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SoSe 05

Set 4
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T IV: Thermodynamik und Statistik
(Prof. E. Frey)

Problem set 4

Problem 4.1 *Biopolymer*

Many biopolymers (e.g. *titin*) have a modular structure, where each module can undergo a transition between two energetically different states (folded and unfolded) in which the modules have different length l_f and l_u, respectively (see figure); for titin $l_f = 4$nm and $l_u = 32$nm. Consider a polymer where N such modular units are arranged in a straight line, N_u of which are in the unfolded state and N_f of which are in the folded state, such that the total length is $L = N_f l_f + N_u l_u$. The folded state with energy ϵ_f is energetically favored with respect to the unfolded state with energy ϵ_u. Derive the relation between the length L of the chain molecule and the tension F applied between both ends of the molecule. Use the canonical ensemble at constant tension.

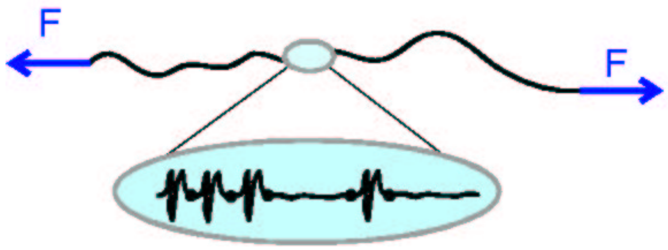

Figure 1: Illustration of a two-state model for a modular biopolymer like titin; see M. Rief et al., Phys. Rev. Lett. **81**, 4764 (1998).

Problem 4.2 *entropy of mixing*

Consider a container at temperature T of volume V separated by an unpermeable fixed wall into subsystems of volume V_A, V_B, containing N_A, N_B particles, respectively. Removing the wall the system reaches a new equilibrium state, where the $N = N_A + N_B$ particles homogeneously fill the total container. Calculate the change of entropy for such a process (mixing entropy) for the case that the particles in V_A and V_B are chemically different/identical. Discuss the problem in particular for equal pressures in the subsystems and underline the significance of the combinatorial factors in the partition sum.

Problem 4.3 *typical states*

Consider a thermodynamic system with discrete energy levels. The canonical ensemble assigns probabilities for the microstates k with corresponding energy E_k according to

$$p_k = Z^{-1} \exp\left(\frac{-E_k}{k_B T}\right), \qquad Z = \sum_k \exp\left(\frac{-E_k}{k_B T}\right).$$

Use the thermodynamic identity $F = -k_B T \ln Z = \langle E \rangle - TS$ to eliminate the partition sum Z in favor of the mean energy $\langle E \rangle$ and the entropy S. Show that the probability for a *typical state* k, i.e. a state with an energy close to the mean one, $|E_k - \langle E \rangle| \leq N\epsilon$, fulfills the bounds

$$e^{-S/k_B} e^{-N\epsilon/k_B T} \leq p_k \leq e^{-S/k_B} e^{N\epsilon/k_B T}.$$

Use the extensivity of the heat capacity

$$C_V = \frac{1}{k_B T^2} \langle (E - \langle E \rangle)^2 = \frac{1}{k_B T^2} \sum_k (E_k - \langle E \rangle)^2 p_k$$

to show that in the thermodynamic limit, $N \to \infty$ the *atypical states* have negligible weight, i.e. $\sum' p_k \to 0$, where the prime indicates that the sum is restricted to atypical states. Argue that in the thermodynamic limit all typical microstates are essentially equiprobable, and that the entropy is a measure for the number of these typical states.

Problem 4.4 *free energy*

Consider the probabilites for microstates k

$$p_k(\beta) = Z(\beta)^{-1} \exp(-\beta E_k), \qquad \beta = 1/k_B T$$

of some thermodynamic system as a function of inverse temperature. Use probabilistic arguments to show

$$Z(\beta) = Z(\beta_0) \langle e^{(\beta_0 - \beta)E} \rangle_0,$$

where $\langle \cdot \rangle_0$ denotes canonical averaging at inverse temperature $\beta_0 = 1/k_B T_0$. Use the definition of the cumulants to show that the corresponding free energies satisfy

$$-\beta F(\beta) = -\beta_0 F(\beta_0) + \sum_{n=1}^{\infty} \kappa_n \frac{(\beta_0 - \beta)^n}{n!}$$

where κ_n are the cumulants of the energy with respect to the probability distribution at β_0.

Problem 4.5 *ideal gas reservoir*

Consider a system of N_1 particles described by a Hamilton function $\mathcal{H}_1$ in weak thermal contact with an ideal gas of N_2 particles. Starting from the microcanonical probability distribution function for the joint system, derive the probability distribution function of the system of the N_1 particles alone by integrating out the degrees of freedom of the ideal gas. Consider, in particular, the limit when the ideal gas acts as a thermal reservoir, i.e. particle number $N_2 \to \infty$ and total energy $E \to \infty$ with fixed energy per particle $\epsilon = E/N_2$.