

Statistical Physics - Paris Physics Master

Home exercices

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November 3, 2020

Your homework should be uploaded as a single pdf file on moodle no later than November 17, 2020. As an alternative, you can send it by email to fabio.pietrucci@sorbonne-universite.fr.

1 Random walk

1.1

Consider a random walk in three dimensions: each step is a vector whose components are three random numbers uniformly distributed in the interval $[-a, +a]$ (x, y components) or $[d - a, d + a]$ (z component), with $a > 0$. What are the average displacement and the mean squared displacement after N steps? Explain your calculations, and propose a possible physical system that could be modelled in this way.

1.2

Explain what we can infer about the long-time displacement of a molecule in a liquid from the central limit theorem, without knowing the detailed interatomic forces. Can we apply the same reasoning to an impurity atom in a solid?

2 Partition functions

2.1

Calculate the electric polarization \mathbf{P} of an ideal gas, consisting of molecules having a constant electric dipole moment \mathbf{p} in a homogeneous external electric field \mathbf{E} at temperature T . What is the dielectric constant of this gas at small fields?

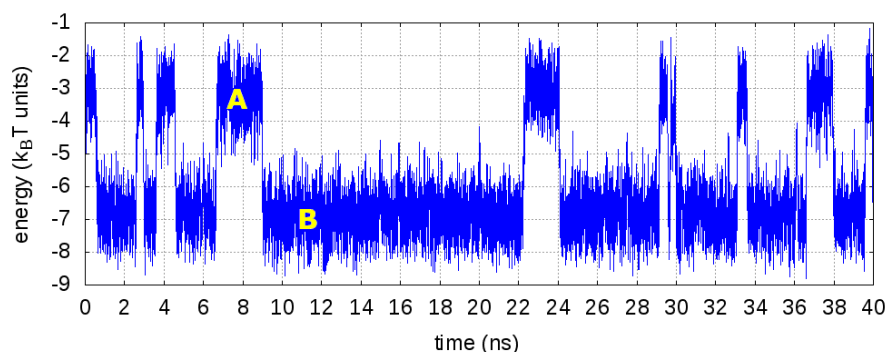
2.2

Consider a system composed of a very large number N of distinguishable atoms at rest and mutually noninteracting, each atom having only two (nondegenerate) energy levels: $0, \epsilon > 0$. Consider the limit $N \rightarrow \infty$. What is the maximum possible value of E/N if the system is in thermal equilibrium at $T > 0$? Compute the entropy per atom S/N as a function of E/N .

3 Free energy landscapes

3.1

The graph here below represents the energy along the trajectory of a metastable system simulated in the NVT ensemble. From the graph, make an approximate estimate of the probability of the two metastable states A and B , and of the transition rates $k_{A \rightarrow B}$ and $k_{B \rightarrow A}$.



3.2

Now estimate ΔF_{AB} (free energy difference), ΔE_{AB} (energy difference), $T\Delta S_{AB}$ (temperature \times entropy difference), explaining your calculation. Which state has larger entropy?

3.3

Suppose that the transition between A and B is described well by an order parameter Q : make a simple sketch of the free energy landscape $F(Q)$, indicating the location of transition state configurations. Give a possible example of such a physical system, and of the corresponding order parameter.

3.4

In this exercise you replaced ensemble averages with another type of averages: define both of them mathematically. What are the conditions for the two types

to give the same results? Give a couple of examples of physical experiments where these conditions hold, and a couple where they do not hold.

3.5

In general, rare transitions between metastable states are well described by Poisson's probability law: why? Compute the mean and the standard deviation of the first passage time (the time we have to wait to observe a transition from one metastable state to another one), considering that its probability density is given by the probability to observe zero jumps between 0 and t multiplied by the probability to observe one jump between t and $t + dt$.

4 Scientific articles

Choose one of the following articles, read it and discuss the most important and most interesting results in a maximum of two written pages. Be critical and describe the connections with the topics studied during the course. The pdf files can be downloaded from moodle.

4.1

D.F. Styer, *Insight into entropy*, American Journal of Physics 68, 1090 (2000)

Abstract: What is the qualitative character of entropy? Several examples from statistical mechanics (including liquid crystal reentrant phases, two different lattice gas models, and the game of poker) demonstrate facets of this difficult question and point toward an answer. The common answer of "entropy as disorder" is regarded here as inadequate. An alternative but equally problematic analogy is "entropy as freedom." Neither simile is perfect, but if both are used cautiously and not too literally, then the combination provides considerable insight.

<https://doi.org/10.1119/1.1287353>

4.2

V. Ambegaokar and A.A. Clerk, *Entropy and time*, American Journal of Physics 67, 1068 (1999)

Abstract: The emergence of a direction of time in statistical mechanics from an underlying time-reversal-invariant dynamics is explained by examining a simple model. The manner in which time-reversal symmetry is preserved and the role of initial conditions are emphasized. An extension of the model to finite temperatures also is discussed.

<https://doi.org/10.1119/1.19084>

4.3

S.K. Ma, *Calculation of Entropy from Data of Motion*, Journal of Statistical Physics, Vol. 26, No. 2 (1981)

Abstract: We discuss the question of determining the entropy given the phase space trajectory which describes the detailed history of a many-body system over a period of observation. Our viewpoint is that the determination of entropy, as well as all other thermodynamic properties, should require no concepts or information other than those given and defined by the trajectory. The counting of coincidence (or repetition) of states along the trajectory is presented as a way to determine entropy given the trajectory. An illustrative program based on the kinetic Ising model is described in detail.

<https://link.springer.com/article/10.1007/BF01013169>

4.4

P.W. Anderson, *More is different: broken symmetry and the nature of the hierarchical structure of science*, Science, Vol. 177, Page 4047 (1972)

The reductionist hypothesis may still be a topic for controversy among philosophers, but among the great majority of active scientists I think it is accepted without question. The workings of our minds and bodies, and of all the animate or inanimate matter of which we have any detailed knowledges are assumed to be controlled by the same set of fundamental laws which except under certain extreme conditions we feel we know pretty well. ... The main fallacy in this kind of thinking is that the reductionist hypothesis does not by any means imply a "constructionist" one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe. In fact, the more the elementary particle physicists tell us about the nature of the fundamental laws the less relevance they seem to have to the very real problems of the rest of science, much less to those of society. ... At each stage entirely new laws, concepts, and generalizations are necessary, requiring inspiration and creativity to just as great a degree as in the previous one. Psychology is not applied biology, nor is biology applied chemistry. ... we have begun to formulate a general theory of just how this shift from quantitative to qualitative differentiation takes place. This formulation, called the theory of "broken symmetry", ...

<https://www.jstor.org/stable/pdf/1734697.pdf>

4.5

S. Jungblut and C. Dellago, *Pathways to self-organization: crystallization via nucleation and growth*, European Physical Journal E, Vol. 39, No. 77 (2016)

Abstract: Crystallization, a prototypical self-organization process during which a disordered state spontaneously transforms into a crystal characterized by a regular arrangement of its building blocks, usually proceeds by nucleation and growth. In the

initial stages of the transformation, a localized nucleus of the new phase forms in the old one due to a random fluctuation. Most of these nuclei disappear after a short time, but rarely a crystalline embryo may reach a critical size after which further growth becomes thermodynamically favorable and the entire system is converted into the new phase. In this article, we will discuss several theoretical concepts and computational methods to study crystallization. More specifically, we will address the rare event problem arising in the simulation of nucleation processes and explain how to calculate nucleation rates accurately. Particular attention is directed towards discussing statistical tools to analyze crystallization trajectories and identify the transition mechanism.

<http://doi.org/10.1140/epje/i2016-16077-6>

(suggestion: only until section 3.1)

4.6

F. Noé and S. Fischer, *Transition networks for modeling the kinetics of conformational change in macromolecules*, Current Opinion in Structural Biology, Vol. 18, Page 154 (2008)

Abstract: The kinetics and thermodynamics of complex transitions in biomolecules can be modeled in terms of a network of transitions between the relevant conformational substates. Such a transition network, which overcomes the fundamental limitations of reaction-coordinate-based methods, can be constructed either based on the features of the energy landscape, or from molecular dynamics simulations. Energy-landscape-based networks are generated with the aid of automated path-optimization methods, and, using graph-theoretical adaptive methods, can now be constructed for large molecules such as proteins. Dynamics-based networks, also called Markov State Models, can be interpreted and adaptively improved using statistical concepts, such as the mean first passage time, reactive flux and sampling error analysis. This makes transition networks powerful tools for understanding large-scale conformational changes.

<http://dx.doi.org/10.1016/j.sbi.2008.01.008>

4.7

D.T. Gillespie, *The mathematics of Brownian motion and Johnson noise*, American Journal of Physics 64, 225 (1996)

Abstract: One reason why Brownian motion and Johnson noise are difficult subjects to teach is that their mathematical requirements transcend the capabilities of ordinary differential calculus. Presented here is an exposition of the needed generalization of calculus, namely continuous Markov process theory, in a form that should be accessible to advanced physics undergraduates. It is shown how this mathematical framework enables one to give clear, concise derivations of all the principal results of Brownian motion and Johnson noise, including fluctuation–dissipation formulas, autocovariance transport formulas, spectral density formulas, Nyquist’s formula, the

notions of white and $1/\sqrt{2}$ noise, and an accurate numerical simulation algorithm. An added benefit of this exposition is a clearer view of the mathematical connection between the two very different approaches to Brownian motion taken by Einstein and Langevin in their pioneering papers of 1905 and 1908.

<https://doi.org/10.1119/1.18210>

(suggestion: only until section D)

4.8

D. Frenkel, *Why colloidal systems can be described by statistical mechanics: some not very original comments on the Gibbs paradox*, Molecular Physics, 112, 2325 (2014)

Abstract: Colloidal particles are distinguishable. Moreover, their thermodynamic properties are extensive. Statistical mechanics predicts such behaviour if one accepts that the configurational integral of a system of N colloids must be divided by $N!$. In many textbooks, it is argued that the factor $N!$ corrects for the fact that identical particles (in the quantum mechanical sense) are indistinguishable. Clearly, this argument does not apply to colloids. This article explains why, nevertheless, all is well. The point has been made before, but has not yet sunk in. I also discuss the effect of polydispersity.

<https://doi.org/10.1080/00268976.2014.904051>