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

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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 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 nature 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]

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

where

$$\mathcal{DPDX} = \prod_{n=1}^{N} \frac{d^3 p_n d^3 x_n}{(2\pi\hbar)^3} \tag{2.2}$$

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

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

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

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

[1] In 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 $[E, E + \Delta E]$.

[2] Alternative definitions of the density of states can be more convenient in certain contexts. For further discussion of this subject, please refer to section 2.3.

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

$$S(E) = k_{\mathrm{B}} \ln g(E), \tag{2.5}$$

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

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

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

$$g(E) = \int dE_1 g_1(E_1) g_2(E - E_1). \tag{2.7}$$

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

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

$$\frac{1}{g_1}\frac{dg_1}{dE_1}\bigg|_{\bar{E}_1} = \frac{1}{g_2}\frac{dg_2}{dE_2}\bigg|_{E-\bar{E}_1}, \tag{2.8}$$

or alternatively in terms of the microcanonical entropy

$$\frac{dS_1}{dE_1}\bigg|_{\bar{E}_1} = \frac{dS_2}{dE_2}\bigg|_{E-\bar{E}_1}. \tag{2.9}$$

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

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

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

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

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

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Computational Methods

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

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Aggregation of Flexible Elastic Homopolymers

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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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