

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 2, 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 inflection-point analysis	10
2.2	The canonical ensemble	11
2.3	Configurational density of states	11
2.4	Generalized ensembles	11
3	Computational Methods	12
3.1	Markov chain Monte Carlo	12
3.1.1	Master equation and detailed balance	12
3.1.2	Metropolis sampling	12
3.2	Generalized ensemble Monte Carlo	12
3.2.1	Parallel tempering	12
3.2.2	Multiple Gaussian modified ensemble	12
3.2.3	Histogram reweighting methods	12
3.2.4	Multicanonical sampling	12
3.3	Simple Monte Carlo updates	12

4	Coarse-grained Homopolymer Model	13
4.1	Flexible elastic homopolymer	13
4.2	Interacting homopolymers	13
5	Confinement Effects on Structural Transitions in Flexible Homopolymers	14
5.1	Introduction	14
5.2	Canonical analysis	14
5.3	Inflection-point analysis	14
5.4	Hyper-phase diagrams	14
6	Impact of Bonded Interactions on the Ground-State Geometries of Flexible Homopolymers	15
6.1	Structural order parameters	15
6.2	15-mer	15
6.3	55-mer	15
7	Aggregation of Flexible Elastic Homopolymers	16
7.1	Introduction	16
7.2	Microcanonical analysis	16
7.2.1	Subphases and subphase transitions	16
7.2.2	Missing subphases and translational entropy	16
7.2.3	Density effects on the latent heat	16
8	Summary and Outlook	17

List of Figures

8.1	Example of a figure.	17
-----	------------------------------	----

List of Tables

8.1	Example of a table.	18
-----	-----------------------------	----

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 a large number 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 motion of most phase space trajectories, collective system properties such as entropy, pressure, or temperature often 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 first 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 $[E, E + \Delta E]$.

²Alternative definitions of the density of states are more convenient in certain contexts. Please see section 2.3 for detailed discussion.

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) . These can be found by setting

³Entropy would be a unitless quantity if temperature was measured in the more natural units of energy.

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

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

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 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.]