

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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Contents

1	Introduction	1
2	Elements of Statistical Mechanics	2
2.1	The microcanonical ensemble	3
2.2	The canonical ensemble	9
2.3	Configurational density of states	9
2.4	Generalized ensembles	9
3	Computational Methods	10
3.1	Markov chain Monte Carlo	10
3.2	Generalized ensemble Monte Carlo	10
3.3	Simple Monte Carlo updates	10
4	Coarse-grained Homopolymer Model	11
4.1	Flexible elastic homopolymer	11
4.2	Interacting homopolymers	11
5	Confinement Effects on Structural Transitions in Flexible Homopolymers	12
5.1	Introduction	12
5.2	Canonical analysis	12
5.3	Inflection-point analysis	12

5.4	Hyper-phase diagrams	12
6	Impact of Bonded Interactions on the Ground-State Geometries of Flexible Homopolymers	13
6.1	Structural order parameters	13
6.2	15-mer	13
6.3	55-mer	13
7	Aggregation of Flexible Elastic Homopolymers	14
7.1	Introduction	14
7.2	Microcanonical analysis	14
8	Summary and Outlook	15
	Bibliography	15

List of Figures

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 <i>first-order</i> transition. The negative-valued peak at $E \approx -24$ corresponds to a <i>second-order</i> transition.	7
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 <i>first-order</i> 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	8
8.1	Example of a figure.	15

List of Tables

8.1	Example of a table.	16
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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 ~ 10 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.

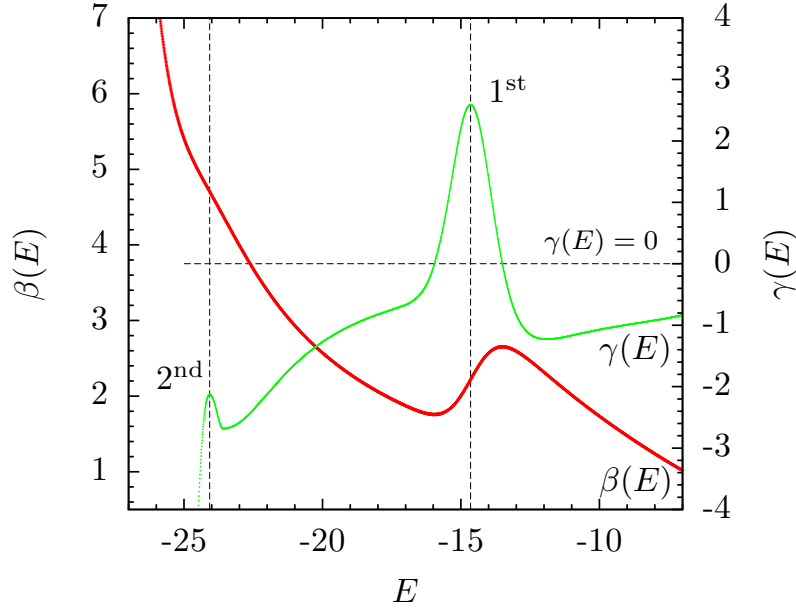


Figure 2.1: Microcanonical inflection-point analysis of the inverse microcanonical temperature $\beta(E)$. The prominent back-bending region in $\beta(E)$, together with the positive-valued peak in its energy derivative $\gamma(E)$ at $E \approx -15$, indicates a *first-order* transition. The negative-valued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

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 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

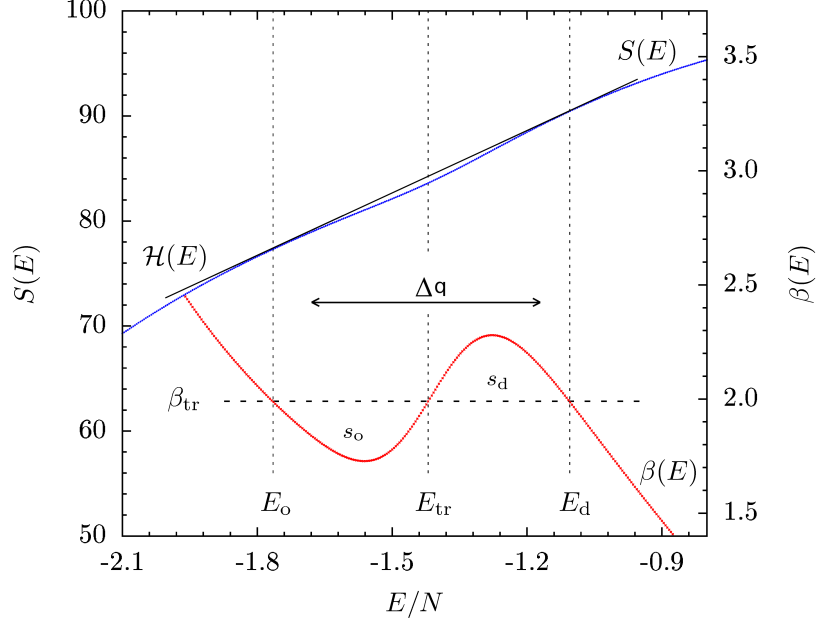


Figure 2.2: The convex region of the microcanonical entropy $S(E)$ and the back-bending of the microcanonical inverse temperature $\beta(E)$ are prominent indicators of *first-order* transitions. The slope of the double-tangent Gibbs hull $\mathcal{H}(E)$ defines the transition temperature β_{tr} . The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

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

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

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

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 pseu-

dophase 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.

Based on the principle of minimal sensitivity and Ehrenfest's original idea of characterizing the order of a transition by the free-energy derivative at which a discontinuity occurs, one can likewise introduce a hierarchy of higher-order transitions microcanonically.

2.2 The canonical ensemble

2.3 Configurational density of states

2.4 Generalized ensembles

Chapter 3

Computational Methods

3.1 Markov chain Monte Carlo

3.1.1 Master equation and detailed balance

3.1.2 Metropolis sampling

3.2 Generalized ensemble Monte Carlo

3.2.1 Parallel tempering

3.2.2 Multiple Gaussian modified ensemble

3.2.3 Histogram reweighting methods

3.2.4 Multicanonical sampling

3.3 Simple Monte Carlo updates

Chapter 4

Coarse-grained Homopolymer Model

4.1 Flexible elastic homopolymer

4.2 Interacting homopolymers

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

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Figure 8.1: Example of a figure.

Table 8.1: Example of a table.
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Bibliography

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