

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,
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MESOSCOPIC POLYMER SYSTEMS

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Structure Forming Processes in 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 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)¹. 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 states²

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

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

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

¹Additional quantities such as the total linear momentum \vec{P} , or angular momentum \vec{J} , may be conserved.

²In the context of computer simulations, the energy space becomes by necessity discretized and the density of states is measured by counting the number of microstates within some finite energy range $[E, E + \Delta E]$.

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

$$S(E) = k_B \ln g(E), \quad (2.5)$$

an *extensive* quantity with dimensions of energy over temperature.³

2.1.1 Microcanonical temperature

Temperature is a fundamental concept in 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 two weakly interacting isolated systems, S_1 and S_2 . The total energy of the combined system is fixed and equals to the sum of energies of the two systems $E = E_1 + E_2$. The probability density for a given pair of energies (E_1, E_2) is given by

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

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 a system with a large number of degrees of freedom, the probability density $\rho(E_1, E_2)$ is sharply peaked around (E'_1, E'_2) . Therefore the equilibrium energies of the two subsystems

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

can be found by setting the energy derivative of the probability density to zero in which case

$$\frac{1}{g_1} \frac{dg_1}{dE_1} \Big|_{E'_1} = \frac{1}{g_2} \frac{dg_2}{dE_2} \Big|_{E-E'_1}, \quad (2.8)$$

or 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 fact that in thermal equilibrium, interacting systems have equal temperatures, we define the microcanonical temperature as

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

In many contexts it is convenient to instead work with the inverse microcanonical temperature, defined as

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

Next we discuss the central role of the inverse microcanonical temperature and its energy derivatives in the identification and 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 Generalized ensembles

Chapter 3

Computational Methods

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3.1.1 Master equation and detailed balance

3.1.2 Metropolis sampling

3.2 Generalized ensemble Monte Carlo

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