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Advanced Statistical Physics II – Problem Sheet 3

Problem 1 – **Einstein relations**

Consider a system where the particle number N is fixed, while the internal energy U and volume V can fluctuate. Gaussian fluctuations are described by a 2×2 matrix $\mathbf{g}$

$$\mathbf{g} = \begin{pmatrix} g_{UU} & g_{UV} \\ g_{UV} & g_{VV} \end{pmatrix} \tag{1}$$

with elements

$$g_{UU} = -\frac{\partial^2 S(U,V,N)}{\partial U^2} = \frac{1}{T^2 c_V}, \tag{2}$$

$$g_{UV} = -\frac{\partial^2 S(U,V,N)}{\partial U \partial V} = \frac{1}{T^2 c_V}\left(p - \frac{\alpha T}{\kappa_T}\right), \tag{3}$$

$$g_{VV} = -\frac{\partial^2 S(U,V,N)}{\partial V^2} = \frac{1}{T^2 c_V}\left(p - \frac{\alpha T}{\kappa_T}\right)^2 + \frac{1}{T\kappa_T V}. \tag{4}$$

a) (3P) Compute the pressure fluctuation $(\Delta(p/T))^2$ of a single water molecule at ambient conditions, i.e. $T = 300$ K, $C_V = 4$ J/(gK), $\kappa_T = 4.6 \times 10^{-10}$ 1/Pa, $\alpha = 0.2 \times 10^{-3}$ 1/K, and $p = 10^5$ Pa.

b) (4P) Show that the fluctuation of the internal energy U is

$$\langle (U - U^*)^2 \rangle = \langle (V - V^*)^2 \rangle \left(p - \frac{\alpha T}{\kappa_T}\right)^2 + \langle (U - U^*)^2 \rangle_V. \tag{5}$$

where $\langle (V - V^*)^2 \rangle = k_B T \kappa_T V$ is the volume fluctuation, and $\langle (U - U^*)^2 \rangle_V = k_B T^2 C_V$ is the energy fluctuation at fixed volume (in the canonical ensemble (N, V, T)).

c) (3P) Now estimate the energy flucutation $\langle (U - U^*)^2 \rangle$ in units of $(\mathrm{k}_B\mathrm{T})^2$ of a single Bacteriorhodopsin molecule at ambient conditions using the material constants of water and $m_{BR} = 64 \times 10^{-21}$ g and $V_{BR} = 64 \times 10^{-27}$ m^3. Compare with the canonical energy fluctuation $\langle (U - U^*)^2 \rangle_V$.

Problem 2 – **Mass Conservation**

Consider a system consisting of k different species (like water, alcohol, citric acid, sugar) described by continuous mass densities $\rho_i(\vec{r}, t)$. Recall the mass of species i within any volume V is given by

$$m_i(t) = \int_V \rho_i(\vec{r}, t) dV. \tag{6}$$

We assume that no chemical reactions can take place, so that there is no interconversion between the different species.
a) (2P) Conservation of mass for the i-th species can be formulated as the statement that for every volume V, the change of mass within V is equal to the net flow through the volume's surface $S(V)$, i.e.

$$\frac{d}{dt} m_i(t) = - \int_S \rho_i(\vec{r}, t) v_i^j(\vec{r}, t) dS^j. \tag{7}$$

Here, v_i^j denotes the j Cartesian component of the velocity vector of species i, $\vec{v}_i$, (which describes the flow of the i-th species of the system). Note that there is (obviously) no sum over i but a sum over j in the above expression. Use Gauss law and the fact that eq. 7 holds for arbitrary volumes to formulate the conservation of mass equation in the differential form, i.e. without integrals.
b) (1P) Now sum over i and write the resulting conservation law for the total mass in terms of the total density ρ and the center-of-mass velocity

$$\vec{v}(\vec{r}, t) = \frac{\sum_i \rho_i(\vec{r}, t) \vec{v}_i(\vec{r}, t)}{\rho(\vec{r}, t)}. \tag{8}$$

c) (2P) Reformulate the conservation law for the total mass using the convective derivative

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{v}(\vec{r}, t)\ \vec{\nabla}, \tag{9}$$

i.e. show that

$$\frac{D\rho(\vec{r}, t)}{Dt} + \rho(\vec{r}, t) \vec{\nabla} \vec{v}(\vec{r}, t) = 0. \tag{10}$$

Problem 3 – **Liouville equation**

(5P) Show that if the probability density in phase space $\rho(q_{3N}, p_{3N}, t)$ fullfills the Liouville equation for a given Hamiltonian $\mathcal{H}$, the entropy,

$$S(t) = - \int dp^{3N} \int dq^{3N}\ \rho(q_{3N}, p_{3N}, t)\ \ln(\rho(q_{3N}, p_{3N}, t)), \tag{11}$$

is extremal, i.e. $dS/dt = 0$.
Hint: Set $\rho = 0$ at the system boundaries and use partial integration.