

Statistical Physics and Computer Simulations
Burkhard Dünweg
Exercise Sheet 6

1. Statistical Errors

Consider a Monte Carlo or Molecular Dynamics simulation that is strictly in equilibrium, and produces a time series of observable values $A(t)$, $t = 1, 2, \dots, T$. The observations have been made at equidistant times. Demonstrate that the time-displaced autocorrelation function of the fluctuations of A is the central quantity that governs the statistical accuracy (i.e. the error bar) of the estimator

$$\bar{A} = T^{-1} \sum_{t=1}^T A(t), \quad (1)$$

and show that the effective number of statistically independent observations is given by

$$T_{eff} = \frac{T}{1 + 2\tau}, \quad (2)$$

where τ is a suitably (how??) defined correlation time.

Hints: Consider the expectation value

$$\left\langle \left(\bar{A} - \langle A \rangle \right)^2 \right\rangle, \quad (3)$$

and introduce

$$\delta A(t) = A(t) - \langle A \rangle. \quad (4)$$

Assume that the simulation time is much longer than the correlation time.

2. Stochastic Dynamics and Hydrodynamic Screening

Consider a simulation where Molecular Dynamics for N particles in a volume V is coupled to a Langevin thermostat (Stochastic Dynamics). The equations of motion are

$$\frac{d}{dt} \vec{r}_i = \frac{1}{m} \vec{p}_i, \quad (5)$$

$$\frac{d}{dt} \vec{p}_i = \vec{F}_i - \frac{\zeta}{m} \vec{p}_i + \vec{f}_i(t), \quad (6)$$

where \vec{F}_i is the conservative force from the particle–particle interactions, ζ is the friction constant, \vec{f}_i is a Gaussian white noise with the properties

$$\langle f_{i\alpha} \rangle = 0, \quad (7)$$

$$\langle f_{i\alpha}(t)f_{j\beta}(t') \rangle = 2\zeta T\delta_{ij}\delta_{\alpha\beta}\delta(t-t'). \quad (8)$$

The Greek letters denote Cartesian indices, and we assume that the system is three–dimensional. Our aim is to study this system under the *nonequilibrium* situation of shear flow. Temperature is defined here in the pragmatic sense as the input parameter of the Langevin thermostat.

- (a) Discretize the equations of motion in terms of the Euler algorithm with a time step h . Calculate the change in energy, $\mathcal{H}(t+h) - \mathcal{H}(t)$. From the limit $h \rightarrow 0$, show that

$$\left\langle \frac{d\mathcal{H}}{dt} \right\rangle = \frac{3}{m}\zeta NT - \frac{\zeta}{m^2} \sum_i \langle \vec{p}_i^2 \rangle, \quad (9)$$

where $\langle \dots \rangle$ refers to the average over the noise (and *not* to a thermal ensemble average). Show that in thermal equilibrium the ensemble average of this expression is zero.

- (b) Under nonequilibrium conditions, the average of the above expression is nonzero. Assume that for a stationary shear flow we have

$$\vec{p}_i = m\vec{u}(\vec{r}_i) + \vec{c}_i, \quad (10)$$

where \vec{u} is the macroscopic (hydrodynamic) velocity flow field (evaluated at the position of particle i), while the \vec{c}_i are the so–called “peculiar momenta” that have the statistical properties (in the sense of nonequilibrium ensemble averages)

$$\langle \vec{c}_i \rangle = 0, \quad (11)$$

$$\langle c_{i\alpha}c_{j\beta} \rangle = \delta_{ij}\delta_{\alpha\beta}mT. \quad (12)$$

Calculate the nonequilibrium ensemble average of $\langle d\mathcal{H}/dt \rangle$. *Hint:* \vec{u} can be considered as a constant when evaluating the averages.

- (c) Assume that the particle number density $n = N/V$ is constant in the sample. Re-write the sum over particles into an integral over space. Show that the thermostat induces a dissipation rate (total energy loss per unit time) of

$$\dot{E}_{thermostat} = \zeta n \int_V d^3\vec{r} \vec{u}^2. \quad (13)$$

- (d) Even for purely Newtonian dynamics one would get dissipation due to the shear viscosity η . From hydrodynamics, we know that it is given by

$$\dot{E}_{Newton} = \eta \int_V d^3\vec{r} (\partial_\alpha u_\beta) (\partial_\alpha u_\beta), \quad (14)$$

where $\partial_\alpha \equiv \partial/\partial x_\alpha$ and summation convention is implied. Assume that \vec{u} is oriented in x direction and depends only on the z coordinate. Impose the boundary conditions $u(z = -L/2) = -u_0$, $u(z = +L/2) = u_0$. Find the velocity profile by minimizing the *total* dissipation rate, and interpret the result in terms of a hydrodynamic screening length λ .

Hint: Recall Lagrangian mechanics!

Remark: The assumption that the dissipation rate should be a minimum often holds in nonequilibrium thermodynamics. It is however not generally valid, in particular not in cases of nonlinear behavior (like turbulence, for instance).