# Theoretische Physik IV: Statistische Mechanik, Exercise 8

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*Prof. Dr. Hans Peter Büchler WS 2013/14, 3. Dezember 2013*

## 1. Skating (Oral)

The popular sport of skating relies on the low friction between the blades of skates and the ice. According to a widespread belief this low friction is due to a thin film of *liquid* water separating blade and ice. This liquid film may be the result of the high pressure exerted by the blades.
Assume that the temperature of the ice is $T = -5\,°\mathrm{C}$, the slope of the phase boundary that separates ice and water is $\frac{\partial p_{fs}}{\partial T} = -138\,\mathrm{at/deg}$ (Why the sign?), and the skater's weight is $M = 69\,\mathrm{kg}$. Is the explanation given above reasonable?

Remark: For further information on this issue see
www.nytimes.com/2006/02/21/science/21ice.html?pagewanted=all.

## 2. Gibbs paradox (Oral)

Entropy is one of the most subtle concepts in physics and responsible for a great deal of confusion. In this exercise we examine the concept of entropy — especially the entropy of an ideal gas — in more detail to gain a deeper understanding of some oddities that arise when gases are allowed to mix; this is usually referred to as "Gibbs paradox". We start with some preliminaries:

(a) Read and understand p. 77-79 in the script by G. Blatter. Show that the entropy of mixing for two boxes ($V_1$, $N_1$ and $V_2$, $N_2$; both temperature $T$ and pressure $p$) of *different* ideal gases reads

$$\Delta S = S_{mixture} - (S_1 + S_2) = k_B \left[ N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] \quad \text{where} \quad V = V_1 + V_2\,.$$

(b) Employ the second law of thermodynamics to argue that $\Delta S = 0$ if the ideal gases in box 1 and 2 are *identical*.
Hint: Contrive a gedankenexperiment which allows a *decrease* in entropy.

(c) Consider the mixing of two ideal gases (as above) which differ *only* in the colour C of their particles. Let $C = 0$ denote black and $C = 1$ white particles (and $0 < C < 1$ the intermediate grey tones). Sketch the (physically expected) entropy of mixing $\Delta S$ as a function of C for $0 \le C \le 1$.

This strange behaviour in combination with the expression for $\Delta S$ in (a) is usually referred to as *Gibbs paradox*. To scrutinise it, let us try to understand why $\Delta S > 0$

in (a) from a mathematical point of view. In the lecture was shown that the entropy for an ideal gas is given by

$$S(T,V) = Nk_B \left[ \ln\left(\frac{T}{T_0}\right)^{3/2} + \ln\left(\frac{V}{V_0}\right) \right] \tag{1}$$

with temperature $T$, (fixed) particle number $N$ and volume $V$. A *homogeneous function* $f$ of order $k$ over $n$ variables $x_1, \ldots, x_n$ is characterized by

$$f(\lambda x_1, \ldots, \lambda x_n) = \lambda^k f(x_1, \ldots, x_n) \quad \text{for all} \quad \lambda \in \mathbb{R}\,. \tag{2}$$

A quantity is called *extensive* if it is homogeneous of order $k = 1$ in its *extensive variables*.

(d) Consider $V$ and $N$ as extensive variables. Show that $S$ as given in Eq. (1) is *not* extensive. This calculation is formally ill-defined. Why?
Hint: It is no coincidence that in Eq. (1) (and in the script) $S = S(T,V)$ is not a function of $N$.

(e) We can make $S$ extensive if we take into account the $N$-dependence (which formally is hidden in the integration constants $T_0$ and $V_0$). Show this by a careful derivation of $S = S(T,V,N)$.
Hint: Calculate $S(T_1,V_1,N) - S(T_2,V_2,N)$ and show that the most general entropy function reads

$$S(T,V,N) = Nk_B \left[ \ln\left(\frac{T}{T_0}\right)^{3/2} + \ln\left(\frac{V}{V_0}\right) \right] + k_B f(N) \tag{3}$$

where $f$ is an arbitrary function of $N$.

(f) Obviously the extensivity of $S$ depends on $f$. *Demand* $S(T,V,N)$ to be extensive in $V$ and $N$. Show that this leads to the functional equation

$$f(\lambda N) = \lambda f(N) - \lambda N \ln \lambda\,. \tag{4}$$

Solve it (Hint: Set $N = 1$ and $f(1) \equiv \ln N_0$ with $N_0$ an arbitrary constant) and show that the now *extensive* entropy $\tilde{S}(T,V,N)$ is given by

$$\tilde{S}(T,V,N) = Nk_B \left[ \ln\left(\frac{T}{T_0}\right)^{3/2} + \ln\left(\frac{VN_0}{NV_0}\right) \right]\,. \tag{5}$$

(g) Derive the entropy of mixing $\Delta\tilde{S}$ for this entropy and show that it vanishes for a "mixture" of identical gases. When is it legitimate to use Eq. (1) and when is it necessary to use the extensive version Eq. (5)? Can you reproduce the result for $\Delta S$ in (a) with the extensive entropy in Eq. (5)?

Remark: The extensive entropy $\tilde{S}$ can be (and will be) derived in the framework of statistical mechanics quite naturally if one takes into account the *indistinguishability* of particles properly.

**3. Permafrost (Written)**

In the lecture the source-free heat equation was derived; it reads

$$(\partial_t - \mathcal{D}\Delta)\, T = 0 \tag{6}$$

with temperature $T = T(\vec{x}, t)$ and thermal diffusivity $\mathcal{D} > 0$. Here we employ Eq. (6) to model the heat flow below the earth's surface. To this end, identify the earth with a (one-dimensional) half space $x \geq 0$ where $x = 0$ corresponds to the surface. The temperature is then a function $T = T(x, t)$ depending on depth $x$ and time $t$. Assume that the surface temperature is oscillatory

$$T|_S = T(x = 0, t) = T_0 \cos \omega t \tag{7}$$

due to daily or annual temperature variations.

(a) Solve Eq. (6) with the boundary condition in Eq. (7). The solution is ambiguous. Introduce another (reasonable) boundary condition to get rid of this ambiguity.
Hint: How did you solve the time evolution of a free particle wave function $\Psi(x, t)$ in quantum mechanics? How does Eq. (6) relate to the free particle Schrödinger equation?

(b) The penetration depth for surface variations of the temperature is defined as $\lambda \equiv \sqrt{2\mathcal{D}/\omega}$. What is the ratio of $\lambda_a/\lambda_d$ for annual and daily temperature variations? Assume the typical thermal diffusivity $\mathcal{D} = 0.006\,\mathrm{cm}^2\mathrm{s}^{-1}$ and calculate $\lambda_a$ and $\lambda_d$. Give an explanation for the phenomenon of permafrost.