UNIVERSITÄT ZU KÖLN

Prof. Dr. Joachim Krug
Dr. Ivan Szendro
Institut für Theoretische Physik
Sommersemester 2012

3. Exercise sheet to the lecture "Statistical Physics Far from Equilibrium"

Exercise 5: The Langmuir lattice gas

Consider a lattice of V sites, each of which is vacant with probability ρ or occupied by a single particle with probability $1-\rho$. Multiple occupancy is not allowed, i.e. the particles are subject to a *hard core interaction.*

a.) Calculate the variance $\langle (N - \langle N \rangle^2 \rangle$ of the particle number N, and use the general relation[1]

$$\langle (N - \langle N \rangle)^2 \rangle = \frac{\langle N \rangle^2}{V} k_{\mathrm{B}} T \kappa_T \tag{1}$$

to determine the isothermal compressibility κ_T of the lattice gas. Compare the result to the compressibility of the ideal classical gas, which you can compute from the ideal gas law using purely thermodynamic relations. In which density regime do the two expressions agree?

b.) Write down an expression for the probability $P(N,V)$ to find exactly N particles in the system. Evaluate this expression in the limit $V \to \infty$ for the following two cases:
(i) Keeping the density ρ constant, show that $P(N,V)$ converges to a Gaussian.
(ii) Keeping the mean particle number $\langle N \rangle = \rho V$ constant, show that $P(N,V)$ converges to a Poisson distribution.

c.) Under Langmuir kinetics, particles are added to empty sites at rate Γ_a and removed from occupied sites at rate Γ_d. Write down the master equation for this two-state system and determine the stationary density ρ as a function of Γ_a and Γ_d.

Exercise 6: Convergence of the master equation to the stationary distribution

A continuous time Markov chain on a finite number of states $i = 1, ..., C$ is governed by the *master equation*

$$\frac{d}{dt} P_i = \sum_{j \neq i} \Gamma_{ji} P_j - \sum_{j \neq i} \Gamma_{ij} P_i = \sum_j A_{ji} P_j, \tag{2}$$

where $P_i(t)$ is the probability to find the system in state i at time t (subject to some initial condition), Γ_{ij} is the transition rate from state i to state j, and the *generator* of the process is the matrix

$$A_{ij} = \begin{cases} \Gamma_{ij} & : \quad i \neq j \\ -\sum_{k \neq i} \Gamma_{ik} & : \quad i = j. \end{cases} \tag{3}$$

[1] The derivation can be found in any textbook on equilibrium statistical mechanics.

We assume that the Markov chain is irreducible, such that a unique, normalizable stationary distribution P_i^* satisfying the relation

$$\sum_j A_{ji} P_j^* = 0 \tag{4}$$

exists.

In this exercise we examine the convergence of the dynamical evolution (2) to the stationary distribution P_i^*. To this end we introduce the *relative entropy*[2]

$$D(\{p_i\}|\{q_i\}) = \sum_i p_i \ln(p_i/q_i) \tag{5}$$

as a measure of the 'distance' between two probability distributions $\{p_i\}$ and $\{q_i\}$.

a.) Show that for any two probability distributions

$$D(\{p_i\}|\{q_i\}) \geq 0, \tag{6}$$

and $D(\{p_i\}|\{q_i\}) = 0$ only if $p_i \equiv q_i$. *Hint:* Use that $\ln x \leq x - 1$ for any x.

b.) Using (2), now show that

$$\frac{d}{dt} D(\{P_i(t)\}|\{P_i^*\}) \leq 0, \tag{7}$$

which implies[3] that $P_i(t)$ approaches P_i^*.

[2] This is also known as the Kullback-Leibler divergence.

[3] Mathematically, D is a *Lyapunov function* for the dynamical evolution (2). To rigorously deduce convergence to P_i^* requires a few additional steps, see e.g. J. Schnakenberg, Rev. Mod. Phys. **48**, 571 (1976).