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

Exercise 3: The Einstein relation

The Einstein relation

$$D = \frac{k_\mathrm{B}T}{\gamma} \tag{1}$$

connects a *microscopic* measure of fluctuations, the diffusion coefficient D of a Brownian particle, to a *macroscopic* transport coefficient, the friction coefficient[1] γ. We derive it here within the framework of Langevin's 1906 approach.

The starting point is a stochastic differential equation for (one component of) the particle velocity v,

$$m\frac{dv}{dt} + \gamma v = \xi(t) \tag{2}$$

where $\xi(t)$ is a stochastic force accounting for the random collisions of the particle with the fluid molecules. We take $\xi(t)$ to be Gaussian white noise with zero mean and covariance

$$\langle \xi(t)\xi(t')\rangle = A\delta(t-t') \tag{3}$$

with an, as yet unspecified, noise amplitude A.

a.) Solve (2) with initial condition $v(0) = 0$ and compute the mean kinetic energy $\frac{1}{2}m\langle v^2\rangle$ for long times. Now the amplitude A can be fixed by comparing the result to the classical equipartition theorem.

b.) The diffusion coefficient D of the particle is defined by the growth of its mean square positional displacement according to

$$\langle [x(t) - x(t')]^2\rangle = 2D|t-t'|. \tag{4}$$

Compute the mean square displacement by integrating over the velocity autocorrelation function, and thus identify D in accordance with (1).

Exercise 4: Invariance of the Onsager relations under linear transformations

The derivation of Onsager's relations is based on a decomposition of the entropy production σ into a sum of products of thermodynamic fluxes J_i and generalized forces X_i,

$$\sigma = \sum_{i=1}^{n} J_i X_i, \tag{5}$$

[1]For a spherical particle of radius R immersed in a fluid of viscosity η, Stokes' formula gives $\gamma = 6\pi\eta R$.

which is however not unique.

Here we want to show that the content of the relations is independent of the precise choice of fluxes and forces. To this end we perform an invertible linear transformation replacing the fluxes J_i by a new set of fluxes $\tilde{J}_i$,

$$\tilde{J}_i = \sum_{k=1}^{n} A_{ik} J_k. \tag{6}$$

Demanding that the entropy production (5) remains invariant under this transformation fixes the corresponding transformation of the generalized forces X_i, and allows to identify a new set of Onsager coefficients $\tilde{L}_{ij}$ entering the transformed linear transport laws

$$\tilde{J}_i = \sum_{k=1}^{n} \tilde{L}_{ik} \tilde{X}_k. \tag{7}$$

Show that symmetry of the L_{ij} implies symmetry of the $\tilde{L}_{ij}$.
Hint: The proof simplifies by using 'quantum mechanical' notation, $\sigma = \langle J|X\rangle = \langle X|\hat{L}|X\rangle$ etc.