

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: Index word or phrase, Index word or phrase, Index word or phrase, Index word, Index word, Index word

STRUCTURE FORMING PROCESSES IN
MESOSCOPIC POLYMER SYSTEMS

by

TOMAS KOCI

B.A., The Juilliard School, 2008

A Dissertation Submitted to the Graduate Faculty
of The University of Georgia in Partial Fulfillment
of the

Requirements for the Degree

DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

2016

©2016

Tomas Koci

STRUCTURE FORMING PROCESSES IN
MESOSCOPIC POLYMER SYSTEMS

by

TOMAS KOCI

Approved:

Major Professor: Michael Bachmann

Committee: Steven P. Lewis
Heinz-Bernd Schuttler

Electronic Version Approved:

Alan Dorsey
Dean of the Graduate School
The University of Georgia
July 2016

Structure Forming Processes in Mesoscopic Polymer Systems

Tomas Koci

May 4, 2016

Acknowledgments

Mention Michael Bachmann, Steven Lewis, Heinz Schuttler, D.P. Landau, Jeff Mike and Shan-Ho, finally all the Links and my family

Contents

1	Introduction	6
2	Elements of Statistical Mechanics	7
2.1	The microcanonical ensemble	8
2.1.1	Microcanonical temperature	9
2.1.2	Microcanonical analysis of phase transitions	10
2.2	The canonical ensemble	12
2.3	Configurational density of states	12
2.4	Generalized ensembles	12
3	Computational Methods	13
3.1	Markov chain Monte Carlo	13
3.1.1	Master equation and detailed balance	13
3.1.2	Metropolis sampling	13
3.2	Generalized ensemble Monte Carlo	13
3.2.1	Parallel tempering	13
3.2.2	Multiple Gaussian modified ensemble	13
3.2.3	Histogram reweighting methods	13
3.2.4	Multicanonical sampling	13
3.3	Simple Monte Carlo updates	13

4	Coarse-grained Homopolymer Model	14
4.1	Flexible elastic homopolymer	14
4.2	Interacting homopolymers	14
5	Confinement Effects on Structural Transitions in Flexible Homopolymers	15
5.1	Introduction	15
5.2	Canonical analysis	15
5.3	Inflection-point analysis	15
5.4	Hyper-phase diagrams	15
6	Impact of Bonded Interactions on the Ground-State Geometries of Flexible Homopolymers	16
6.1	Structural order parameters	16
6.2	15-mer	16
6.3	55-mer	16
7	Aggregation of Flexible Elastic Homopolymers	17
7.1	Introduction	17
7.2	Microcanonical analysis	17
7.2.1	Subphases and subphase transitions	17
7.2.2	Missing subphases and translational entropy	17
7.2.3	Density effects on the latent heat	17
8	Summary and Outlook	18

List of Figures

8.1	Example of a figure.	18
-----	------------------------------	----

List of Tables

8.1	Example of a table.	19
-----	-----------------------------	----

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 over a range of values of some external control parameter⁵ 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, typically marked

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

by abrupt changes in macroscopic properties in response to a minute change in an external control parameter. 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 the thermodynamic observables and their derivatives are found only in systems which satisfy the thermodynamic limit. In mesoscopic and microscopic systems, due to finite size effects, divergences are replaced by peaks and discontinuities become smoothed over. For clarity, we designate the term *pseudophase transition* to represent significant conformational changes in finite systems. Likewise, a thermodynamic phase in a finite system shall be referred to as a *pseudophase*. 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 temperature is an inherent property of the system. As such, it contains all the information about the interplay of entropy and energy, and can be used to locate and classify all structural transitions of the system. In fact a transition occurs when $\beta(E)$ responds least sensitively to changes in E . This is embodied by the inflection-point analysis method [?, ?]. In this scheme, the convex-to-concave inflection points of $\beta(E)$ locate an energetic transition point between ensembles of macrostates that can be crossed by a change in energy. We call these ensembles “phases” (sometimes referred to as pseudophases or structural phases), because this microcanonical behavior remains also valid in the thermodynamic limit. If we introduce $\gamma(E) = d\beta(E)/dE$, a transition is defined to be of *first order* if $\gamma(E)$ has a positive peak

value at the inflection point. In case the peak value is negative, the transition is classified as of *second order*. This is schematically depicted in Fig. ?? . 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

[You could put a picture here.]

Figure 8.1: Example of a figure.

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