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SoSe 05

Set 3
5/02/05

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

Problem set 3

Problem 3.1 *Liouville's theorem*

Show that the time evolution for a classical system in terms of Hamilton's equations leaves the phase space density $\rho(\{q_i, p_i\})$ for the microcanonical/canonical ensemble invariant. Introduce new generalized coordinates $Q_l = Q_l(\{q_i, p_i\})$ and generalized momenta $P_l = P_l(\{q_i, p_i\})$ such that the transformation is canonical, i.e. the Poisson brackets fulfill

$$\{Q_k, Q_l\} = 0\,, \qquad \{P_k, P_l\} = 0\,, \qquad \{P_k, Q_l\} = \delta_{kl}$$

Recall that Hamilton's equations are covariant under such transformations and show that the phase space density remains stationary if expressed in terms of the new variables.

Problem 3.2 *variational principle*

Find the distribution function of momenta $f(\mathbf{p})$ that maximizes the functional

$$H = -\int d^3p f(\mathbf{p}) \ln f(\mathbf{p})\,.$$

with the constraint that $f(\mathbf{p})$ is normalized to $\int d^3p f(\mathbf{p}) = n$ and the kinetic energy is fixed to $n^{-1} \int d^3p f(\mathbf{p}) p^2/2m = \epsilon$.

Problem 3.3 *Harmonic oscillator*

The Hamilton function of a classical harmonic oscillator in an external field $\mathbf{F}$ is given by

$$\mathcal{H} \;=\; \frac{\mathbf{p}^2}{2m} + \frac{m\omega^2}{2}\mathbf{r}^2 - \mathbf{F}\cdot\mathbf{r}$$

1. Assuming that the oscillator is in contact with a thermal reservoir at fixed temperature T calculate the free energy of the oscillator using the canonical ensemble. Derive expressions for the energy and entropy of the oscillator.
2. Evaluate the mean elongation $\langle \mathbf{r} \rangle$ in the canonical ensemble.
3. Evaluate the moment generating function for the spatial coordinate $\langle \exp(\mathbf{f}\cdot\mathbf{r})\rangle$ and the corresponding cumulant generating function and relate them to the partition sum and free energy. Evaluate all cumulants.

Problem 3.4 *Dipoles*

Consider a non-interacting gas of N identical rod-like molecules, each with mass m, moment of inertia I and electric dipole moment μ. The configuration of each molecule is described by 5 generalized coordinates, i.e. the location of the center of mass $\mathbf{r}$ and the two spherical angles defining the direction of the rod θ, ϕ (see figure). From classical mechanics we know that the Lagrangian of an individual molecule in an electric field $\mathcal{E}$ (pointing along the z-axis) is given by

$$\mathcal{L} = \frac{m}{2}\dot{\mathbf{r}}^2 + \frac{I}{2}(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta) + \mu\mathcal{E}\cos\theta$$

(a) Derive the corresponding Hamilton function in terms of the generalized momenta $\mathbf{p}, p_\theta$ and p_ϕ.

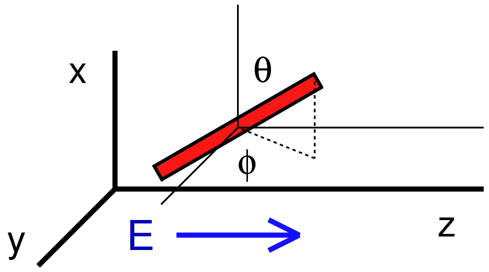
(b) Calculate the canonical partition integral of N non-interacting dipoles

$$Z(T,V,N) = \frac{1}{N!h^{5N}} \int \left[\prod_{i=1}^{N} d^3\mathbf{r}_i d\theta_i d\phi_i d^3\mathbf{p}_i dp_{i,\theta} dp_{i,\phi}\right] \exp(-\mathcal{H}/k_B T)$$

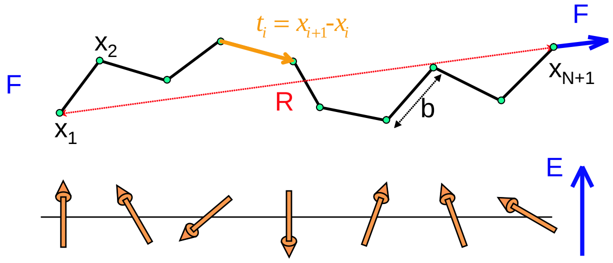
(c) Calculate the pressure and average total energy. Discuss your results and, in particular, compare with an ideal gas of point-like molecules for $\mathcal{E} = 0$.

(d) Calculate the average polarisation $\mathcal{P} = \sum_{i=1}^{N} \langle \mu \cos\theta_i \rangle$; plot $\mathcal{P}$ as a function of the external field and temperature and discuss the limits of small and large electric fields.

(e)* How can you map the statistical mechanics of a freely jointed chain (N rods of length b connected by free hinges; see figure), where a force F is applied at both ends, to the above results?



Rod-like molecule in an external field $\mathcal{E}$



Freely jointed chain under tension

Problem 3.5 *Kinetic energy*

For a fluid of N structureless classical particles the Hamilton function reads

$$\mathcal{H} = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2M} + \mathcal{V}\,.$$

Here the potential energy $\mathcal{V}$ depends only on the coordinates $\mathbf{r}_i$. Calculate the probability distribution of the kinetic energy in the canonical ensemble, i.e with a phase space density

$$\rho(\{\mathbf{p}_i, \mathbf{r}_i\}) = Z^{-1} \exp(-\beta\mathcal{H})\,.$$

Note that the phase space integrals factorize into a kinetic and potential part.