Advanced statistical mechanics

(WS 12/13, FU Berlin)

Problem sheet 4

Due date: November 21, 2012

Problem 12: Joule Expansion (2+1+2+2)

A gas is allowed to freely expand from a container of volume, V_i, to a larger volume V_f. The containers are thermally isolated, so no heat flows in or out, and no mechanical work is extracted in the expansions process. The *Joule*-coefficient, denoted θ, is the resulting change in temperature with respect to volume through this process, i.e., $\theta = \left(\frac{\partial T}{\partial V}\right)_U$. Assume throughout that the specific heat capacity under constant volume, denoted $C_V = \left(\frac{\partial U}{\partial T}\right)_V$, is independent of volume and temperature.

a) Making use of Gibbs' fundamental equation show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{1}$$

Hint: Results of previous problem sheets can be used, see e.g. Problem 9.

b) Use the above and the Maxwell-relation $\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial U}\right)_T = -1$ to deduce that

$$\theta = \frac{1}{C_V}\left(p - T\left(\frac{\partial p}{\partial T}\right)_V\right) \tag{2}$$

For the remainder of this question assume that the gas obeys the van der Waals equation of state

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{3}$$

where a and b are non-negative constants and $n = N/N_A$ where N_A is the Avogadro constant.

c) Show that for a van der Waals gas the Joule-coefficient is

$$\theta = \frac{an^2}{C_V V^2} \tag{4}$$

d) Find the change in temperature $\Delta T = (T_f - T_i)$ in terms of V_f and V_i and comment on the limit of an ideal gas.

Problem 13: Basic probability theory (2+1+1+1)

A *probability measure* μ on $\mathbb{R}^n$ is a function obeying

(i) $\mu(A) \in [0, 1]$

(ii) $\mu(\mathbb{R}^n) = 1$

(iii) $\mu(A \cup B) = \mu(A) + \mu(B)$

for all (suitable) disjoint subsets $A, B \subset \mathbb{R}^n$ (and where (iii) can be iterated countably many times). Every subset A is called an *event* and $\mu(A)$ is called *probability of the event* A.

There are two very important classes of probability measures:

Absolutely continuous measures: μ can be written in terms of a *probability density (function)*, i.e.,

$$\mu(A) = \int_A \rho(x)\ \mathrm{d}x \tag{5}$$

for some function $\rho : \mathbb{R}^n \to \mathbb{R}$ and suitable sets $A \subset \mathbb{R}^n$.

Discrete measures: μ is a discrete probability measure, i.e., there are $p_j \in [0, 1]$ with $\sum_j p_j = 1$ and $x_j \in \mathbb{R}^n$ such that

$$\mu(A) = \sum_{x_j \in A} p_j. \tag{6}$$

a) What two condition does ρ in Eq. (5) need to satisfy in order to be a proper probability density, i.e., that μ in Eq. (5) is indeed a probability measure? Show that under these conditions μ is indeed a probability measure.

b) Show that μ as given in Eq. (6) is also indeed a probability measure.

c) Show that any convex combination $\mu_p = p\,\mu_1 + (1-p)\,\mu_2$, $p \in [0,1]$, of two probability measures μ_1 and μ_2 is again a probability measures.

Consider a continuous function $X : \mathbb{R}^n \to \mathbb{R}^m$ and a probability measure μ on $\mathbb{R}^n$, then X is called a *random variable*.

d) Show that μ_X defined by

$$\mu_X(A) := \mu(X^{-1}(A)) \tag{7}$$

is a probability measure for the two cases given by Eq. (5) and (6).
Hint: $X^{-1}(A)$ denotes the preimage of A, i.e., the set of elements that are mapped to A.

The measure μ_X is the measure *induced* by the random variable X.

Problem 14: Fair dice (1+1+1+1+2+1)

We consider a fair die and identify its sample space or state space with $\Gamma = \{1, 2, \ldots, 6\}$.

a) What is the state space of two dice?

b) Let X_1 and X_2 be the random variables associated to the outcomes of the first and second die respectively. What subset of the sample space corresponds to the event that the sum of the two dice yields 6, i.e., $X_1 + X_2 = 6$?

c) What set/event corresponds to the event that at least one of the dice yields 2?

In situations like this one, where there clearly is a natural measure μ, the uniform one in this case, one often writes $\mathbb{P}(A)$ for the probability of the event A. It is then also useful to introduce the *conditional probability* $\mathbb{P}(A|B)$ of A given B, for $\mathbb{P}(B) > 0$, which is defined by

$$\mathbb{P}(A|B) := \frac{\mathbb{P}(A \cap B)}{\mathbb{P}(B)}. \tag{8}$$

d) Calculate $\mathbb{P}(X_1 = 2 \text{ OR } X_2 = 2 | X_1 + X_2 = 6)$, i.e. the probability that at least one die yields a 2 conditioned on their sum being 6.

A set of events $\{A_j\}$ is said to be *pairwise independent* iff

$$\mathbb{P}(A_j \cap A_k) = \mathbb{P}(A_j)\,\mathbb{P}(A_k) \quad \forall\, j \neq k. \tag{9}$$

and *mutually independent* iff

$$\mathbb{P}\Big(\bigcap_{A \in \mathcal{A}} A\Big) = \prod_{A \in \mathcal{A}} \mathbb{P}(A) \quad \forall\, \mathcal{A} \subseteq \{A_j\}. \tag{10}$$

e) Prove that the three events

$$A_1 = \{X_1 \text{ is even}\} \tag{11}$$

$$A_2 = \{X_2 \text{ is even}\} \tag{12}$$

$$A_3 = \{X_1 + X_2 \text{ is even}\} \tag{13}$$

are pairwise independent but not mutually independent.

The notion of statistical independence can be extended from events to random variables. A set of random variables $\{X_j : \mathbb{R}^n \to \mathbb{R}^m\}$ is said to be *pairwise/mutually independent* iff the associated set of events $\{X_j < \alpha_j\}$ is pairwise/mutually independent for all values of the parameters α_j.

f) Argue that the set of random variables $\{X_1, X_2, X_1 + X_2\}$ is neither pairwise, nor mutually independent.