

## 4 Task Theoretical Physics VI - Statistics

### 4.1 (Spin lattice)

At each site of a isolated lattice an unpaired electron with spin  $1/2$  is localized. External magnetic field  $\vec{B} = B\vec{e}_z$ , spins parallel or anti-parallel to magnetic field ( $s_{z,i} = \pm\frac{1}{2}$ ). Energy of state  $r$  given by:

$$E_r(B) = -2\mu_B B \sum_{i=1}^N s_{z,i}$$

(a)

$n$  spins parallel to magnetic field  $\Rightarrow N - n$  spins anti-parallel. Energy in dependance of  $n$ :

$$\begin{aligned} E_n(B) &= -2\mu_B B \left( \frac{1}{2} \sum_{i=1}^n 1 - \frac{1}{2} \sum_{i=n+1}^N 1 \right) \\ &= -2\mu_B B \left( \frac{1}{2} \sum_{i=1}^n 1 - \frac{1}{2} \sum_{i=1}^{N-n} 1 \right) \\ &= -2\mu_B B \left( n - \frac{N}{2} \right) \end{aligned}$$

Number of states given through binomial distribution:

$$\Omega_n(E_n) = \frac{N!}{n!(N-n)!}$$

with:

$$n(E_n) = \frac{N}{2} \left( 1 - \frac{E_n(B)}{N\mu_B B} \right)$$

this leads to:

$$\Omega_n(E_n) = \frac{N!}{\left( \frac{N}{2} \left( 1 - \frac{E_n(B)}{N\mu_B B} \right) \right)! \left( \frac{N}{2} \left( 1 + \frac{E_n(B)}{N\mu_B B} \right) \right)!}$$

(b)

Applying Stirling's formula to  $\Omega_n(E_n)$ , with  $N - n \gg 1 \Rightarrow N \gg n$  and  $n \gg 1$ :

$$\Omega_n(E_n) = \frac{\left(\frac{N}{e}\right)^N}{\left(\frac{n}{e}\right)^n \left(\frac{N-n}{e}\right)^{N-n}} = \frac{N^N e^n e^{-N} e^{N-n}}{n^n (N-n)^{N-n}} = \frac{N^N}{n^n (N-n)^{N-n}}$$

Logarithmus naturalis:

$$\ln \Omega_n(E_n) = N \ln N - n \ln n - (N - n) \ln(N - n)$$

inserting  $n(E_n)$ :

$$\begin{aligned} \ln \Omega_n(E_n) &= N \ln N - \frac{N}{2} \left(1 - \frac{E_n(B)}{N\mu_B B}\right) \ln \frac{N}{2} \left(1 - \frac{E_n(B)}{N\mu_B B}\right) \\ &\quad - \left(N - \frac{N}{2} \left(1 - \frac{E_n(B)}{N\mu_B B}\right)\right) \ln \left(N - \frac{N}{2} \left(1 - \frac{E_n(B)}{N\mu_B B}\right)\right) \\ &= N \ln N - \frac{N}{2} \left(1 - \frac{E}{N\mu_B B}\right) \ln \left[N \left(\frac{1}{2} - \frac{E}{2N\mu_B B}\right)\right] \\ &\quad - \frac{N}{2} \left(1 + \frac{E}{N\mu_B B}\right) \ln \left[N \left(\frac{1}{2} + \frac{E}{2\mu_B B}\right)\right] \\ &= N \ln N - \frac{N}{2} \left(1 - \frac{E}{N\mu_B B}\right) \left\{ \ln N + \ln \left(\frac{1}{2} - \frac{E}{2N\mu_B B}\right) \right\} \\ &\quad - \frac{N}{2} \left(1 + \frac{E}{N\mu_B B}\right) \left\{ \ln N + \ln \left(\frac{1}{2} + \frac{E}{2\mu_B B}\right) \right\} \\ &= N \ln N - \left(\frac{N}{2} - \frac{E}{2\mu_B B}\right) \ln N - \frac{N}{2} \left(1 - \frac{E}{N\mu_B B}\right) \ln \left(\frac{1}{2} - \frac{E}{2N\mu_B B}\right) \\ &\quad + - \left(\frac{N}{2} + \frac{E}{2\mu_B B}\right) \ln N - \frac{N}{2} \left(1 + \frac{E}{N\mu_B B}\right) \ln \left(\frac{1}{2} + \frac{E}{2\mu_B B}\right) \\ &= -\frac{N}{2} \left(1 - \frac{E}{N\mu_B B}\right) \ln \left(\frac{1}{2} - \frac{E}{2N\mu_B B}\right) - \frac{N}{2} \left(1 + \frac{E}{N\mu_B B}\right) \ln \left(\frac{1}{2} + \frac{E}{2\mu_B B}\right) \\ &\quad + \left(N - \frac{N}{2} + \frac{E}{2\mu_B B} - \frac{N}{2} - \frac{E}{2\mu_B B}\right) \ln N \\ &= -\frac{N}{2} \left(1 - \frac{E}{N\mu_B B}\right) \ln \left(\frac{1}{2} - \frac{E}{2N\mu_B B}\right) - \frac{N}{2} \left(1 + \frac{E}{N\mu_B B}\right) \ln \left(\frac{1}{2} + \frac{E}{2\mu_B B}\right) \end{aligned}$$

□

## 4.2 (Mixture of ideal gases)

Mixture of ideal gases with  $N_i$  particles of the kind  $i$  ( $i = 1, \dots, m$ ) in a vessel of volume  $V$ .

Definition of entropy:

$$S = -k_B \ln W(E)$$

with  $W(E) = \frac{\Omega(E)}{N! h^{3N}}$ , for indistinguishable particles with  $c_N = \frac{1}{N! h^{3N}}$ .

For the total system we can write:

$$\Omega(N_1, \dots, N_m) = \frac{N!}{\prod_{i=1}^m N_i!} \prod_{i=1}^m \Omega_i^{N_i}$$

Inserting this into definition of the Entropie:

$$\begin{aligned}
S &= -k_B \ln \frac{\Omega(N_1, \dots, N_m)}{N! h^{3N}} \\
&= -k_B \ln \frac{N! \prod_{i=1}^m \Omega_i^{N_i}}{N! h^{3N}} \\
&= -k_B \left( \ln \frac{N!}{\prod_{i=1}^m N_i!} + \sum_{i=1}^m N_i \ln \Omega_i - \ln N! h^{3N} \right)
\end{aligned}$$

Applying Stirling formula  $N! / \prod_{i=1}^m N_i! = \prod_{i=1}^m \left(\frac{N}{e}\right)^{N_i} \approx \prod_{i=1}^m \left(\frac{N}{N_i}\right)^{N_i}$ :

$$\begin{aligned}
S_{\text{ensemble}} &= -k_B \left( \ln \prod_{i=1}^m \left(\frac{N}{N_i}\right)^{N_i} + \sum_{i=1}^m N_i \ln \Omega_i - \ln N! h^{3N} \right) \\
&= -k_B \left( \ln \prod_{i=1}^m \left(\frac{N}{N_i}\right)^{N_i} + \sum_{i=1}^m N_i \ln \frac{\Omega_i}{N! h^{3N}} \right) \\
&= -k_B \sum_{i=1}^m N_i \ln \frac{N}{N_i} - k_B \sum_{i=1}^m N_i \ln \frac{\Omega_i}{N! h^{3N}} \\
&= -k_B \sum_{i=1}^m N_i \ln \frac{N}{N_i} + S \\
&= S_{\text{Mix}} + S
\end{aligned}$$

Entropy of an ideal gas (Sackur-Tetrode-equation):

$$S(E, V, N) = k_B N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{4\pi m E}{3N h^2} \right) + \frac{5}{2} \right]$$

leads to:

$$\begin{aligned}
S(E, V, N_1, N_2, \dots, N_m) &= \sum_{i=1}^m S_i + S_{\text{Mix}} \\
&= \sum_{i=1}^m k_B N_i \left[ \ln \left( \frac{V}{N_i} \right) + \frac{3}{2} \ln \left( \frac{4\pi m_i E_i}{3N_i h^2} \right) + \frac{5}{2} \right] - k_B \sum_{i=1}^m N_i \ln \frac{N}{N_i} \\
&= \sum_{i=1}^m k_B N_i \left( \ln \frac{V}{N_i} - \ln \frac{N}{N_i} + \frac{3}{2} \ln \left( \frac{4\pi m_i E_i}{3N_i h^2} \right) + \frac{5}{2} \right) \\
&= \sum_{i=1}^m k_B N_i \left( \ln \left( \frac{V}{N_i} \frac{N_i}{N} \right) + \frac{3}{2} \ln \left( \frac{4\pi m_i E_i}{3N_i h^2} \right) + \frac{5}{2} \right) \\
&= \sum_{i=1}^m k_B N_i \left( \ln \frac{V}{N} + \frac{3}{2} \ln \left( \frac{4\pi m_i E_i}{3N_i h^2} \right) + \frac{5}{2} \right) \\
&= k_B N \ln \frac{V}{N} + \sum_{i=1}^m k_B N_i \frac{3}{2} \ln \left( \frac{4\pi m_i E_i}{3N_i h^2} \right) + \frac{5}{2} k_B N
\end{aligned}$$

Definition of pressure:

$$p = T \left. \frac{\partial S}{\partial V} \right|_{E,N}$$

inserting  $S$ :

$$p = k_B T \frac{1}{V} N = \frac{1}{\beta} \frac{N}{V} = \frac{\rho}{\beta} \Leftrightarrow pV = Nk_B T$$

### 4.3 (Ideal gas in a centrifuge)

Radius =  $R$ , height =  $L$ , centrifuge frequency =  $\omega$  and mass of particle =  $m$ . The  $z$ -axis is parallel to the axis of the centrifuge. One particle Hamiltonian:

$$H = \frac{p^2}{2m} - \omega (xp_y - yp_x)$$

(a)

To show:

$$Z_1 = \left( \frac{2\pi m}{h^2 \beta} \right)^{3/2} \frac{2\pi L}{m\beta\omega^2} \left( e^{m\beta\omega^2 R^2/2} - 1 \right)$$

partition function for one particle of the gas.  
Definition of partition function:

$$Z_N = c_N \int d^{3N} q d^{3N} p e^{-\beta H(\vec{q}_N, \vec{p}_N)}$$

with  $c_N = \frac{1}{N! h^{3N}}$  for identical particles.  
Inserting Hamiltonian:

$$Z_1 = \frac{1}{1! h^3} \int d^3 q d^3 p e^{-\beta \frac{p^2}{2m} + \beta \omega (xp_y - yp_x)}$$

Integrating over momentum:

$$Z_1 = \frac{1}{1! h^3} \int d^3 q \int_{-\infty}^{\infty} dp_x e^{-\frac{\beta}{2m} p_x^2 - \beta \omega y p_x} \int_{-\infty}^{\infty} dp_y e^{-\frac{\beta}{2m} p_y^2 + \beta \omega x p_y} \int_{-\infty}^{\infty} dp_z e^{-\frac{\beta}{2m} p_z^2}$$

with:

$$\begin{aligned} \int_{-\infty}^{\infty} dp_z e^{-\frac{\beta}{2m} p_z^2} &= \sqrt{\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp\left(-\frac{\beta}{2m} (x^2 + y^2)\right)} \\ &= \sqrt{\int_0^{\infty} dr \int_0^{2\pi} d\varphi r \exp\left(-\frac{\beta}{2m} r^2\right)} \\ &= \sqrt{\frac{2m}{\beta} \pi \int_0^{\infty} du \exp(-u)} \\ &= \sqrt{\frac{2m\pi}{\beta}} \end{aligned}$$

$$\begin{aligned}
\int_{-\infty}^{\infty} dp_x e^{-\frac{\beta}{2m}p_x^2 - \beta\omega y p_x} &= \int_{-\infty}^{\infty} dp_x e^{-\left(\frac{\beta}{2m}p_x^2 + \beta\omega y p_x + \frac{m\beta}{2}\omega^2 y^2\right) + \frac{m\beta}{2}\omega^2 y^2} \\
&= e^{\frac{m\beta}{2}\omega^2 y^2} \cdot \int_{-\infty}^{\infty} dp_x e^{-\left(\sqrt{\frac{\beta}{2m}}p_x + \sqrt{\frac{m\beta}{2}}\omega y\right)^2} \\
&= \sqrt{\frac{2m}{\beta}} e^{\frac{m\beta}{2}\omega^2 y^2} \cdot \int_{-\infty}^{\infty} du e^{-u^2} \\
&= \sqrt{\frac{2m}{\beta}} e^{\frac{m\beta}{2}\omega^2 y^2} \cdot \sqrt{\pi} \\
&= \sqrt{\frac{2m\pi}{\beta}} e^{\frac{m\beta}{2}\omega^2 y^2}
\end{aligned}$$

$$\begin{aligned}
\int_{-\infty}^{\infty} dp_y e^{-\frac{\beta}{2m}p_y^2 + \beta\omega x p_y} &= \int_{-\infty}^{\infty} dp_y e^{-\left(\frac{\beta}{2m}p_y^2 - \beta\omega x p_y + \frac{m\beta}{2}\omega^2 x^2\right) + \frac{m\beta}{2}\omega^2 x^2} \\
&= e^{\frac{m\beta}{2}\omega^2 x^2} \cdot \int_{-\infty}^{\infty} dp_y e^{-\left(\sqrt{\frac{\beta}{2m}}p_y - \sqrt{\frac{m\beta}{2}}\omega x\right)^2} \\
&= \dots \text{equivalent to } p_x \dots \\
&= \sqrt{\frac{2m\pi}{\beta}} e^{\frac{m\beta}{2}\omega^2 x^2}
\end{aligned}$$

We get:

$$Z_1 = \frac{1}{h^3} \left( \sqrt{\frac{2m\pi}{\beta}} \right)^3 \int d^3q e^{\frac{m\beta}{2}\omega^2 y^2} e^{\frac{m\beta}{2}\omega^2 x^2}$$

Using cylindrical coordinates:

$$\begin{aligned}
Z_1 &= \left( \frac{2m\pi}{h^2\beta} \right)^{3/2} \int_0^R dr \int_0^{2\pi} d\varphi \int_0^L dz r e^{\frac{m\beta}{2}\omega^2 r^2} \\
&= \left( \frac{2m\pi}{h^2\beta} \right)^{3/2} 2\pi L \int_0^{m\beta\omega^2 R^2/2} \frac{du}{2m\beta\omega^2 r/2} r e^u \\
&= \left( \frac{2m\pi}{h^2\beta} \right)^{3/2} \frac{2\pi L}{m\beta\omega^2} \cdot [e^u]_0^{m\beta\omega^2 R^2/2} \\
&= \left( \frac{2m\pi}{h^2\beta} \right)^{3/2} \frac{2\pi L}{m\beta\omega^2} \cdot \left( e^{m\beta\omega^2 R^2/2} - 1 \right)
\end{aligned}$$

□

(b)

Using  $N$  identical particles we get:

$$Z_N = \frac{1}{N!h^{3N}} \int d^{3N}q d^{3N}p e^{-\beta \sum_{i=1}^N \left( \frac{p_i^2}{2m} - \omega(x_i p_{y,i} - y_i p_{x,i}) \right)}$$

Momentum integration:

$$\begin{aligned}
Z_N &= \frac{1}{N!h^{3N}} \int d^{3N}q \\
&\cdot \int_{-\infty}^{\infty} d^N p_x e^{-\beta \sum_{i=1}^N \left( \frac{p_{x,i}^2}{2m} + \omega y_i p_{x,i} \right)} \\
&\cdot \int_{-\infty}^{\infty} d^N p_y e^{-\beta \sum_{i=1}^N \left( \frac{p_{y,i}^2}{2m} - \omega x_i p_{y,i} \right)} \\
&\cdot \int_{-\infty}^{\infty} d^N p_z e^{-\beta \sum_{i=1}^N \frac{p_{z,i}^2}{2m}}
\end{aligned}$$

with:

$$\begin{aligned}
\int_{-\infty}^{\infty} dp_z e^{-\frac{\beta}{2m} \sum_{i=1}^N p_{z,i}^2} &= \left[ \int_{-\infty}^{\infty} dp_z e^{-\frac{\beta}{2m} p_z^2} \right]^N \\
&= \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^N
\end{aligned}$$

$$\begin{aligned}
\int_{-\infty}^{\infty} d^N p_x e^{-\beta \sum_{i=1}^N \left( \frac{p_{x,i}^2}{2m} + \omega y_i p_{x,i} \right)} &= \left[ \int_{-\infty}^{\infty} dp_x e^{-\frac{\beta}{2m} p_x^2 - \beta \omega y p_x} \right]^N \\
&= \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^N e^{N \frac{m\beta}{2} \omega^2 y^2}
\end{aligned}$$

$$\int_{-\infty}^{\infty} d^N p_y e^{-\beta \sum_{i=1}^N \left( \frac{p_{y,i}^2}{2m} - \omega x_i p_{y,i} \right)} = \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^N e^{N \frac{m\beta}{2} \omega^2 x^2}$$

leads to:

$$\begin{aligned}
Z_N &= \frac{1}{N!h^{3N}} \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{3N} \int d^{3N}q e^{N \frac{m\beta}{2} \omega^2 y^2} e^{N \frac{m\beta}{2} \omega^2 x^2} \\
&= \frac{1}{N!h^{3N}} \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{3N} \left[ \int d^3q e^{\frac{m\beta}{2} \omega^2 (x^2 + y^2)} \right]^N
\end{aligned}$$

Using result from **(a)**:

$$Z_N = \frac{1}{N!} \left[ \frac{2m\pi}{h^2 \beta} \right]^{\frac{3N}{2}} \left[ \frac{2\pi L}{m\beta \omega^2} \right]^N \cdot \left( e^{m\beta \omega^2 R^2/2} - 1 \right)^N$$

(c)

Definition of free energy:

$$F(T, V, N) = -\frac{1}{\beta} \ln Z_N(T, V)$$

inserting  $Z_N$  from **(b)**:

$$\begin{aligned} F(T, V, N) &= -\frac{1}{\beta} \ln \left[ \frac{1}{N!} \left[ \frac{2m\pi}{h^2\beta} \right]^{\frac{3N}{2}} \left[ \frac{2\pi L}{m\beta\omega^2} \right]^N \cdot \left( e^{m\beta\omega^2 R^2/2} - 1 \right)^N \right] \\ &= -\frac{1}{\beta} \left[ -\ln N! + \frac{3}{2}N \cdot \ln \left[ \frac{2m\pi}{h^2\beta} \right] + N \ln \left[ \frac{2\pi L}{m\beta\omega^2} \right] + N \ln \left( e^{m\beta\omega^2 R^2/2} - 1 \right) \right] \end{aligned}$$

**(d)**

Definition:

$$p = -\frac{\partial F}{\partial V}$$

Volume of a cylinder:

$$V = \pi R^2 L$$

Since there is no direct  $V$  dependance in  $F$  and pressure is going to vary in dependance of  $R$  and  $L$  we calculate two different pressures  $p_R$  and  $p_L$ . Therefore one of them stays in as a variable.

$$p_R = -\frac{\partial F}{\partial V} \Big|_L = -\frac{\partial F}{\partial R} \frac{\partial R}{\partial V} \Big|_L = -\frac{1}{2\sqrt{\pi V L}} \frac{\partial F}{\partial R} \Big|_L = -\frac{1}{2\pi R L} \frac{\partial F}{\partial R} \Big|_L$$

inserting  $F$  from **(c)**  $L = const.$ :

$$\begin{aligned} p_R &= -\frac{1}{2\pi R L} \frac{\partial}{\partial R} \left( -\frac{1}{\beta} \left[ -\ln N! + \frac{3}{2}N \cdot \ln \left[ \frac{2m\pi}{h^2\beta} \right] + N \ln \left[ \frac{2\pi L}{m\beta\omega^2} \right] + N \ln \left( e^{m\beta\omega^2 R^2/2} - 1 \right) \right] \right) \\ &= \frac{1}{2\beta\pi R L} \left\{ N \frac{\partial}{\partial R} \ln \left[ \left( e^{m\beta\omega^2 R^2/2} - 1 \right) \right] \right\} \\ &= \frac{N}{2\beta\pi R L} \left( \frac{e^{m\beta\omega^2 R^2/2}}{e^{m\beta\omega^2 R^2/2} - 1} \cdot \frac{m\beta\omega^2}{2} \cdot 2R \right) \\ &= \frac{N}{2\pi L} \left( \frac{m\omega^2}{1 - e^{-m\beta\omega^2 R^2/2}} \right) \end{aligned}$$

This converges to  $p_R V = N k_B T$  for  $\omega \rightarrow 0$ , this can be seen using L'Hospital.

$p_L$ :

$$p_L = -\frac{\partial F}{\partial V} \Big|_R = -\frac{\partial F}{\partial L} \frac{\partial L}{\partial V} \Big|_R = -\frac{1}{\pi R^2} \frac{\partial F}{\partial L} \Big|_R$$

with  $F$ ,  $R = const.$ :

$$\begin{aligned}
p_L &= -\frac{1}{\pi R^2} \frac{\partial}{\partial L} \left\{ -\frac{1}{\beta} - \frac{N}{\beta} \ln \left[ \frac{L\sqrt{m}}{h^3 \omega^2 N} \cdot (e^{m\beta\omega^2 R^2/2} - 1) \right] - \frac{5N}{2\beta} \ln \left[ \frac{2\pi}{\beta} \right] \right\} \\
&= \frac{N}{\beta \pi R^2} \frac{\partial}{\partial L} \left( \ln \frac{L\sqrt{m}}{h^3 \omega^2 N} \right) \\
&= \frac{N}{\beta \pi R^2 L} \\
&= \frac{1}{\beta} \frac{N}{V}
\end{aligned}$$

This is the ideal gas relation  $p_L V = N k_B T$ , which seems likely for the  $z$ -axis, since there is no reason for any other dependence there (especially there is no dependence of  $\omega$ ).

Total force at outer walls:

$$\begin{aligned}
F &= p \cdot A \\
&\text{with} \\
F_R &= p_R A_R \\
&= \frac{N}{2\pi L} \left( \frac{m\omega^2}{1 - e^{-m\beta\omega^2 R^2/2}} \right) \pi R^2 \\
F_R &= \frac{N}{2L} \left( \frac{m\omega^2 R^2}{1 - e^{-m\beta\omega^2 R^2/2}} \right) \\
&\text{and} \\
F_L &= p_L A_L \\
&= \frac{1}{\beta} \frac{N}{\pi R^2 L} 2\pi R L \\
F_L &= \frac{2N}{R\beta}
\end{aligned}$$

#### 4.4 (Doppler broadening)

Atoms with mass  $m$ , temperature  $T$  emit light in  $x$ -direction, moving with  $v_x$  leads to doppler effect:

$$\nu = \nu_0 \left( 1 + \frac{v_x}{c} \right)$$

Using  $v_x = \frac{p_x}{m}$  and Hamiltonian for free particle  $H = \sum_{i=1}^N \frac{p_i^2}{2m}$ :

$$\nu = \nu_0 \left( 1 + \frac{p_x}{mc} \right)$$

(a)

Definition:

$$\langle A \rangle = \frac{\int d^{3N} q \int d^{3N} p A(\vec{q}_N, \vec{p}_N) e^{-\beta H(\vec{q}_N, \vec{p}_N)}}{\int d^{3N} q \int d^{3N} p e^{-\beta H(\vec{q}_N, \vec{p}_N)}}$$



inserting given problem conditions:

$$\begin{aligned}
\langle \nu \rangle &= \nu_0 \frac{\int d^{3N} q \int d^{3N} p \left(1 + \frac{p_x}{mc}\right) e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}}{\int d^{3N} q \int d^{3N} p e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}} \\
&= \nu_0 \frac{\int d^{3N} q \int d^{3N} p e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}}{\int d^{3N} q \int d^{3N} p e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}} + \frac{\nu_0}{mc} \frac{\int d^{3N} q \int d^{3N} p p_x e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}}{\int d^{3N} q \int d^{3N} p e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}} \\
&= \nu_0
\end{aligned}$$

second term vanishes because of symmetry reasons (integrating over symmetric intervall, but  $p_x$  is odd, while exponent ( $p^2 = p_x^2 + p_y^2 + p_z^2$ )  $p_x^2$  is even).

(b)

Definition:

$$\Delta \nu = \sqrt{\langle (\nu - \langle \nu \rangle)^2 \rangle} = \sqrt{\langle \nu^2 - 2\nu \langle \nu \rangle + \langle \nu \rangle^2 \rangle} = \sqrt{\langle \nu^2 \rangle - \langle \nu \rangle^2}$$

$\langle \nu^2 \rangle$  calculation:

$$\begin{aligned}
\langle \nu^2 \rangle &= \nu_0^2 \frac{\int d^{3N} q \int d^{3N} p \left(1 + \frac{p_x}{mc}\right)^2 e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}}{\int d^{3N} q \int d^{3N} p e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}} \\
&= \nu_0^2 + \frac{\nu_0^2}{(mc)^2} \frac{\int d^{3N} q \int d^{3N} p p_x^2 e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}}{\int d^{3N} q \int d^{3N} p e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}}}
\end{aligned}$$

$\left(1 + \frac{p_x}{mc}\right)^2 = \left(1 + 2\frac{p_x}{mc} + \left(\frac{p_x}{mc}\right)^2\right)$ , first term leads to  $\nu_0^2$ , while numerator and denominator integrals are the same, second term cancels because of symmetry. Integrals of last term have to be calculated:

denominator:

$$\int d^{3N} q \int d^{3N} p e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} = \int d^{3N} q \left[ \int_{-\infty}^{\infty} dp e^{-\beta \frac{p^2}{2m}} \right]^{3N} = \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{3N} \int d^{3N} q$$

numerator:

$$\begin{aligned}
\int d^{3N} q \int d^{3N} p p_x^2 e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} &= \int d^{3N} q \int_{-\infty}^{\infty} dp_x p_x^2 e^{-\frac{\beta}{2m} \sum_{i=1}^N p_{x,i}^2} \left[ \int_{-\infty}^{\infty} dp e^{-\frac{\beta}{2m} p^2} \right]^{2N} \\
&= \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{2N} \int d^{3N} q \left[ \int_{-\infty}^{\infty} dp_x p_x^2 e^{-\frac{\beta}{2m} p_x^2} \right]^N
\end{aligned}$$

solving one dimensional integral:

$$\begin{aligned}
\int_{-\infty}^{\infty} dp_x p_x^2 e^{-\frac{\beta}{2m}p_x^2} &= \int_{-\infty}^{\infty} dp_x p_x \cdot p_x e^{-\frac{\beta}{2m}p_x^2} \\
&= \left[ -p_x \cdot \frac{m}{\beta} e^{-\frac{\beta}{2m}p_x^2} \right]_{-\infty}^{\infty} + \frac{m}{\beta} \int_{-\infty}^{\infty} dp_x e^{-\frac{\beta}{2m}p_x^2} \\
&= \frac{m}{\beta} \sqrt{\frac{2m\pi}{\beta}}
\end{aligned}$$

inserting in numerator integral:

$$\begin{aligned}
\int d^{3N}q \int d^{3N}p p_x^2 e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} &= \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{2N} \left[ \frac{m}{\beta} \sqrt{\frac{2m\pi}{\beta}} \right]^N \int d^{3N}q \\
&= \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{3N} \left( \frac{m}{\beta} \right)^N \int d^{3N}q
\end{aligned}$$

inserting numerator and denominator integral:

$$\begin{aligned}
\langle \nu^2 \rangle &= \nu_0^2 + \frac{\nu_0^2}{(mc)^2} \frac{\left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{3N} \left( \frac{m}{\beta} \right)^N \int d^{3N}q}{\left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{3N} \int d^{3N}q} \\
&= \nu_0^2 \cdot \left( 1 + \frac{m^N}{(mc)^2 \beta^N} \right)
\end{aligned}$$

This leads to:

$$\Delta\nu = \sqrt{\langle \nu^2 \rangle - \langle \nu \rangle^2} = \sqrt{\nu_0^2 + \frac{m^N}{(mc)^2 \beta^N} \cdot \nu_0^2 - \nu_0^2} = \frac{m^{\frac{N}{2}}}{mc\beta^{\frac{N}{2}}} \cdot \nu_0$$

with  $N = 1$ , this is what we need, since we only have a look at one “average”-particle:

$$\Delta\nu = \sqrt{\frac{k_B T}{mc^2}} \cdot \nu_0$$

(c)

Using Maxwell velocity distribution:

$$w(\vec{v}) d^3v = \left( \frac{m\beta}{2\pi} \right)^{\frac{3}{2}} \exp\left( -\frac{\beta m v^2}{2} \right) d^3v$$

we get the velocity distribution for  $v_x$ :

$$w(v_x) dv_x = \left( \frac{m\beta}{2\pi} \right)^{\frac{3}{2}} \exp\left( -\frac{\beta m v_x^2}{2} \right) \int_{-\infty}^{\infty} dv_y \exp\left( -\frac{\beta m v_y^2}{2} \right) \int_{-\infty}^{\infty} dv_z \exp\left( -\frac{\beta m v_z^2}{2} \right)$$

$$\begin{aligned}
&= \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{\beta m v_x^2}{2}\right) \left[\int_{-\infty}^{\infty} dv \exp\left(-\frac{\beta m}{2} v^2\right)\right]^2 \\
&= \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{\beta m v_x^2}{2}\right) \left[\sqrt{\frac{2\pi}{\beta m}}\right]^2 \\
&= \left(\frac{m\beta}{2\pi}\right)^{\frac{1}{2}} \exp\left(-\frac{\beta m v_x^2}{2}\right)
\end{aligned}$$

while we got the direct correlation  $I(\nu) d\nu = w(v_x) dv_x$  with

$$v_x = \frac{c}{\nu_0} (\nu - \nu_0) \quad \text{and} \quad dv_x = \frac{c}{\nu_0} d\nu$$

we get:

$$I(\nu) d\nu = \frac{1}{\sqrt{\pi}} \left(\frac{mc^2\beta}{2\nu_0^2}\right)^{\frac{1}{2}} \exp\left(-\frac{\beta mc^2 (\nu - \nu_0)^2}{2\nu_0^2}\right) d\nu$$

For the non relativistic case  $k_B T \ll mc^2$ , with  $\beta = \frac{1}{k_B T}$ , we have to consider, that  $\beta mc^2 \rightarrow \infty$ . While the squareroot term will diverge the exponential term will converge to zero. Substituting  $x = \sqrt{\frac{mc^2\beta}{2\nu_0^2}}$  we get:

$$I(\nu) = \frac{x}{\sqrt{\pi}} \exp\left(-x^2 (\nu - \nu_0)^2\right)$$

which is a representation of the delta function for  $x \rightarrow \infty$ :

$$\lim_{x \rightarrow \infty} I(\nu) = \delta(\nu - \nu_0)$$

This means, we only get an intensity at  $\nu_0 = \nu$ , while  $\nu_0$  is the emitted frequency of the atoms. This means, the velocity of the atoms doesn't have any effect and the doppler effect doesn't occur. Meaning  $v_x \ll c$ :

$$\nu = \nu_0 \left(1 + \underbrace{\frac{v_x}{c}}_{\rightarrow 0}\right) \approx \nu_0$$