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Übungen zu Theoretische Physik IV

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http://www.th.physik.uni-bonn.de/people/forste/exercises/ws1213/tp4

–Class Exercises–

A 6.1 Ideal Gases with Inner Degrees of Freedom

When we looked at gases in the previous exercises, we always treated them as mass points or hard spheres without any inner degrees of freedom. However, most of the gases consist of molecules which can have inner motions like rotations or vibrations. Here we want to look at the impact of these features on the thermodynamic properties of such gases. We will assume the inner degrees of freedom to be independent of each other, such that we can write the Hamilton function of a single molecule as

$$H = H_{\text{trans}}(Q, P) + H_{\text{rot}}(\phi_i, p_{\phi_i}) + H_{\text{vib}}(q, p)\,.$$

Here H_{trans} describes the motion of the center of mass of the molecule, H_{rot} is the rotational energy and depends on the *Euler angles* $\phi_i \in \{\theta, \phi, \psi\}$ and the corresponding angular momenta p_{ϕ_i} and H_{vib} describes the energy of the oscillations of the molecule, which depend on the generalized coordinates of the f normal modes and the corresponding momenta. The canonical single-particle partition function

$$Z(T,V,1) = \frac{1}{h^{6+f}} \int \mathrm{d}^3R \int \mathrm{d}^3P \int \mathrm{d}^3\phi \int \mathrm{d}^3p_\phi \int \mathrm{d}^fq \int \mathrm{d}^fp\, \exp\{-\beta\,(H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}})\}\,,$$

then factorizes according to

$$Z(T,V,1) = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}\,,$$

where

$$Z_{\text{trans}} = \frac{1}{h^3} \int \mathrm{d}^3R \int \mathrm{d}^3P\, \exp\{-\beta H_{\text{trans}}\}\,,$$
$$Z_{\text{rot}} = \frac{1}{h^3} \int \mathrm{d}^3\phi \int \mathrm{d}^3p_\phi\, \exp\{-\beta H_{\text{rot}}\}\,,$$
$$Z_{\text{vib}} = \frac{1}{h^f} \int \mathrm{d}^fq \int \mathrm{d}^fp\, \exp\{-\beta H_{\text{vib}}\}\,.$$

Furthermore we assume the gas to be non-interacting, such that the canonical partition function of the gas with N particles is given by

$$Z(T,V,N) = \frac{1}{N!}[Z(T,V,1)]^N = \frac{1}{N!} Z_{\text{trans}}^N Z_{\text{rot}}^N Z_{\text{vib}}^N\,.$$

Moreover we will neglect the contributions of the vibrational energy.

(a) Assume $H_{\text{trans}}(Q,P) = \frac{P^2}{2M}$ and show that

$$Z_{\text{trans}} = V\left(\frac{2\pi MkT}{h^2}\right)^{3/2}$$

and that the free energy fulfills

$$F_{\text{trans}} = -NkT\left[\log\left\{\frac{Z_{\text{trans}}(T,V,1)}{N}\right\} + 1\right].$$

Hence F_{trans} is exactly the free energy of an ideal gas.

Now we want to calculate Z_{rot}. The Lagrange function of a symmetric gyroscope with the momenta of inertia I_1, $I_2 = I_1$ and I_3 is given by

$$L_{\text{rot}} = \frac{I_1}{2}\left(\dot{\theta}^2 + \dot{\phi}\sin^2\theta\right) + \frac{I_3}{2}\left(\dot{\psi} + \dot{\phi}\cos\theta\right)^2.$$

Here $\theta \in [0,\pi]$, $\phi \in [0,2\pi]$, $\psi \in [0,2\pi]$.

(b) Show that by going to the canonical momenta $p_{\phi_i} = \frac{\partial L}{\partial \dot{\phi}_i}$ one gets the Hamilton function

$$H_{\text{rot}} = \frac{p_\theta^2}{2I_1} + \frac{p_\psi^2}{2I_3} + \frac{(p_\phi - p_\psi\cos\theta)^2}{2I_1\sin^2\theta},$$

where we assume $I_1, I_3 \neq 0$.

(c) Show that Z_{rot} is given by

$$Z_{\text{rot}} = \frac{(2\pi)^3}{h^3}\sqrt{\frac{2\pi I_1}{\beta}}\sqrt{\frac{2\pi I_1}{\beta}}\sqrt{\frac{2\pi I_3}{\beta}}.$$

(d) Consider a diatomic molecule. Argue that for this special case

$$Z_{\text{rot}} = \frac{8\pi^2}{h^2}\frac{I_1}{\beta}$$

holds. How does Z_{rot} change in the case of a homonuclear diatomic molecule?

(e) Show that the free energy fulfills

$$E = \begin{cases} \frac{5}{2}NkT & \text{for diatomic gases,} \\ 3NkT & \text{for multiatomic gases} \end{cases}.$$

Now one can calculate the *specific heat* $C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N}$ and get an impressing agreement with experimental data for gases of e.g. He, Ar, O_2, N_2, H_2, CO_2 and N_2O, which differ by at most 7%.

–HOMEWORK–

H 6.1 Isothermal-Isobaric Ensemble *(7+3=10) Points*

Consider, analogously to the grand canonical ensemble, a small subsystem 1, which is embedded in a big system 2. The number of particles of both systems, N_1 and N_2 are fixed. The volume V_1 of the subsystem is variable, while the total volume $V_1 + V_2 = V$ is kept constant. Furthermore we allow energy exchange between the two system at constant total energy $E = E_1 + E_2$. An example of such a system is given by a balloon filled with gas in a thermal bath.

(a) Show, by performing steps similar to those used to deduce the grand canonical density matrix, that the density matrix of this ensemble is given by

$$\rho_{\mathrm{II}} = Z_{\mathrm{II}}^{-1} \mathrm{e}^{-\beta(H_1 + pV_1)} = \frac{\mathrm{e}^{-\beta(H_1+pV_1)}}{\mathrm{Sp}\ \mathrm{e}^{-\beta(H_1+pV_1)}} ,$$

where p describes the pressure and $T = \frac{1}{k\beta}$ the temperature in the equilibrium state. *Hint: The pressure is defined as* $p = kT\frac{\partial}{\partial V}\log\Omega(E,N,V)$.

(b) Define $G = -kT \log Z_{\mathrm{II}}$ and show the relation

$$G = \bar{E} + p\bar{V} - TS_{\mathrm{II}} ,$$

where we suppress the indices referring to the subsystem 1. G is the *free enthalpy* or the *Gibbs' free energy*, which we will encounter again in the context of thermodynamics.

H 6.2 Energy Density of a Canonical Ensemble *(3+2+3+2=10) Points*

Consider a canonical ensemble, which possesses the equation of state

$$PV = \alpha E(T,V) ,$$

where α is a positive constant.

(a) Use the integrability condition of the free energy F,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V ,$$

to show the following partial differential equation for $E(T,V)$

$$\left(\frac{\partial E}{\partial V}\right)_T = -\frac{\alpha}{V}E + \frac{\alpha T}{V}\left(\frac{\partial E}{\partial T}\right)_V .$$

(b) Verify, that this differential equation is solved by the Ansatz

$$E(T,V) = V^{-\alpha}\phi(TV^{\alpha}) ,$$

where ϕ is an arbitrary differentiable function. Note (without proof), that this is the general solution of the partial differential equation.

(c) Show, that the entropy must be of the form $S = \psi(TV^\alpha)$, where the function ψ fulfills the relation $\phi'(x) = x\,\psi'(x)$.

(d) Assume that the energy density E/V only depends on T. Show that in this case

$$\frac{E}{V} = \sigma T^{\frac{1+\alpha}{\alpha}}$$

must be fulfilled, where σ is a proportionality constant. For $\alpha = 1/3$ one gets the Stefan-Boltzmann law for black body radiation.