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Hand in on May 8th 2015 before the lecture

Advanced Statistical Physics II – Problem Sheet 3

Problem 1 – **Functions of expectation values and Jensen's inequality**

Throughout the tasks the Einstein's summation convention is used. As in our discussion on fluctuations in the lecture, consider the probability distribution obtained by Taylor-expanding the entropy around its maximum at $(U^*, V^*, N_1^*, .., N_k^*)$:

$$\rho(\vec{x}) \equiv \rho(x_1, ..., x_{k+2}) = A \exp\left[S(U^*, V^*, N_1^*, .., N_k^*) - \frac{g_{ij}}{2k_B} x_i x_j\right] \tag{1}$$

with normalization constant

$$A = e^{-S^*/k_B} \left(\frac{det(g)}{(2\pi k_B)^{k+2}}\right)^{1/2}. \tag{2}$$

In the lecture, we defined the forces $f_i = -g_{ij}x_j$ and found the following three relations:

$$\langle x_i f_j \rangle = -k_B \delta_{ij}, \tag{3}$$
$$\langle f_i f_j \rangle = \quad k_B g_{ij}, \tag{4}$$
$$\langle x_i x_j \rangle = \quad k_B (g^{-1})_{ij}. \tag{5}$$

a) Let $(\lambda_i)_{1\leq i\leq k+2}$ be real numbers and define

$$H(\vec{x}) \equiv H(x_1, ..., x_{k+2}) = e^{\lambda_i x_i}. \tag{6}$$

Show that

$$\langle H(\vec{x})\rangle \equiv \langle e^{\lambda_i x_i}\rangle = e^{1/2 \lambda_i \lambda_j \langle x_i x_j \rangle}. \tag{7}$$

Would you have expected this (from naive Taylor expansion of the left hand side of equation (7))?

b) Use your result from a) to verify that for a generic (i.e. not necessarily gaussian) function h and random variable y, the equality

$$h(\langle y\rangle) = \langle h(y)\rangle \tag{8}$$

does **not** hold.

c) For convex functions h, however, there is Jensen's inequality which states that

$$h(\langle y\rangle) \leq \langle h(y)\rangle. \tag{9}$$

Prove this for the special case where the function is $H(x_1, ..., x_{k+2}) = e^{\lambda_i x_i}$. For what values of $(\lambda_1, ..., \lambda_{k+2})$ is this function convex? Is Jensen's inequality consistent with your results from part b)?

Problem 2 – **Concavity of the entropy**

In the lecture we already showed that $S(U, V, N)$ is concave in V. Now we want to show that S is also concave in N:

$$\frac{\partial^2 S(U, V, N)}{\partial N^2} \leq 0. \tag{10}$$

a) Express $\frac{\partial^2 S(U,V,N)}{\partial N^2}$ in terms of $\left(\frac{\partial \mu}{\partial N}\right)_{U,V}$ and $\left(\frac{\partial T}{\partial N}\right)_{U,V}$.

b) Derive an expression for $\left(\frac{\partial T}{\partial N}\right)_{U,V}$

c) Derive an expression for $\left(\frac{\partial \mu}{\partial N}\right)_{U,V}$

d) Put everything together and argue why the entropy S is strictly concave in N.

Problem 3 – **Energy and volume fluctuations**

Consider a system where the particle number N is fixed, while the internal energy U and volume V can fluctuate. We then have a 2×2 matrix g with the elements

$$g_{UU} = -\frac{\partial^2 S(U,V,N)}{\partial U^2}, \quad (11)$$

$$g_{UV} = -\frac{\partial^2 S(U,V,N)}{\partial U \partial V}, \quad (12)$$

$$g_{VV} = -\frac{\partial^2 S(U,V,N)}{\partial V^2}. \quad (13)$$

a) By using the second derivative expressions for $S(U,V,N)$ given in the lecture, find g_{UU}, g_{UV} and g_{VV} in terms of T, C_V, κ_T, V, α and p.

b) Use your result from a) and eq. 5 to show that the fluctuations read

$$\langle (U-U^*)^2 \rangle = \langle (V-V^*)^2 \rangle \left(p - \frac{\alpha T}{\kappa_T}\right)^2 + \langle (U-U^*)^2 \rangle_V, \quad (14)$$

$$\langle (U-U^*)(V-V^*) \rangle = \langle (V-V^*)^2 \rangle \left(\frac{\alpha T}{\kappa_T} - p\right), \quad (15)$$

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 canonical ensemble (N,V,T)).

c) Consider 1 litre of liquid water at $T = 300$ K, $C_V = 4097.5$ J/K, $\kappa_T = 4.6 \times 10^{-10}$ 1/Pa, $\alpha = 0.2 \times 10^{-3}$ 1/K, and $p = 10^5$ Pa. Estimate the energy flucutation $\langle (U-U^*)^2 \rangle$ and compare with the canonical energy fluctuation $\langle (U-U^*)^2 \rangle_V$. Also estimate $\langle (U-U^*)(V-V^*) \rangle$ and $\langle (V-V^*)^2 \rangle$.

d) In order to more practically see how large are the energy fluctuations, convert the energy fluctuation $\langle (U-U^*)^2 \rangle_V$ into the temperature fluctuation $\langle (T-T^*)^2 \rangle = k_B T^2 / C_V$. Estimate $\langle (T-T^*)^2 \rangle$ for 1 litre of liquid water with $C_V = 4097.5$ J/K at $T = 300$ K, and $\langle (T-T^*)^2 \rangle$ for one water molecule with $C_V = 1.2 \times 10^{-22}$ J/K at $T = 300$ K.