do not act independently but rather behave in a cooperative fashion. The goal is then to find the minimal set of degrees of freedom which would allow for an accurate description of a given physical process. In the context of biomolecules, this typically amounts to replacing individual atoms by coarse-grained interaction sites and exact quantum many-body interactions by effective potentials [Fig. 4.1]. The new interaction sites are often referred to as *monomers*.

Individual conformations of a coarse-grained model with N monomers can be represented by a $3N$ -dimensional vector $\mathbf{Q} = (q_1, q_2, \dots, q_{3N})$ in the reduced coordinate system. The components q_i represent the relevant degrees of freedom and are defined in terms of the map

$$\tilde{q}_i(\mathbf{X}) : \mathbf{X} \rightarrow \mathbf{Q} \quad (4.1)$$

between the full conformational space \mathbf{X} and the reduced space \mathbf{Q} . In the full conformational space, the canonical partition function is defined as

$$Z_{\text{can}} = \int \mathcal{D}\mathcal{X} e^{-\beta V(\mathbf{X})}, \quad (4.2)$$

where $V(\mathbf{X})$ is the exact inter-atomic potential. In order to express Z_{can} in terms of the coarse-grained coordinates, we begin by integrating out the microscopic degrees of freedom

$$Z_{\text{can}} = \int \mathcal{D}\mathcal{Q} \int \mathcal{D}\mathcal{X} \prod_{i=1}^{3N} [\delta(q_i - \tilde{q}_i(\mathbf{X}))] e^{-\beta V(\mathbf{X})}. \quad (4.3)$$

Next we replace $V(\mathbf{X})$ by an effective potential

$$\tilde{V}(\mathbf{Q}) = -k_{\text{B}} T \ln \int \mathcal{D}\mathcal{X} \prod_{i=1}^{3N} [\delta(q_i - \tilde{q}_i(\mathbf{X}))] e^{-\beta V(\mathbf{X})}. \quad (4.4)$$

and write

$$Z_{\text{can}} = \int \mathcal{D}\mathcal{Q} e^{-\beta \tilde{V}(\mathbf{Q})}. \quad (4.5)$$

In principle, $\tilde{V}(\mathbf{X})$ contains the combined effects of the exact inter-atomic potentials and hence should allow for an accurate description of the thermodynamic and structural properties of the original system. However in reality, effective potentials are often only crude approximations to the definition introduced in Eq. 4.4. The perhaps surprising fact, that a wide range of physical phenomena can be studied by the means of drastically simplified models, suggests that physical properties that arise through cooperative behaviors do not depend sensitively on microscopic details.

4.2 Flexible elastic homopolymer

The generic model of a flexible, elastic, homopolymer is suitable for the investigation of the thermodynamic properties of polymer chains on a coarse-grained level. The polymer is represented by a linear chain of elastically bonded coarse-grained interaction sites, i.e., monomers [Fig. 4.3]. Individual monomers have neutral electric charges and do not interact via Coulomb forces. Instead, all structure forming processes are primarily driven by effective dipole-dipole interactions represented by the van Der Waals forces.

The potential energy of a dipole-dipole interaction between a pair of monomers (i, j) separated by the distance r is given by

$$V_{\text{dip}}(r) = \frac{1}{4\pi\epsilon_0} \frac{1}{r^3} [\mathbf{p}_i \cdot \mathbf{p}_j - 3(\mathbf{p}_i \cdot \hat{\mathbf{r}})(\mathbf{p}_j \cdot \hat{\mathbf{r}})], \quad (4.6)$$

where \mathbf{p}_i is the dipole moment of the i th monomer and $\hat{\mathbf{r}}$ is the unit vector in the direction given by the separation vector between the two monomers [39]. However the strength of the potential decreases with the third power of the distance which is not consistent with the $1/r^6$ decay typically observed in experiments. In fact, the problem must be treated quantum mechanically to account for the existing overlap between electron wave functions. The potential $V_{\text{dip}}(r)$ is replaced by a dipole-dipole operator \hat{H}_{dip} , which is then introduced as a perturbation to a system of two non-interacting monomers. The first non-trivial term in the perturbation expansion of the ground state energy yields the desired $1/r^6$ dependence [1]. In addition to this generic long range attraction, interacting bodies experience strong short range repulsion due to repelling electronic clouds. Both effects are contained in the famous Lennard-Jones potential [40]

$$U_{\text{LJ}}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (4.7)$$

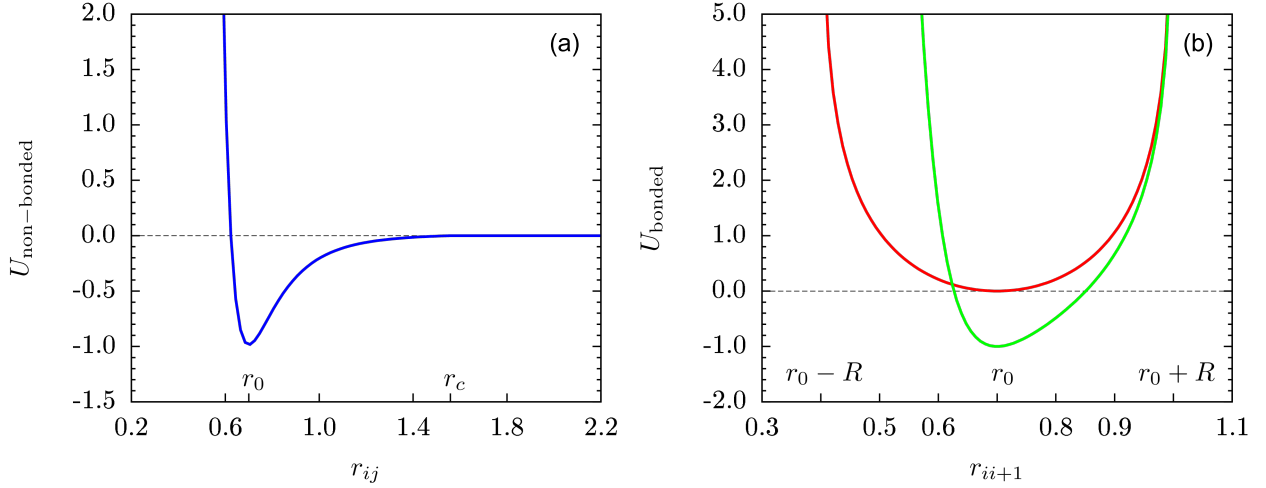


Figure 4.2: (a) Non-bonded interactions in the generic model of an elastic homopolymer are represented by the Lennard-Jones potential. Interacting monomers experience strong repulsion below the equilibrium distance r_0 , and are weakly attracted over the interval (r_0, r_c) where r_c marks the cutoff distance. (b) The nonlinear FENE potential (red) is a symmetric representation of the bonded interactions. As a possible variant, the symmetry of the bonded potential can be broken by combining the FENE and the Lennard-Jones potentials (green).

where ϵ sets the energy scale of the interaction while the relevant length scale is given by the van der Waals distance σ [Fig. 4.2(a)].

The bonds between adjacent monomers are represented by an elastic potential which allows for longitudinal bond vibrations. The simplest approximation is given by the harmonic spring potential (Rouse model), however the linearity of the interaction force allows for large separation between the bonded monomers. This problem can be avoided by introducing a potential which diverges for $|r - r_0| \geq R$, where r_0 is the equilibrium bond length and R controls the allowed fluctuation width. A particularly suitable choice is the finitely extensible nonlinear elastic (FENE) potential [Fig. 4.2] [41–43]

$$U_{\text{FENE}}(r_{ii+1}) = -\frac{K}{2}R^2 \ln \left[1 - \left(\frac{r_{ii+1} - r_0}{R} \right)^2 \right]. \quad (4.8)$$

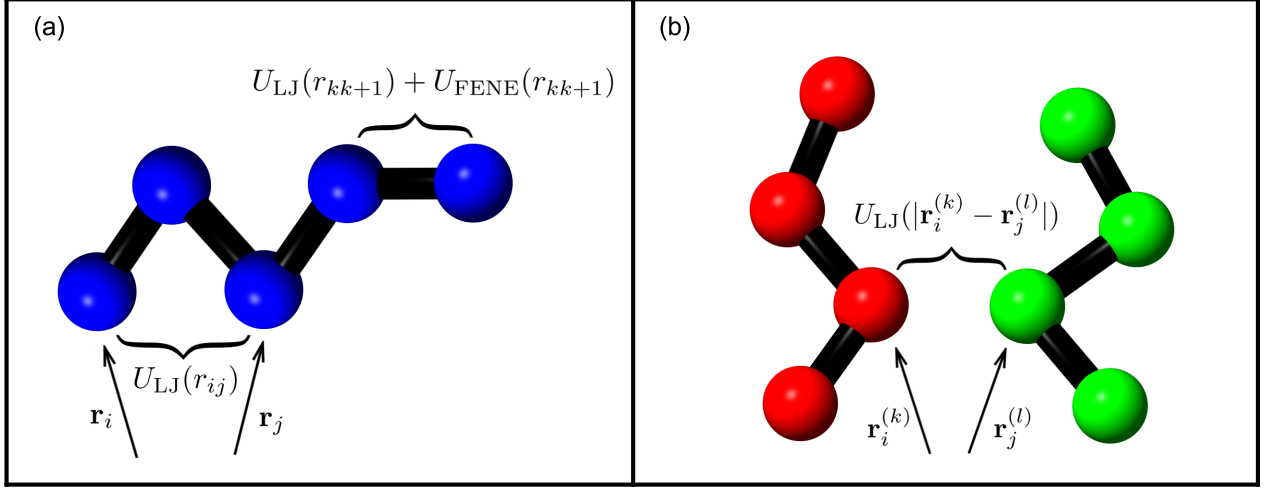


Figure 4.3: (a) Generic model of a flexible elastic homopolymer. All monomers interact via a pairwise Lennard-Jones potential (LJ). Bonded interactions include an additional finitely extensible nonlinear elastic potential (FENE). (b) In a multi-chain system, the interactions between monomers belonging to different chains are also represented by the (LJ) potential.

4.2.1 Single elastic chain

In the following, we will define the model for a single elastic polymer chain which will be used for the remainder of this thesis [Fig. 4.3]. The specific values of the model parameters will be provided individually in the later chapters. The energy of a polymer chain of length N in a conformation $\mathbf{X} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ is given by the sum of non-bonded and bonded contributions

$$E(\mathbf{X}) = \sum_{i < j+1}^N U_{\text{non-bonded}}(r_{ij}) + \sum_{i=1}^{N-1} U_{\text{bonded}}(r_{ii+1}). \quad (4.9)$$

All non-bonded interactions are represented by the Lennard-Jones potential introduced in Eq. 4.7. In order to reduce the number of required calculations in a computer simulation, it is a standard procedure to introduce a cutoff distance r_c and set $U_{\text{LJ}} = 0$ for all $r \geq r_c$. The truncated LJ potential must also be shifted vertically by the constant $U_{\text{LJ}}(r_c)$ to prevent

a discontinuity at r_c . Hence the non-bonded interactions are represented by

$$U_{\text{non-bonded}}(r_{ij}) = U_{\text{LJ}}^{\text{trunc}}(r_{ij}) = \begin{cases} U_{\text{LJ}}(r_{ij}) - U_{\text{LJ}}(r_c), & r_{ij} \leq r_c, \\ 0, & r_{ij} > r_c. \end{cases} \quad (4.10)$$

In addition to the FENE potential [Eq. 4.8], bonded interactions contain an additional Lennard-Jones term

$$U_{\text{bonded}}(r_{ii+1}) = U_{\text{FENE}}(r_{ii+1}) + U_{\text{LJ}}^{\text{trunc}}(r_{ii+1}). \quad (4.11)$$

The short range repulsive part of the LJ potential ensures that the resultant potential is asymmetric. The shapes of the bonded and non-bonded potentials are shown in Fig. 4.2.

4.2.2 Interacting elastic chains

A system of interacting elastic homopolymer chains is a suitable model for the study of generic features of macromolecular aggregation. The energy of M interacting chains, each consisting of N identical monomers, can be separated into intra-chain and inter-chain pairwise interactions

$$E_{\text{total}} = E_{\text{intra}} + E_{\text{inter}}. \quad (4.12)$$

The intra-chain contribution

$$E_{\text{intra}} = \sum_{k=1}^M \sum_{i=1}^{N-1} U_{\text{bonded}}(r_{ii+1}^{(k)}) + \sum_{k=1}^M \sum_{i < j}^N U_{\text{non-bonded}}(r_{ij}^{(k)}) \quad (4.13)$$

consists of both bonded and non-bonded interactions, as defined in Sec. 4.2.1, and $r_{ij}^{(k)}$ is the distance between the pair of monomers (i,j) of the k -th chain. The inter-chain contribution

$$E_{\text{inter}} = \sum_{k < l}^M \sum_{i,j}^N U_{\text{LJ}}^{\text{trunc}}(|\mathbf{r}_i^{(k)} - \mathbf{r}_j^{(l)}|), \quad (4.14)$$

consists solely of non-bonded Lennard-Jones interactions. Schematic depiction of the model is provided in Fig. 4.3 (b).

4.3 Structural order parameters

The formalism of the microcanonical inflection-point analysis, as introduced in section 2.1.2, provides a systematic approach for the identification and classification of pseudophase transitions in mesoscopic systems. Further insight into the thermodynamic and structural properties of polymer systems can be obtained by identifying the set of conformations which are dominant in a given pseudophase. This can be accomplished either by visual inspection of sample structures, or more systematically, by introducing a suitable set of structural order parameters.

An example of a useful and easily computable structural quantity is the radius of gyration

$$r_{\text{gyr}}(\mathbf{X}) = \sqrt{\frac{1}{N} \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{\text{com}})^2}, \quad (4.15)$$

where

$$\mathbf{r}_{\text{com}} = \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i \quad (4.16)$$

is the center-of-mass of the polymer conformation. The average $\langle r_{\text{gyr}} \rangle$ is a measure of the compactness of the dominant conformations found at a given canonical temperature.

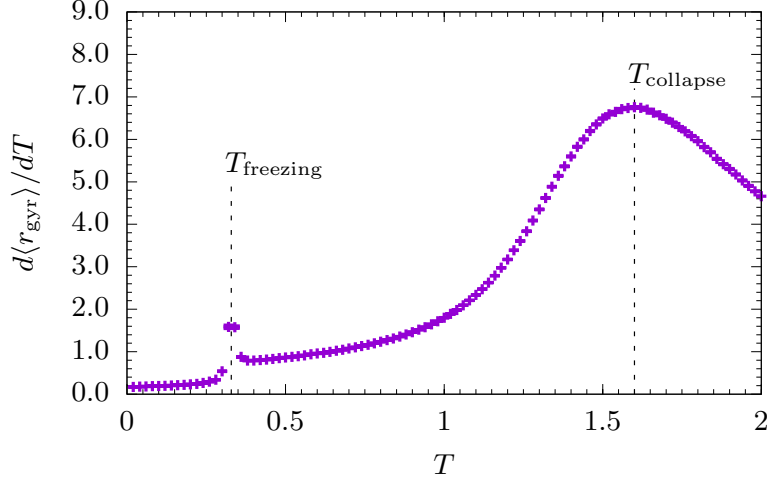


Figure 4.4: The thermal fluctuations of the radius of gyration obtained from a Monte Carlo simulation of an elastic 55mer. The distinct peaks indicate the locations of the freezing and collapse transitions at the temperatures T_{freezing} and T_{collapse} respectively.

Signals, such as peaks and shoulders, in the temperature derivative

$$\frac{d\langle r_{\text{gyr}} \rangle}{dT} = \frac{\langle r_{\text{gyr}} E \rangle - \langle r_{\text{gyr}} \rangle \langle E \rangle}{k_B T^2} \quad (4.17)$$

indicate locations of heightened thermodynamic activity and are routinely used to identify pseudophase transitions [Fig. 4.4].

Alternatively, a wide range of polymer conformation geometries can be identified using the set of rotationally invariant order parameters

$$Q_l = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^l |\rho_{l,m}|^2 \right]^{1/2}, \quad (4.18)$$

where

$$\rho_{l,m} = \frac{1}{N} \sum_{i=0}^N Y_{l,m}(\mathbf{r}_i) \quad (4.19)$$

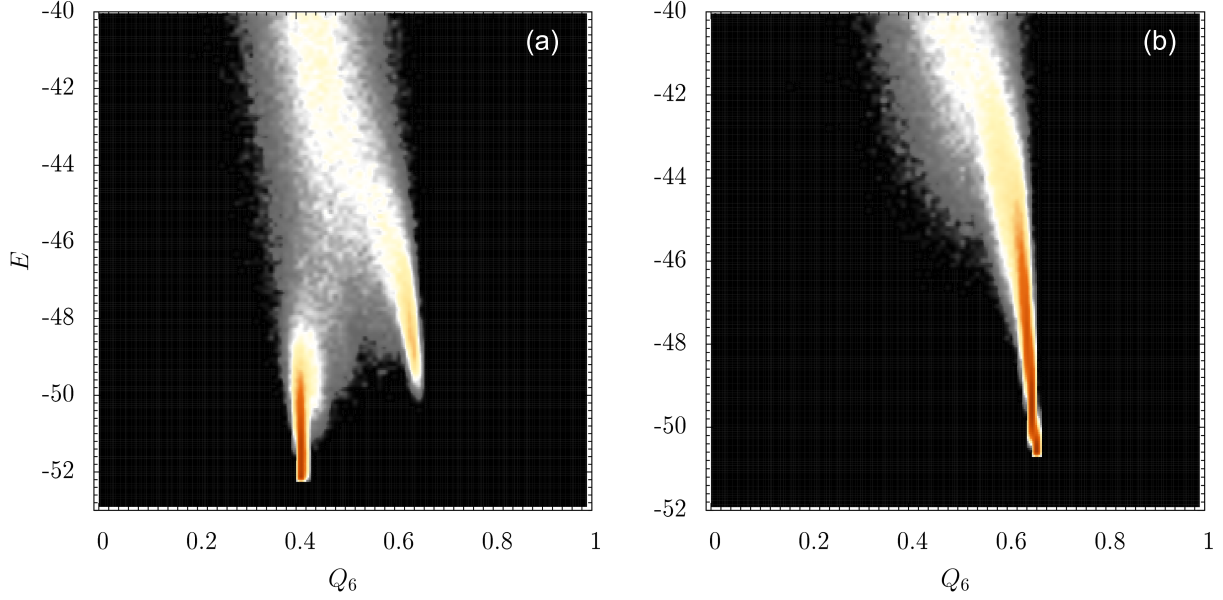


Figure 4.5: Intensity plots of the rotationally invariant order parameter Q_6 for two variants of a coarse-grained model of an elastic 15mer. The shading indicates the probability of detecting a configuration with a given value of the order parameter, red being the maximum probability and black being the lowest. In figure (a), the two prominent low energy branches reveal the existence of two solid pseudophases with distinct conformational geometries. Whereas in (b), only a single solid phase is detected.

is the average of the real spherical harmonics¹ evaluated at positions of the individual monomers [44]. This approach has been particularly effective in the investigations of polymer systems exhibiting multiple solid pseudophases at low energies [45].

¹The real harmonics can be expressed in terms of the better known complex harmonics as

$$Y_{lm}(\mathbf{r}_i) = \begin{cases} \frac{i}{\sqrt{2}} [Y_l^m(\mathbf{r}_i) - (-1)^m Y_l^{-m}(\mathbf{r}_i)] & \text{if } m < 0, \\ Y_l^m(\mathbf{r}_i) & \text{if } m = 0, \\ \frac{1}{\sqrt{2}} [Y_l^{-m}(\mathbf{r}_i) + (-1)^m Y_l^m(\mathbf{r}_i)] & \text{if } m > 0. \end{cases} \quad (4.20)$$

Chapter 5

Confinement Effects on Structural Transitions in Flexible Homopolymers

5.1 Introduction

5.2 Canonical analysis

5.3 Inflection-point analysis

5.4 Hyper-phase diagrams

Chapter 6

Impact of Bonded Interactions on the Ground-State Geometries of Flexible Homopolymers

6.1 Structural order parameters

6.2 15-mer

6.3 55-mer

Chapter 7

Aggregation of Flexible Elastic Homopolymers

7.1 Introduction

7.2 Microcanonical analysis

7.2.1 Subphases and subphase transitions

7.2.2 Missing subphases and translational entropy

7.2.3 Density effects on the latent heat

Chapter 8

Summary and Outlook

Table 8.1: Example of a table.
[The contents of the table would go here.]

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