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Hand in on November 14th 2016 before the lecture

Advanced Statistical Physics II – Problem Sheet 4

Problem 1 – **Einstein relations**

Consider a system where the energy U and the volume V can fluctuate at a constant particle number N. In the following we determine the matrix

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

a) (1P) Determine the differential $\mathrm{d}S(U,V)$ and show that $g_{UU} = 1/(T^2 C_V)$.
b) (2P) Give an expression for g_{UV} that depends on $\left(\frac{\partial T}{\partial V}\right)_U$. Show that

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) . \tag{2}$$

In order to do this, first determine the differential $\mathrm{d}U(T,V)$ using the response functions α, κ_T and C_V.
Hint: You can use the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$.
c) (2P) Give an expression for g_{UV} that depends on $\left(\frac{\partial p}{\partial V}\right)_U$. Show that

$$\left(\frac{\partial p}{\partial V}\right)_U = -\frac{1}{\kappa_T V} + \frac{\alpha}{\kappa_T C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) . \tag{3}$$

In order to do this, first determine the differential $\mathrm{d}V(T,p)$ and use your result for $\mathrm{d}U(T,V)$ from b).
d) (1P) Calculate the inverse matrix $\mathbf{g}^{-1}$.
e) (1P) Consider 1 liter of liquid water at $T = 300$ K, $C_V = 4097.5$ J/K, $\kappa_T = 4.6\times10^{-10}$ 1/Pa, $\alpha = 0.2\times10^{-3}$ 1/K, and $p = 10^5$ Pa. Estimate the energy flucutation $\langle \Delta U^2\rangle = \langle (U-U^*)^2\rangle$ and compare with the canonical energy fluctuation $\langle (U-U^*)^2\rangle_V = k_B T^2 C_V$. Also estimate $\langle (U-U^*)(V-V^*)\rangle$ and $\langle \Delta V^2\rangle = \langle (V-V^*)^2\rangle$.
f) (1P) Compute the same quantities for a system of 100 water molecules assuming that the heat capacity of water is proportional to the number of molecules $C_V \sim N$. What are the relative fluctuations in the volume $\sqrt{\langle \Delta V^2\rangle}/V$ for both systems?

Problem 2 – **Mass Conservation**

Consider a system of k components described by the continuous mass densities $\rho^i(\vec{r},t)$. Recall that by definition of the ρ^i, the mass of component i within any volume V is given by

$$m^i(V) = \int_V \rho^i dV. \tag{4}$$

We assume that no chemical reactions can take place, so that there is no interconversion between the different components.

a) (2P) Conservation of mass for the i-th component 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, i.e.

$$\frac{\partial}{\partial t} m^i(V) = -\int_S \rho^i v^i_j dS_j. \tag{5}$$

Here, v^i_j denotes the j-component of the velocity vector $\vec{v}^i$ (which describes the flow of the i-th component 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. 5 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

$$v_j = \frac{\sum_i \rho^i v_j^i}{\rho}. \tag{6}$$

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

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + v_j \nabla_j, \tag{7}$$

i.e. show that

$$\frac{d\rho}{dt} + \rho \nabla_j v_j = 0. \tag{8}$$

Problem 3 – **Momentum balance and energy balance**
Assume the balance of momentum is given by

$$\frac{\partial(\rho v_i)}{\partial t} + \nabla_j (v_j \rho v_i) = \rho F_i \tag{9}$$

when no stresses are considered.

a) (2P) Derive *Newton's 2nd law*

$$\rho \frac{Dv_i}{Dt} = \rho F_i \tag{10}$$

from equation (9). Note: The derivative is given in terms of Eq. (7)!

b) (4P) We want to derive the balance of energy

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho v_i^2 + \rho\psi\right) + \nabla_j \left[v_j \left(\frac{1}{2}\rho v_i^2 + \rho\psi\right)\right] = \rho \frac{\partial \psi}{\partial t}, \tag{11}$$

where $F_i = -\nabla_i \psi(\vec{x}, t)$ is given by its potential function.

Hint: Multiply equation (9) *by* v_i *and derive expressions for* $\frac{\partial}{\partial t}\left(\frac{1}{2}\rho v_i^2\right)$ *and* $\nabla_j \left(\frac{1}{2} v_j \rho v_i^2\right)$ *and remember the conservation of mass.*

c) (1P) Interpret the terms in Eq. (11). Is the energy conserved?