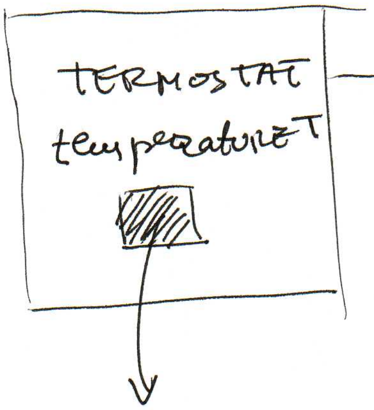
Kanonski ansambl



Za celinu važe pravila mikrokanonskog ansambla

(pod) sistem od interesa

Makroskopski uslovi za podsistem

V, N - fiksirani

Sistem razmenjuje energiju sa termostatom

fazna gustina verovatnoće
$$f(\vec{p},\vec{q}) = \frac{e^{-\beta \mathcal{H}(\vec{p},\vec{q})}}{Z}$$

$Z \rightarrow$ statistička suma (faktor normiranja)

$$Z = \int_{\Gamma} e^{-\beta \mathcal{H}(\vec{p},\vec{q})}\, d\Gamma \quad ; \quad Z = Z(T,V,N)$$

$\beta = \frac{1}{kT} \rightarrow$ modul kanonske raspodele

Veza sa termodinamikom

$$F(T,V,N) = -kT \ln Z$$

Entropija i pritisak su dati kao

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad , \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$\downarrow$ Kalorična j-na stanja

$\uparrow$

$U = F + TS$

$\downarrow$ Termička j-na stanja

— Očekivana vrednost

$$\langle B \rangle = \int_{\Gamma(E)} B\, f\, d\Gamma = \frac{1}{Z} \int B\, e^{-\beta \mathcal{H}}\, d\Gamma$$

1. Polazeći od definicije za statističku sumu Z u kanonskom ansamblu pokazati da je tačan sledeći izraz za toplotni kapacitet pri stalnoj zapremini:

$$C_V = \left[\frac{\partial}{\partial T}\left(kT^2 \frac{\partial}{\partial T} \ln Z \right) \right]_V$$

$$Z(T,V,N) = \int_\Gamma e^{-\frac{1}{kT}\mathcal{H}(\vec{p},\vec{q})}\, d\Gamma$$

$$\frac{\partial Z}{\partial T} = \int_\Gamma \frac{1}{kT^2}\mathcal{H}(\vec{p},\vec{q})\, e^{-\frac{1}{kT}\mathcal{H}(\vec{p},\vec{q})}\, d\Gamma$$

$$kT^2\frac{\partial Z}{\partial T} = \int_\Gamma \mathcal{H}(\vec{p},\vec{q})\, e^{-\frac{1}{kT}\mathcal{H}(\vec{p},\vec{q})}\, d\Gamma \quad \Big/ \frac{1}{Z}$$

$$\frac{kT^2}{Z}\frac{\partial Z}{\partial T} = \langle \mathcal{H} \rangle = U$$

$$kT^2\frac{\partial \ln Z}{\partial T} = U$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\left(kT^2 \frac{\partial \ln Z}{\partial T}\right)\right]_V$$

$\boxed{//}$

2. Idealan gas od N jednoatomskih molekula nalazi se u kontaktu sa termostatom temperature T. Odrediti entropiju i termičnu i kaloričnu j-nu stanja ovog sistema. Pretpostaviti da je u pitanju klasičan idealan gas i u relativističkom i u kvantno-mehaničkom smislu.

- U pitanju su jednoatomski molekuli, što znači da se ne uzimaju u obzir unutrašnji stepeni slobode čestice (vibracioni, rotacioni)
- Klasičan idealni gas u gornjem smislu znači da su brzine molekula daleko manje od brzine svjetlosti i da je srednje rastojanje među molekulima daleko veće od termalne talasne dužine → prokomentarisati!
- Posmatrani gas spada u nelokalizovane sisteme, a budući da je idealan, čestice su neinteragujuće i važi

$$Z_N = \frac{(Z_1)^N}{N!}$$

$$\mathcal{H}(\vec{p},\vec{q}) = \sum_{i=1}^{N} \mathcal{H}_i(\vec{p}_i,\vec{q}_i)$$

$$Z_N = \int_\Gamma e^{-\beta \sum_{i=1}^{N} \mathcal{H}_i(\vec{p}_i, \vec{q}_i)} \, d\Gamma$$

$$d\Gamma = \prod_{i=1}^{N} \frac{d\vec{p}_i \, d\vec{q}_i}{h^{3N} N!}$$

$$Z_N = \frac{1}{N!} \prod_{i=1}^{N} \underbrace{\int e^{-\beta \mathcal{H}_1(\vec{p}_1, \vec{q}_1)} \frac{d\vec{p}_1 \, d\vec{q}_1}{h^3}}_{Z_1}$$

$$\boxed{Z_N = \frac{1}{N!} Z_1^N}$$

$$Z_1 = \int e^{-\beta \mathcal{H}(\vec{p}, \vec{q})} \, d\Gamma$$

$$d\Gamma = \frac{d\vec{p} \, d\vec{q}}{h^3}$$

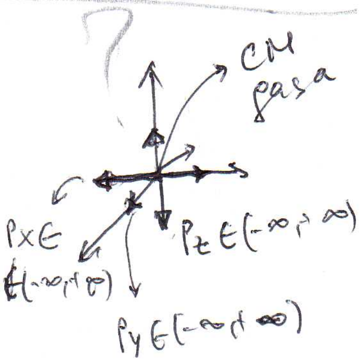
$$Z_1 = \frac{1}{h^3} \int e^{-\beta \frac{\vec{p}^2}{2m}} \, d\vec{p} \, d\vec{q}$$

$$= \frac{V}{h^3} \int_{-\infty}^{+\infty} e^{-\frac{\beta \vec{p}^2}{2m}} \, d\vec{p}$$

Pitanje za studente

Zašto te granice, a ne neke druge?

$$\boxed{\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}}$$



$$= \frac{V}{h^3} \prod_{i=x}^{\cancel{z}} \int_{-\infty}^{+\infty} e^{-\frac{\beta}{2m} p_i^2} \, dp_i$$

Sistem se nalazi van spoljašnjeg polja pa je zato moguće razbijanje gornjeg integrala na int. po osama

$$Z_1 = \frac{V}{h^3}(2\pi m kT)^{\frac{3}{2}}$$

$$Z = \frac{Z_1^N}{N!} = \frac{V^N}{N!\,h^{3N}}(2\pi m kT)^{\frac{3N}{2}}$$

$F = -kT \ln Z$ + Stirlingova aproksimacija

$$F = -kT\left[\ln\frac{V^N}{h^{3N}} - N\ln N + N + \frac{3}{2}N\ln(2\pi m kT)\right]$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \ldots \quad \text{Domaći}$$

$$= \frac{5}{2}NK + Nk\left[\ln\frac{V}{Nh^{3N}} + \frac{3}{2}\ln(2\pi m kT)\right]$$

Kalorična j-na stanja

$$U = F + TS$$

Za Domaći! $\left(U = \frac{3}{2}NKT\right)$

Termička j-na stanja

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \ldots\ldots = \frac{kTN}{V}$$

Domaći!

TERMALNA TALASNA DUŽINA

$$\lambda_T = \frac{h}{\sqrt{2\pi m kT}}$$

3. Posmatrati sistem čestica koje se nalaze u termostatu temperature T i međusobno ne interaguju. Odrediti verovatnoću da energija jedne čestice bude između ε i $\varepsilon + d\varepsilon$ za slučaj:

a) klasične nerelativističke čestice, $\varepsilon = \frac{p^2}{2m}$

b) ultrarelativističke čestice, $\varepsilon = cp$.

Za slučaj pod a) pokazati da najverovatnija energija idealnog gasa od N nerelativističkih čestica nije jednaka zbiru najverovatnijih energija čestica. Ispit Da li je srednja vrednost energije gasa jednaka zbiru srednjih vrednosti energija čestica.

Kanonska fazna gustina verovatnoće za jednu česticu

$$f = \frac{e^{-\beta \mathcal{H}}}{Z}, \quad f = \frac{dw}{d\Gamma}$$

$$dw = f\, d\Gamma = \frac{e^{-\beta \mathcal{H}}}{Z} d\Gamma \qquad (*)$$

$$d\Gamma = \frac{\partial \Gamma}{\partial \varepsilon} d\varepsilon = \Omega(\varepsilon)\, d\varepsilon$$

$$Z = \int e^{-\beta \mathcal{H}} d\Gamma = \int_0^{+\infty} e^{-\beta \varepsilon}\, \Omega(\varepsilon)\, d\varepsilon \qquad (**)$$

(*) i (**) $\Rightarrow$

$$dw = \frac{e^{-\beta\varepsilon}\,\Omega(\varepsilon)\,d\varepsilon}{\int_0^{+\infty} e^{-\beta\varepsilon}\,\Omega(\varepsilon)\,d\varepsilon} \qquad (1)$$

a) $\Gamma(\varepsilon) = \int \cdots \int d\Gamma = \int \cdots \int d\vec{p}\, d\vec{q}$

$= V \int \cdots \int d\vec{p} = 4\pi V \int_0^{\sqrt{2m\varepsilon}} p^2 dp = \ldots =$

$= \frac{4\pi V}{3} (2m)^{\frac{3}{2}} \varepsilon^{\frac{3}{2}}$

$\Omega(\varepsilon) = \frac{\partial \Gamma(\varepsilon)}{\partial \varepsilon} = \ldots = k\, \varepsilon^{\frac{1}{2}}$

Onda (1) daje

$$dw = \frac{e^{-\beta\varepsilon}\,\varepsilon^{\frac{1}{2}}\,d\varepsilon}{(kT)^{\frac{3}{2}}\,\Gamma\left(\frac{3}{2}\right)}$$

b) $\Gamma(\varepsilon) = \int \cdots \int d\Gamma = 4\pi V \int_0^{\varepsilon/c} p^2 dp = \frac{4\pi V}{c^3} \varepsilon^3$

$\Omega(\varepsilon) = \frac{\partial \Gamma(\varepsilon)}{\partial \varepsilon} = \ldots = k\varepsilon^2$

$$dw = \frac{e^{-\beta\varepsilon}\,\varepsilon^2\,d\varepsilon}{(kT)^3\,\Gamma(3)}$$

c) $f^{(\varepsilon)}(\varepsilon) = \frac{dw}{d\varepsilon} = \frac{e^{-\beta\varepsilon}\,\varepsilon^{\frac{1}{2}}}{(kT)^{\frac{3}{2}}\,\Gamma\left(\frac{3}{2}\right)}$

$\frac{d f^{(\varepsilon)}(\varepsilon)}{d\varepsilon} = 0 \Rightarrow \varepsilon = \frac{1}{2} kT$

Zbir najverovatnijih energija $E = \frac{N}{2} kT$

Najverovatnija energija sistema od N čestica

$$\Gamma(E) = V^N \underbrace{\int \cdots \int}_{3N} \prod_{i=1}^{N} d\vec{p}_i$$

$$\sum_i \vec{p}_i^{\,2} \le 2mE \Rightarrow R = \sqrt{2mE}$$

$$V_n = \frac{\pi^{\frac{n}{2}} R^n}{\Gamma\left(\frac{n}{2}+1\right)}$$

$$\Gamma(E) = \frac{V^N \pi^{\frac{3N}{2}} (2mE)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)}$$

$$\Omega(E) = k\, E^{\frac{3N}{2}-1}$$

$$dw = \frac{e^{-\beta E} E^{\frac{3N}{2}-1} dE}{\int_0^{+\infty} e^{-\beta E} E^{\frac{3N}{2}-1} \cancel{dE}}$$

$$\frac{dw}{dE} = \frac{e^{-\beta E} E^{\frac{3N}{2}-1}}{(kT)^{\frac{3N}{2}} \Gamma\left(\frac{3N}{2}\right)} = f^{(E)}(E)$$

$$\frac{d f^{(E)}(E)}{dE} = 0 \Rightarrow E = kT\left(\frac{3N}{2} - 1\right)$$

Ispit

$$\langle \varepsilon \rangle = \int_0^{\infty} \varepsilon f^{(\varepsilon)}(\varepsilon)\, d\varepsilon$$

$$\langle E \rangle = \int_0^{+\infty} E f^{(E)}(E)\, dE$$

$$\langle E \rangle \overset{?}{=} N \langle \varepsilon \rangle$$

4. Dat je gas koji se sastoji od međusobno neinteragujućih čestica, od kojih svaka ima energiju $\varepsilon = \varepsilon_0 + \alpha p^3$, gde su ε_0 i α konstante, a p je intenzitet impulsa čestice. Naći Z ovog gasa, pa na osnovi toga izračunati koliki rad vrši jedan mol gasa pri adijabatskoj ekspanziji iz stanja u kome je zapremina sistema V_1 i temperatura T_1 u stanje u kome je zapremina V_2. Kolika je temperatura gasa nakon ekspanzije?

$$Z_N = \frac{1}{N!\,h^{3N}} \int \cdots \int e^{-\beta \mathcal{H}} \prod_{i=1}^{N} d\vec{r}_i\, d\vec{p}_i$$

$$\mathcal{H} = \sum_{i=1}^{N} \varepsilon_i$$

$$\varepsilon_i = \varepsilon_0 + \alpha p_i^3, \quad \forall i$$

$$Z_N = \frac{V^N}{N!\,h^{3N}} \int \cdots \int e^{-\beta \sum_{i=1}^{N} \varepsilon_i} \prod_{i=1}^{N} d\vec{p}_i$$

$$Z_N = \frac{V^N}{N!\,h^{3N}} \int \cdots \int \underbrace{\prod_{i=1}^{N} e^{-\beta \varepsilon_i}\, d\vec{p}_i}_{\text{istog oblika } \forall i}$$

$$Z_N = \frac{V^N}{N!\,h^{3N}} \left[\int e^{-\beta \varepsilon}\, d\vec{p} \right]^N ; \quad d\vec{p} = 4\pi p^2 dp$$

$$Z_N = \frac{(4\pi V)^N}{N!\,h^{3N}} \left[\int_0^\infty e^{-\beta(\varepsilon_0 + \alpha p^3)}\, p^2 dp \right]^N$$

$$I = \int_0^{+\infty} e^{-\beta(\varepsilon_0 + \alpha p^3)} p^2 dp$$

$$I = \frac{kT}{3\alpha} e^{-\frac{\varepsilon_0}{kT}}$$

$$Z_N = \frac{(4\pi V)^N}{N!\, h^{3N}} \left[\frac{kT}{3\alpha} e^{-\frac{\varepsilon_0}{kT}} \right]^N$$

$$= \frac{1}{N!} \left[\frac{4\pi V kT}{3\alpha h^3} e^{-\frac{\varepsilon_0}{kT}} \right]^N$$

$$F = -kT \ln Z_N = -kT \ln \left[\frac{4\pi V}{3\alpha h^3} kT \right] + N\varepsilon_0 + kT \ln N!$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\downarrow$$

$$p = \frac{NkT}{V}$$

Adijabatska ekspanzija $\quad S = \text{Const}$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk \ln \left[\frac{4\pi V}{3\alpha h^3} kT \right] + Nk - k \ln N!$$

$$S = \text{const} \Rightarrow VT = \text{const}$$

$$W = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{NkT}{V} dV = \int_{V_1}^{V_2} \frac{NkTV}{V^2} dV$$

$$= \text{Const}\, Nk \int_{V_1}^{V_2} \frac{dV}{V^2} = \ldots = \text{Const}\, Nk \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

U isto vreme, ovo je i promena unutrašnje energije: $dU = -\delta W$

Temperatura gasa nakon ekspanzije, zbog $TV = const$ je

$$T_1 V_1 = T_2 V_2 \Rightarrow \boxed{T_2 = \frac{T_1 V_1}{V_2}}$$

5. Sistem se nalazi u stanju toplotne ravnoteže sa okolinom. Dokazati da je srednje kvadratno odstupanje (disperzija) energije određeno relacijom:

$$D(\mathcal{H}) = kT^2 C_V$$

gde je C_V toplotni kapacitet pri stalnoj zapremini. Na osnovi ovog rezultata pokazati da se energija makroskopskog sistema u stanju toplotne ravnoteže može smatrati konstantnom.

$$D(\mathcal{H}) = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2$$

$\langle \mathcal{H} \rangle = ?$

$\langle \mathcal{H}^2 \rangle = ?$

$$\langle \mathcal{H} \rangle = \frac{1}{Z} \int_{\Gamma} \mathcal{H} e^{-\beta \mathcal{H}} d\Gamma$$

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} = \left(-\frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \right) \int_{\Gamma} \mathcal{H} e^{-\beta \mathcal{H}} d\Gamma$$

$$- \frac{1}{Z} \int_{\Gamma} \mathcal{H}^2 e^{-\beta \mathcal{H}} d\Gamma$$

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} = -\langle \mathcal{H}^2 \rangle - \frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \int_{\Gamma} \mathcal{H} e^{-\beta \mathcal{H}} d\Gamma$$

$$Z = \int_\Gamma e^{-\beta \mathcal{H}} d\Gamma$$

$$\frac{\partial Z}{\partial \beta} = -\int_\Gamma \mathcal{H} e^{-\beta \mathcal{H}} d\Gamma = -Z\langle \mathcal{H} \rangle$$

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} = -\langle \mathcal{H}^2 \rangle - \frac{1}{Z^2}\left(-Z\langle \mathcal{H} \rangle\right)\int \mathcal{H} e^{-\beta \mathcal{H}} d\Gamma$$

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} = -\langle \mathcal{H}^2 \rangle + \frac{1}{Z}\langle \mathcal{H} \rangle \int \mathcal{H} e^{-\beta \mathcal{H}} d\Gamma$$

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} = -\langle \mathcal{H}^2 \rangle + \langle \mathcal{H} \rangle^2 = -D(\mathcal{H}) \quad (*)$$

Sa druge strane

$$C_V = \frac{\partial \langle \mathcal{H} \rangle}{\partial T} = \frac{\partial \langle \mathcal{H} \rangle}{\partial \beta}\frac{\partial \beta}{\partial T} = \frac{-1}{kT^2}\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} \quad (**)$$

$$(*) \wedge (**) \Rightarrow \boxed{D(\mathcal{H}) = C_V k T^2}$$

Budući da je

$$\frac{\sqrt{D(\mathcal{H})}}{\langle \mathcal{H} \rangle} = \frac{\sqrt{C_V k T^2}}{U}$$

$D(\mathcal{H})$ – disperzija
$\sigma(\mathcal{H}) = \sqrt{D(\mathcal{H})}$ – standardna devijacija

a C_V i U su ekstenzivne veličine proporcionalne broju čestica N, onda važi

$$\frac{\sqrt{D(\mathcal{H})}}{\langle \mathcal{H} \rangle} \sim \frac{1}{\sqrt{N}}$$

Za N veliko relativne fluktuacije postaju zanemarljive, pa se kanonski ansambl nalazi o stanju sa energijom praktično jednakoj $\langle \mathcal{H}$

Domaći!

Pokazati da važi $\langle (\mathcal{H} - \langle \mathcal{H} \rangle)^3 \rangle =$

$$= k^2 T^2 \left(T^2 \frac{\partial C_V}{\partial T} + 2 T C_V \right)$$

Rešenje!

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} = -\frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \int_\Gamma \mathcal{H} e^{-\beta \mathcal{H}} d\Gamma - \frac{1}{Z} \int_\Gamma \mathcal{H}^2 e^{-\beta \mathcal{H}} d\Gamma$$

$$\frac{\partial^2 \langle \mathcal{H} \rangle}{\partial \beta^2} = -\left(-\frac{2}{Z^3} \left(\frac{\partial Z}{\partial \beta} \right)^2 + \frac{1}{Z^2} \frac{\partial^2 Z}{\partial \beta^2} \right) \int_\Gamma \mathcal{H} e^{-\beta \mathcal{H}} d\Gamma$$

$$+ \frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \int_\Gamma \mathcal{H}^2 e^{-\beta \mathcal{H}} d\Gamma - \left(-\frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \right) \int_\Gamma \mathcal{H}^2 e^{-\beta \mathcal{H}} d\Gamma$$

$$+ \frac{1}{Z} \int \mathcal{H}^3 e^{-\beta \mathcal{H}} d\Gamma$$

$$\frac{\partial^2\langle\mathcal{H}\rangle}{\partial\beta^2} = \frac{2}{Z^3}\left(\frac{\partial Z}{\partial\beta}\right)^2 \int_\Gamma \mathcal{H} e^{-\beta\mathcal{H}} d\Gamma -$$

$$-\frac{1}{Z^2}\frac{\partial^2 Z}{\partial\beta^2}\int_\Gamma \mathcal{H} e^{-\beta\mathcal{H}} d\Gamma + \frac{1}{Z^2}\frac{\partial Z}{\partial\beta}\int_\Gamma \mathcal{H}^2 e^{-\beta\mathcal{H}} d\Gamma$$

$$+\frac{1}{Z^2}\frac{\partial Z}{\partial\beta}\int_\Gamma \mathcal{H}^2 e^{-\beta\mathcal{H}} d\Gamma + \frac{1}{Z}\int \mathcal{H}^3 e^{-\beta\mathcal{H}} d\Gamma$$

$$Z = \int e^{-\beta\mathcal{H}} d\Gamma$$

$$\frac{\partial Z}{\partial\beta} = -\int \mathcal{H} e^{-\beta\mathcal{H}} d\Gamma = -Z\langle\mathcal{H}\rangle$$

$$\frac{\partial^2 Z}{\partial\beta^2} = \int \mathcal{H}^2 e^{-\beta\mathcal{H}} d\Gamma = Z\langle\mathcal{H}^2\rangle$$

$$\frac{\partial^2\langle\mathcal{H}\rangle}{\partial\beta^2} = \frac{2}{Z^3}\left(-Z\langle\mathcal{H}\rangle\right)^2 \int_\Gamma \mathcal{H} e^{-\beta\mathcal{H}} d\Gamma$$

$$-\frac{1}{Z^2} Z\langle\mathcal{H}^2\rangle \int \mathcal{H} e^{-\beta\mathcal{H}} d\Gamma + \frac{2}{Z^2}\left(-Z\langle\mathcal{H}\rangle\right)\cdot$$

$$\cdot\int_\Gamma \mathcal{H}^2 e^{-\beta\mathcal{H}} d\Gamma + \frac{1}{Z}\int_\Gamma \mathcal{H}^3 e^{-\beta\mathcal{H}} d\Gamma$$

$$\frac{\partial^2\langle\mathcal{H}\rangle}{\partial\beta^2} = 2\langle\mathcal{H}\rangle^2\langle\mathcal{H}\rangle - \langle\mathcal{H}^2\rangle\langle\mathcal{H}\rangle$$

$$-2\langle\mathcal{H}\rangle\langle\mathcal{H}^2\rangle + \langle\mathcal{H}^3\rangle = 2\langle\mathcal{H}\rangle^3 - 3\langle\mathcal{H}^2\rangle\langle\mathcal{H}\rangle +$$

$$+\langle\mathcal{H}^3\rangle$$

$$D_3(\mathcal{H}) = \langle (\mathcal{H} - \langle \mathcal{H} \rangle)^3 \rangle$$

$$\vdots$$

$$= \langle \mathcal{H}^3 \rangle - 3 \langle \mathcal{H}^2 \rangle \langle \mathcal{H} \rangle + 2 \langle \mathcal{H} \rangle^3$$

$$\frac{\partial^2 \langle \mathcal{H} \rangle}{\partial \beta^2} = D_3(\mathcal{H})$$

$$\frac{\partial \langle \mathcal{H} \rangle}{\partial \beta} = \dots = -kT^2 C_V$$

$$\frac{\partial^2 \langle \mathcal{H} \rangle}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left(-kT^2 C_V \right)$$

$$= \frac{\partial}{\partial T} \frac{\partial T}{\partial \beta} \left(-kT^2 C_V \right)$$

$$= -\frac{1}{\beta^2 k} (-k) \frac{\partial}{\partial T} \left(T^2 C_V \right)$$

$$= k^2 T^2 \left(2T C_V + T^2 \frac{\partial C_V}{\partial T} \right)$$

Damit,

$$D_3(\mathcal{H}) = k^2 T^2 \left(2T C_V + T^2 \frac{\partial C_V}{\partial T} \right)$$

$\boxed{}$

6. Razmatrati sistem od N klasičnih harmonijskih oscilatora. iste mase i frekvencije! Pretpostavljajući da oscilatori zanemarljivo slabo interaguju ~~i da su identični~~ odrediti Z, F, S i $\langle \mathcal{H} \rangle$.

$$\mathcal{H} = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{1}{2} m\omega^2 q_i^2 \right)$$

Isto m i ω za sve oscilatore!

$$Z = \frac{1}{N!\,h^N} \int \dots \int e^{-\beta \mathcal{H}}\, dq_1 \dots dq_N\, dp_1 \dots dp_N$$

$$= \frac{1}{N!\,h^N} \left[\int_{-\infty}^{+\infty} e^{-\beta \frac{p_1^2}{2m}} dp_1 \int_{-\infty}^{+\infty} e^{-\beta \frac{m\omega^2 q_1^2}{2}} dq_1 \right]^N$$

Poisson-ov integral

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$Z = \frac{1}{N!\,h^N} \left[\sqrt{\frac{\pi}{\frac{\beta}{2m}}} \cdot \sqrt{\frac{\pi}{\frac{\beta m\omega^2}{2}}} \right]^N$$

$$Z = \frac{1}{N!\,h^N} \left[\sqrt{\frac{2m\pi}{\beta}} \sqrt{\frac{2\pi}{\beta m\omega^2}} \right]^N = \frac{1}{N!\,h^N} \left[\frac{2\pi}{\beta\omega} \right]^N$$

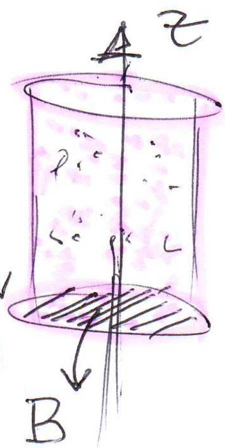
Ispitati da li je ispunjeno

$$\lim_{T \to 0+} S = 0 \ ?$$

Da li je sistem klasičnih LHO realan sistem na niskim temperaturama?

14. Idealan gas se sastoji od N jednoatomskih molekula. Gas se nalazi u beskonačno visokom cilindru (osnove B) pod uticajem homogenog gravitacionog polja. Pretpostavljajući da se gas nalazi u stanju toplotne ravnoteže izračunati statističku sumu, slobodnu energiju i specifičnu toplotu gasa. Masa svakog molekula je m.

$$\mathcal{H} = \sum_{i=1}^{N} \left(\frac{\vec{p}_i^{\,2}}{2m} + mgz_i \right)$$



$$Z = \frac{1}{N!\,h^{3N}} \left[\iint e^{-\beta\left(\frac{\vec{p}^{\,2}}{2m} + mgz\right)} d^3\vec{p}\, d^3\vec{r} \right]^N$$

$$= \frac{1}{N!\,h^{3N}} \left[\int e^{-\beta \frac{\vec{p}^{\,2}}{2m}} d^3\vec{p} \iint_B dx\,dy \int_0^{\infty} e^{-\beta m g z} dz \right]^N$$

$$= \frac{1}{N!\,h^{3N}} (2\pi m kT)^{\frac{3N}{2}} B^N \left(\frac{kT}{mg}\right)^N = \frac{1}{N!} \frac{B^N}{\lambda_T^{3N}} \left(\frac{kT}{mg}\right)^N$$

$$\lambda_T = \frac{h}{\sqrt{2\pi m kT}}$$

Poissonov integral

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

ali ne $d\vec{p}\,d\vec{r}$

$\rightarrow d\vec{r} = dx\,\vec{e}_x + dy\,\vec{e}_y + dz\,\vec{e}_z$

13. Pokazati da je srednja vrednost projekcije vektora polarizacije $\vec{P}$ idealnog gasa od N molekula, na pravac spoljnog električnog polja $\vec{E}$, određena izrazom:

$$\langle P \rangle = \frac{N}{V}\, b \left\{ \mathrm{cth}\left(\frac{bE}{kT}\right) - \frac{kT}{bE} \right\}, \quad (b = |\vec{b}|),$$

gde je $\vec{b}$ dipolni moment molekula, V je zapremina gasa.

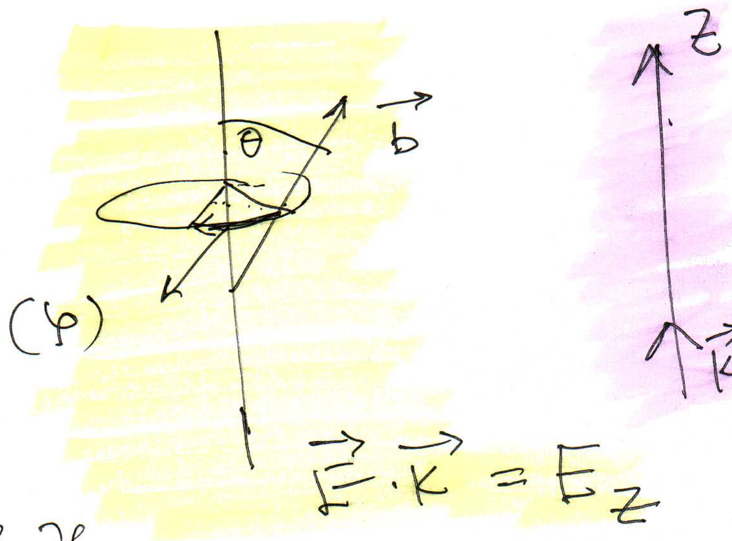
$$\mathcal{H} = -\vec{b}\cdot\vec{E} = -bE\cos\theta = -E b_z$$

$$\vec{b} = (b_x, b_y, b_z)$$

$$b_x = b\sin\theta\cos\varphi$$

$$b_y = b\sin\theta\sin\varphi$$

$$b_z = b\cos\theta$$



$$f = \frac{e^{-\beta\mathcal{H}}}{Z} = \frac{e^{-\beta\mathcal{H}}}{\int e^{-\beta\mathcal{H}}\, d\Gamma}$$

$$dw = \frac{e^{-\beta\mathcal{H}}\, d\Gamma}{\int e^{-\beta\mathcal{H}}\, d\Gamma} \Rightarrow dw' = \frac{e^{-\beta\mathcal{H}}\, d\Omega}{\int e^{-\beta\mathcal{H}}\, d\Omega}$$

$$d\Gamma = d\Gamma_T\, d\Gamma_R \qquad d\Omega = \sin\theta\, d\theta\, d\varphi$$

napomenuti da je prointegraljeno i po radiusu

$\langle \vec{b} \rangle$

$$\langle \vec{B} \rangle = \sum_{i=1}^{N} \langle \vec{b_i} \rangle = N \langle \vec{b} \rangle$$

$$\langle \vec{P} \rangle = \frac{\langle \vec{B} \rangle}{V} = \frac{N}{V} \langle \vec{b} \rangle$$

$$\langle \vec{P} \rangle = \frac{N}{V} \langle b_z \rangle \vec{K} \Big/ \vec{K}$$

$$\Downarrow$$

$$\langle P \rangle = \frac{N}{V} \langle b_z \rangle$$

Domaći:

$$\langle b_x \rangle = \int \dots \int b_x \, d\omega' = \frac{\int \dots \int b_x \, e^{+\beta E b_z} d\Omega}{\int \dots \int e^{\beta E b_z} d\Omega}$$

$$= \dots 0$$

$$\langle b_y \rangle = \int \dots \int b_y \, d\omega' = \dots = 0$$

$$\langle b_z \rangle = \int \dots \int b_z \, d\omega'$$

$$\langle b_z \rangle = \frac{\iint b\cos\theta \, e^{\beta b E \cos\theta} \sin\theta \, d\theta \, d\varphi}{\iint e^{\beta b E \cos\theta} \sin\theta \, d\theta \, d\varphi}$$

$$\langle b_z \rangle = b \frac{\int_0^{2\pi} d\varphi \int_0^{\pi} \cos\theta \, e^{\beta b E \cos\theta} \sin\theta \, d\theta}{\int_0^{2\pi} d\varphi \int_0^{\pi} e^{\beta b E \cos\theta} \sin\theta \, d\theta}$$

$$\langle b_z \rangle = \frac{b \cdot \cancel{2\pi} \int_0^{\pi} \cos\theta \, e^{\beta b E \cos\theta} \, d(\cos\theta)}{\cancel{2\pi} \int_0^{\pi} e^{\beta b E \cos\theta} \, d(\cos\theta)}$$

$$\langle b_z \rangle = b \frac{\int_0^{\pi} \cos\theta \, e^{\beta b E \cos\theta} \, d(\cos\theta)}{\int_0^{\pi} e^{\beta b E \cos\theta} \, d(\cos\theta)}$$

Smena $\cos\theta = \xi$ $\quad \theta \in [0, \pi] \to x \in [1, -1]$

$$\langle b_z \rangle = b \frac{\int_1^{-1} x \, e^{\beta b E x} \, dx}{\int_1^{-1} e^{\beta b E x} \, dx}$$

Domaći! Rešiti integrale!

Rezultat

$$\langle b_z \rangle = b \underbrace{\left(\operatorname{cth} \beta b E - \frac{1}{\beta b E} \right)}_{\text{Langevin-ova f-ja: } L(\beta b E)}$$

$$P = \frac{N}{V} \langle b_z \rangle = \frac{N}{V} b L(\beta b E)$$

8. Pokazati da je srednja vrednost projekcije vektora polarizacije $\vec{P}$ idealnog gasa od N molekula, na pravac spoljašnjeg električnog polja $\vec{E}$, određena izrazom:

$$\langle P \rangle = \frac{N}{V} b \left\{ \operatorname{cth}\left(\frac{bE}{kT}\right) - \frac{kT}{bE} \right\}, \quad (b = |\vec{b}|)$$

gde je $\vec{b}$ dipolni moment molekula, V je zapremina gasa.

Energija jednog dipola

$$\varepsilon = -\vec{b}\cdot\vec{E},$$

a srednja vrednost energije je:

$$\langle \varepsilon \rangle = \frac{\int_{-bE}^{bE} \varepsilon\, e^{-\varepsilon/kT}\, d\varepsilon}{\int_{-bE}^{bE} e^{-\varepsilon/kT}\, d\varepsilon}.$$

Kako je

$$\varepsilon = -bE\cos\theta \Rightarrow d\varepsilon = bE\sin\theta\, d\theta$$

granice u integralu se menjaju sa $\int_{-bE}^{bE}$ na $\int_{0}^{\pi}$

pa će biti

$$\langle \varepsilon \rangle = \frac{-b^2E^2 \int_0^\pi e^{bE\cos\theta/kT} \cos\theta \sin\theta\, d\theta}{bE \int_0^\pi e^{bE\cos\theta/kT} \sin\theta\, d\theta}$$

Nakon integracije

$$\langle \varepsilon \rangle = - \frac{\left(1+e^{2bE/kT}\right) bE + \left(1-e^{2bE/kT}\right) kT}{e^{2bE/kT} - 1}$$

Pomnoživši brojilac i imenilac sa $e^{-bE/kT}$ sledi

$$\langle \varepsilon \rangle = kT - bE \, \mathrm{cth}\left(\frac{bE}{kT}\right)$$

Polarizacija je data izrazom

$$\vec{P} = \frac{N}{V} \langle \vec{b} \rangle$$

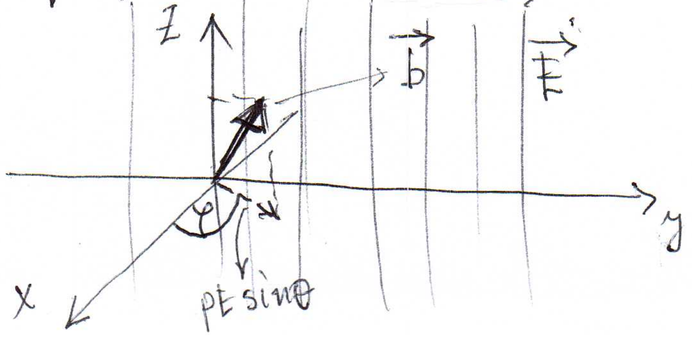
Sa druge strane, $\langle \varepsilon \rangle = - \langle \vec{b} \cdot \vec{E} \rangle$ pa će biti:

$$\frac{N}{V} \langle \varepsilon \rangle = - \frac{N}{V} \langle \vec{b} \cdot \vec{E} \rangle$$

$$= - \langle \vec{P} \cdot \vec{E} \rangle$$

$$= - \underbrace{\langle P E \rangle}_{*} = - \langle P \rangle E \, .$$

Red označen zvezdicom se može dedukovati na osnovi slike, ako se uzme da je homogeno električno polje duž z-ose:



Kao što se sa slike vidi, projekcija na xy ravan je $pE\sin\theta$ i zaklapa ugao φ sa x osom. Kako φ ne utiče na energiju, sve vrednosti ugla φ su podjednako verovatne za svaku posebnu vrednost θ. Dakle, srednja vrednost normalne componente je nula i sledi da je $\langle \vec{p} \rangle$ (antiparalelno) paralelno sa $\vec{E}$.

Iz poslednjeg izraza i izraza za $\langle \varepsilon \rangle$ sledi:

$$\langle p \rangle = -\frac{N}{VE} \langle \varepsilon \rangle$$

$$= \frac{Np}{V} \operatorname{cth}\left(\frac{pE}{kT}\right) - \frac{NkT}{VE}$$

$$\boxed{\langle p \rangle = \frac{Np}{V}\left[\operatorname{cth}\left(\frac{pE}{kT}\right) - \frac{kT}{pE}\right]}$$

9. Posmatrati gas (~~klasični~~, idealni) koji se sastoji od N idealnih čestica. Energija jedne čestice je data kao $\varepsilon = cp$. Naći F, S i $\langle \mathcal{H} \rangle$ za ovaj gas!

$$Z = \frac{(Z_1)^N}{N!} \quad \text{– NElokalizovan sistem}$$

$$Z_1 = \frac{V}{h^3} \int \cdots \int e^{-\beta \mathcal{H}} d\vec{p}$$

$$Z_1 = \frac{V}{h^3} 4\pi \int_0^{+\infty} e^{-\beta p c} p^2 dp$$

$$Z_1 = \frac{V}{h^3} 4\pi \frac{1}{(\beta c)^3} \int_0^{\infty} e^{-\beta c p} (\beta c p)^2 d(\beta c p)$$

$$\beta c p = \xi$$

$$Z_1 = \frac{V}{h^3} \frac{4\pi}{(\beta c)^3} \int_0^{\infty} e^{-x} x^2 dx$$

$$= \frac{V}{h^3} \frac{4\pi}{(\beta c)^3} \Gamma(3) = \frac{8\pi V}{h^3} \frac{1}{(\beta c)^3}$$

$$Z = \frac{1}{N!\, h^{3N}} \left[\frac{8\pi V}{(\beta c)^3} \right]^N$$

$$\langle \mathcal{H} \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$\ln Z = N \ln \frac{8\pi V}{(\beta c)^3} - \ln N! \, h^{3N}$$

$$\frac{\partial \ln Z}{\partial \beta} = N \frac{1}{\frac{\cancel{8\pi V}}{(\beta c)^3}} \frac{\cancel{8\pi V}}{\cancel{c^3}} \left(-\frac{3}{\beta^4}\right)$$

$$= \frac{-3N\beta^3}{\beta^4} = -\frac{3N}{\beta}$$

$\langle \mathcal{H} \rangle = 3NkT$ (kalorička j-na stanja)

Domaći

$F = -kT \ln Z = \ldots$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{1}{kT^2}\left(\frac{\partial F}{\partial \beta}\right)_V$$

Kako glasi termička j-na stanja?

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \rightarrow [pV = NkT]$$

Uporediti sa zadatkom iz MKA!

10. Dokazati važenje Daltonovog zakona, za smešu od n idealnih gasova

$$p = \sum_{i=1}^{n} p_i$$

(ОВО ЈЕ ЗА канонски ансамбл

$$\mathcal{H}(q,p) = \sum_{i=1}^{n} \mathcal{H}_i(\vec{q},\vec{p})$$

$$d\Gamma = \prod_{i=1}^{N} d\Gamma_i$$

$$Z = \int e^{-\beta \mathcal{H}(\vec{p},\vec{q})} d\Gamma$$

$$= \int e^{-\beta \sum_{i=1}^{n} \mathcal{H}_i(\vec{p},\vec{q})} \prod_{i=1}^{n} d\Gamma_i =$$

$$= \prod_{i=1}^{n} Z_i$$

ostatak za domaći

$$F = -kT \ln Z$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$