Sistemi sa diskretnim energijama

MKA
KA
VKA

} i klasični i kvantni sistemi

MKA

$$S(E) = k \ln \Omega^*(E) \simeq k \ln \Gamma^*(E)$$

↳ normalni sistemi u statističko-TD smislu

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \qquad \frac{p}{T} = \left(\frac{\partial S(E)}{\partial V}\right)_{E,N}$$

KA

$$w_n = \frac{e^{-\beta E_n}}{Z}, \qquad Z = \sum_n e^{-\beta E_n}$$

$$Z = \sum_{\{E_n\}} g(E_n)\, e^{-\beta E_n}$$

$$F = -kT \ln Z$$

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

↳ kalorička j-na stanja

↳ termička j-na stanja

$U = F + TS$

ОЧЕКИВАНА ВРЕДНОСТ

$$\langle B \rangle = \sum_n B_n w_n \qquad \left(w_n = \frac{e^{-\beta E_n}}{Z} \right)$$

VKA

$$w_n = \frac{e^{-\beta (E_{N,n} - \mu N)}}{\Xi}$$

$$\Xi = \sum_{N=0}^{\infty} \lambda^N Z_N \quad , \quad Z_N = \sum_n e^{-\beta E_{n,N}}$$

$$Z_N = \sum_{\{E_n\}} g(E_n)\, e^{-\beta E_{n,N}}$$

$$\Omega = -kT \ln \Xi$$

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} , \quad p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} , \quad \langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$$

+ sistem nezavisnih kvantnih čestica

8. Razmatrati sistem od N kvantnih harmonijskih oscilatora. Pretpostavljajući da oscilatori zanemarljivo slabo interaguju i da su identični, odrediti Z, F, S i $\langle \mathcal{H} \rangle$

Moguće vrednosti energije kvantnomehaničkog oscilatora

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad ; \; n = 0, 1, 2, \dots$$

Oscilatori međusobno NE interaguju

lokalizovan

$$\boxed{Z_N = Z_1^N} = \left(\sum_{n=0}^{\infty} e^{-\beta \varepsilon_n}\right)^N$$

sumiranje po stanjima

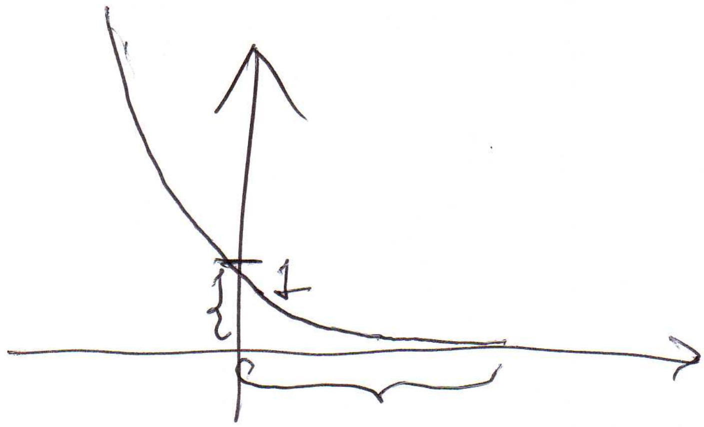
$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta \varepsilon_n} = \sum_{n=0}^{\infty} e^{-\beta \left(n+\frac{1}{2}\right)\hbar\omega}$$

$$= e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n \hbar\omega}$$

$$= e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n$$

$\beta\hbar\omega > 0$ $\quad kT, \omega$

$$\beta\hbar\omega = \frac{\hbar\omega}{kT} > 0 \quad \Rightarrow \quad e^{-\beta\hbar\omega} < 1$$



$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \qquad |x| < 1$$

$$Z_1 = e^{-\frac{\beta\hbar\omega}{2}} \cdot \frac{1}{1-e^{-\beta\hbar\omega}} \; ;$$

$$= \frac{e^{\frac{\beta\hbar\omega}{2}}}{e^{\beta\hbar\omega}-1} = \frac{1}{2\,\mathrm{sh}\left(\frac{\beta\hbar\omega}{2}\right)}$$

$$Z_N = \left[2\,\mathrm{sh}\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-N}$$

$$\left.\begin{array}{l} F \\ S \end{array}\right\} \text{Domadi}$$

$$\langle \mathcal{H} \rangle = -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta}$$

Domaci

tj. $\langle \mathcal{H} \rangle = -\frac{\partial \ln Z_N}{\partial \beta}$

V

Uporediti sa klasičnom slučajem (zadatak br. 6 i sa rezultatom u odeljku "Mikrokanonski ansambl".

Da li je ovo realan sistem na niskim temperaturama?

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

Srednja energija jednog oscilatora

$$\langle \varepsilon \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}$$

Dakle, $\langle \mathcal{H} \rangle = N \langle \varepsilon \rangle$

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2. Izingov model. Statistički sistem je opisan pomoću Hamiltonijana → Detaljnije u ZZ

$$\mathcal{H} = -\sum_{i=1}^{N-1} J_i S_i S_{i+1} \qquad (*)$$

gde su J_i konstante, a veličine S_i mogu imati samo dve vrednosti: $+1$ i -1. Odrediti statističku sumu, slobodnu energiju i entropiju sistema određenog hamiltonijanom (*) u slučaju kada indeks i numeriše čvorove neke 1D kristalne rešetke

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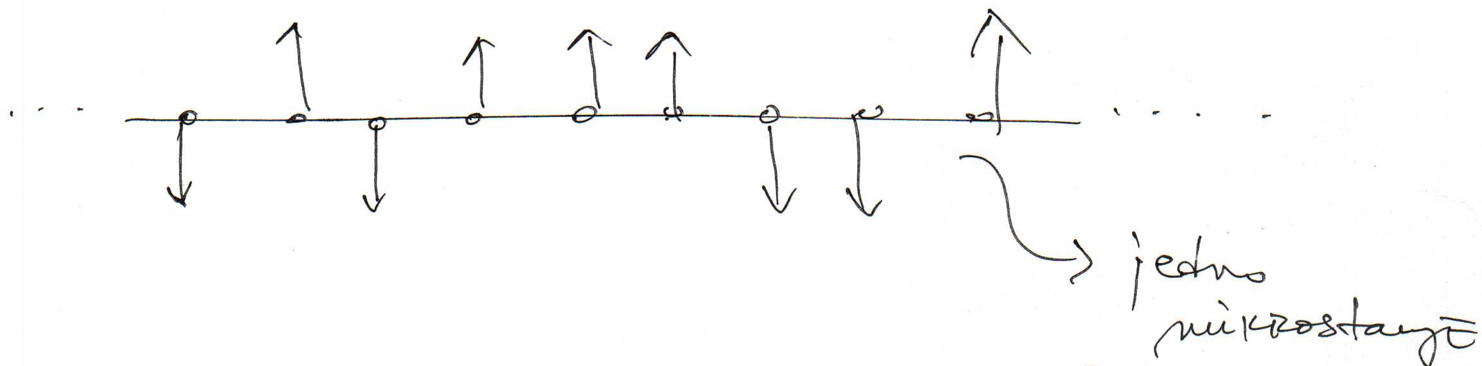
Lokalizovan sistem čestica



$$Z_N = \sum_{S_1=-1}^{1} \sum_{S_2=-1}^{1} \cdots \sum_{S_N=-1}^{1} e^{\beta \sum_{i=1}^{N-1} J_i S_i S_{i+1}}$$

Za jednu česticu $Z_1 = 2$

Nalaženje statističke sume pomoću rekurzije jer pošto su u pitanju interagujuće čestice neće moći preko obrasca $Z_N = Z_1^N$

$$Z_{N+1} = \sum_{S_1=-1}^{1} \sum_{S_2=-1}^{1} \cdots \sum_{S_{N+1}=-1}^{1} e^{\beta \sum_{i=1}^{N} J_i S_i S_{i+1}}$$

$$= \sum_{S_1=-1}^{1} \sum_{S_2=-1}^{1} \cdots \sum_{S_{N+1}=-1}^{1} e^{\beta \sum_{i=1}^{N-1} J_i S_i S_{i+1} + \beta J_N S_N S_{N+1}}$$

$$= Z_N \sum_{S_{N+1}=-1}^{1} e^{\beta J_N S_N S_{N+1}}$$

$$= Z_N \left(e^{-\beta J_N S_N} + e^{\beta J_N S_N} \right)$$

$$= Z_N \cdot 2 \operatorname{ch}(\beta J_N)$$

Dalle

$$Z_{N+1} = Z_N \cdot 2 \operatorname{ch}(\beta J_N)$$

$$Z_N = Z_{N-1} \, 2 \operatorname{ch}(\beta J_{N-1})$$

$$Z_{N-1} = Z_{N-2} \, 2 \operatorname{ch}(\beta J_{N-2})$$

$$\vdots$$

$$\frac{Z_{N+1}}{Z_N} = 2 \operatorname{ch}(\beta J_N)$$

$$\frac{Z_N}{Z_{N-1}} = 2 \operatorname{ch}(\beta J_{N-1})$$

$$\frac{Z_{N-1}}{Z_{N-2}} = 2\,\mathrm{ch}(\beta J_{N-2})$$

$$\vdots$$

$$\Downarrow$$

$$\prod_{i=1}^{N} \frac{Z_{i+1}}{Z_i} = 2^N \prod_{i=1}^{N} \mathrm{ch}(\beta J_i)$$

$$\frac{Z_{N+1}}{Z_1} = 2^N \prod_{i=1}^{N} \mathrm{ch}(\beta J_i)$$

$$Z_{N+1} = 2^{N+1} \prod_{i=1}^{N} \mathrm{ch}(\beta J_i)$$

$$\Downarrow$$

$$\boxed{Z_N = 2^N \prod_{i=1}^{N-1} \mathrm{ch}(\beta J_i)}$$

Za Domaći

$F = ?$

$S = -\frac{\partial F}{\partial T} = ?$

$\lim_{T \to 0+} S = ? \longrightarrow$ (Da li je ovaj model 1D kristalne resetke realan na niskim temperaturama)

3. Nivoi energije oscilatora frekvencije ν su oblika

$$E_n = \left(n+\frac{1}{2}\right)h\nu \qquad (n=0,1,2,\dots)$$

Za sistem koji se sastoji od N oscilatora zanemarljive međusobne interakcije naći entropiju sistema, kao i vezu između temperature sistema T i energije E. Sistem tretirati kvantno.

Totalna energija

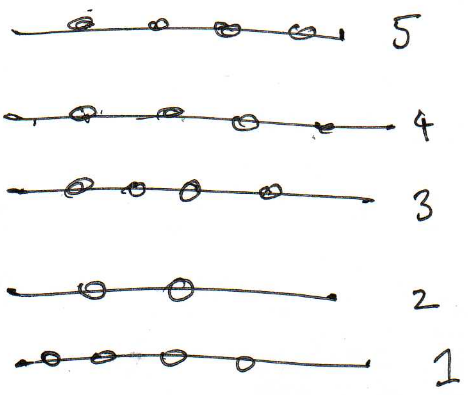
$$E = \sum_{i=1}^{N} E_{n_i} = \sum_{i=1}^{N} \left(n_i + \frac{1}{2}\right)h\nu$$

$$= \sum_{i=1}^{N} n_i h\nu + \frac{1}{2} N h\nu$$

$$= M h\nu + \frac{1}{2} N h\nu$$

M predstavlja broj kvanata $h\nu$ koje sistem "poseduje". Očigledno, $M \geq N$. Primer:

Šta bi značilo $M=N$?



$\rightarrow$ $N = 18$

$M = 1\cdot 4 + 2\cdot 2 + 3\cdot 4 + 4\cdot 4 + 5\cdot 4 = 56$

$n = \overline{1,5}$

[redacted]

Kako se može raspodeliti ovih M kvanata $h\nu$ na N oscilatora? Oscilatori su nerazličivi (sistem tretiramo kvantno), pa poredak nije važan ⇒ kombinacije sa ponavljanjem

$$\Gamma^*(E) = \binom{N+M-1}{M}$$

$$\Gamma^*(E) = \frac{(N+M-1)!}{M!\,(N-1)!}$$

$$S = k \ln \Gamma^*(E)$$

⋮

Za pomoći : $M, N \gg 1$, Stirlingova aproksimacija

$$S = k\{(N+M)\ln(N+M) - M\ln M - N\ln N\}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

$$\frac{1}{T} = \frac{\partial S}{\partial M}\frac{\partial M}{\partial E} = \frac{1}{h\nu}\frac{\partial S}{\partial M}$$

⋮

$$\frac{1}{T} = \frac{k}{h\nu}\ln\frac{N+M}{M}$$

$$E = \frac{1}{2}Nh\nu + Mh\nu$$

$$\Downarrow$$

$$M = \frac{E - \frac{1}{2}Nh\nu}{h\nu} = \frac{E}{h\nu} - \frac{1}{2}N$$

$$\frac{1}{T} = \frac{k}{h\nu}\ln\left(\frac{N}{M} + 1\right)$$

$$= \frac{k}{h\nu}\ln\left(\frac{N}{\frac{E}{h\nu} - \frac{1}{2}N} + 1\right)$$

$$\vdots$$

$$E = \frac{Nh\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{1}{2}Nh\nu$$

$$\Downarrow \Rightarrow \boxed{M = \frac{N}{e^{\frac{h\nu}{kT}} - 1}}$$

Na visokim temperaturama

$$\frac{h\nu}{kT} \ll 1 \qquad h\nu \ll kT$$

$$e^{\frac{h\nu}{kT}} \approx 1 + \frac{h\nu}{kT}$$

$$\vdots$$

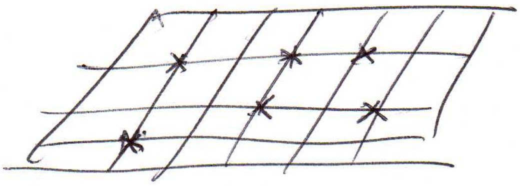
kvantno-mehanički član

$$E \approx NkT + \frac{1}{2}Nh\nu$$ (uporediti sa klasičnim slučajem)

4 Na površini, na kojoj se nalazi N_0 centara adsorpcije, adsorbovano je N molekul gasa ($N \leq N_0$). Pokazati da je hemijski potencijal molekula (množina) μ dat izrazom

$$\mu = kT\left\{\ln\frac{\langle N\rangle}{N_0-\langle N\rangle} - \ln a(T)\right\},$$

gde je $a(T)$ statistička suma jednog adsorbovanog molekula. Pretpostaviti da svaki adsorbovani molekul ima istu energiju ε i da je interakcija adsorbovanih molekula zanemarljiva



N $\downarrow$ broj adsorbovanih

$N_0 - N$ $\downarrow$ broj slobodnih mesta

$$Z_N = \frac{N_0!}{N!(N_0-N)!}\sum_{\{E_n\}} e^{-\beta E_{Nn}}$$

fizička situacija je takva da N adsorbovanih molekula ima jednu energiju sa $\frac{N_0!}{N!(N_0-N)!}$ mikrostanja, pa nema potrebe ni pisati sumu.

$$E_N = \varepsilon_1 + \varepsilon_2 + \dots \varepsilon_N \approx N\varepsilon$$

Dodatna aproksimacija

$$Z_N = \frac{N_0!}{N!(N_0-N)!}\, e^{-\beta N\varepsilon}$$

$$Z_N = \frac{N_0!}{N!\,(N_0-N)!}\left(e^{-\beta\epsilon}\right)^N$$

$$a(T) = e^{-\beta\epsilon}$$ — statistička suma jednog adsorbovanog molekula

$$Z_N = \frac{N_0!}{N!\,(N_0-N)!}\,a^N$$

$$\Xi = \sum_{N=0}^{N_0} \lambda^N Z_N = \sum_{N=0}^{N_0} \frac{N_0!}{N!\,(N_0-N)!}(a\lambda)^N$$

$$= (1+a\lambda)^{N_0}$$

$$\Omega = -kT\ln \Xi$$

$$\Omega = -kTN_0\ln(1+a\lambda)$$

$$\langle N\rangle = -\frac{\partial\Omega}{\partial\mu} = -\frac{\partial\Omega}{\partial\lambda}\frac{\partial\lambda}{\partial\mu} = -\beta\lambda\frac{\partial\Omega}{\partial\lambda}$$

$$\langle N\rangle = \cancel{-\beta}\lambda\,(-\cancel{kT}N_0)\,\frac{1}{1+a\lambda}\cdot a$$

$$= \frac{N_0\lambda a}{1+\lambda a}$$

$$\langle N \rangle = \frac{N_0 \lambda a}{1+\lambda a}$$

$$\frac{\langle N \rangle}{N_0} = \frac{\lambda a + 1 - 1}{1+\lambda a} = 1 - \frac{1}{1+\lambda a}$$

$$\frac{1}{1+\lambda a} = 1 - \frac{\langle N \rangle}{N_0}$$

$$1+\lambda a = \frac{N_0}{N_0 - \langle N \rangle}$$

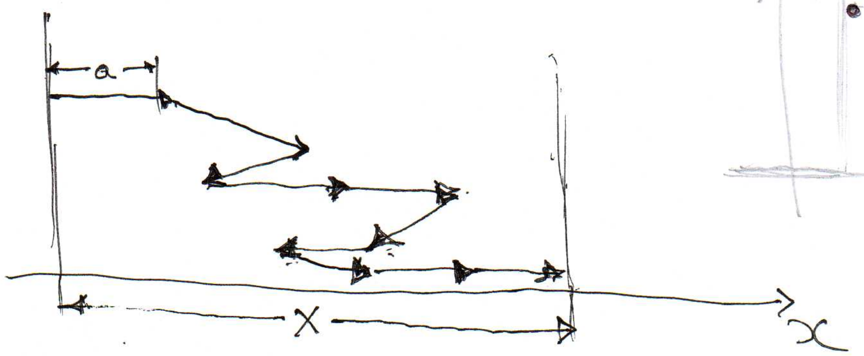
$$\lambda a = \frac{N_0}{N_0 - \langle N \rangle} - 1$$

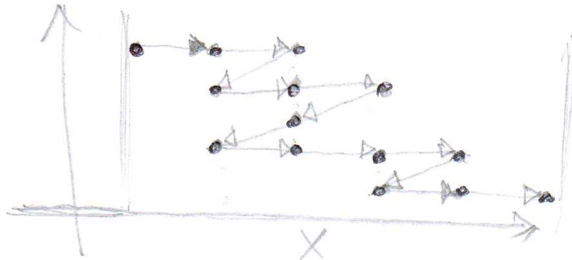
$$\lambda = \frac{1}{a} \frac{\langle N \rangle}{N_0 - \langle N \rangle} \Rightarrow e^{\beta\mu} = \frac{1}{a} \frac{\langle N \rangle}{N_0 - \langle N \rangle}$$

$$\Rightarrow \beta\mu = \ln \frac{\langle N \rangle}{N_0 - \langle N \rangle} - \ln a$$

$$\mu = kT \left\{ \ln \frac{\langle N \rangle}{N_0 - \langle N \rangle} - \ln a \right\}$$

5 Jednodimenzioni lanac se sastoji iz velikog broja ($N \gg 1$) elemenata. Dužina svakog elementa je a. Rastojanje između krajeva lanca je x. Elementi mogu slobodno da se okreću oko spojnih tačaka.





a) Naći entropiju ovog lanca u f-ji x

b) Naći vezu između temperature T i generalisane sile (napona) koja je potrebna da bi se krajevi lanca zadržali na rastojanju x.

Prvo tražimo broj mikrostanja za ovaj fizični sistem

Broj elemenata u pravcu x ose obeležimo sa n_+, a broj elemenata u suprotnom pravcu sa n_-

U pitanju su permutacije sa ponavljanjem, jer učestvuju svi elementi (nema klase!)

$$\Gamma^*(E) = \frac{N!}{n_+!\, n_-!} = \frac{N!}{n_+!\,(N-n_+)!}$$

$$n_+ + n_- = N \qquad (n_+ - n_-)a = x$$

$$\Downarrow$$

$$n_+ = \frac{1}{2}\left(N + \frac{x}{a}\right) \qquad n_- = \frac{1}{2}\left(N - \frac{x}{a}\right)$$

$$\Gamma^*(E) = \frac{N!}{\left[\frac{1}{2}\left(N+\frac{x}{a}\right)\right]!\left[\frac{1}{2}\left(N-\frac{x}{a}\right)\right]!}$$

$$S = k \ln \Gamma^*(E)$$

+ Stirlingova f-la

$$\ln N! \approx N \ln N - N$$

$\vdots \longleftarrow$ Domaći

$$S = Nk\left\{\ln 2 - \frac{1}{2}\left(1+\frac{x}{Na}\right)\ln\left(1+\frac{x}{Na}\right) - \frac{1}{2}\left(1-\frac{x}{Na}\right)\ln\left(1-\frac{x}{Na}\right)\right\}$$

Primetiti iz izraza za entropiju
da je $S = S(N, X) = S(E, X)$

X – spoljašnji parametar koji se menja
sporo $\frac{dx}{dt} \to 0$

$$\mathcal{H}(\vec{q}_i, \vec{p}_i, x) \longrightarrow \mathcal{H}(\vec{q}_i, \vec{p}_i, x + dx)$$

$\downarrow$

kvazistatički adijabatski proces

$\downarrow$ $\frac{dx}{dt} \to 0$

$\downarrow$ Mikrokanonski ansambl, $\delta Q = 0$

U opštem slučaju

$$\delta W = \langle X \rangle dx$$

$\downarrow$ generalisana sila

Adijabatski proces

$$dE = -\langle X \rangle dx$$

$$dS = \left(\frac{\partial S}{\partial E}\right)_X dE + \left(\frac{\partial S}{\partial x}\right)_E dx$$

$\frac{dx}{dt} \to 0$ $\quad \frac{dS}{dx} \to 0$

$$\frac{dS}{dx} = \left(\frac{\partial S}{\partial E}\right)_x \frac{dE}{dx} + \left(\frac{\partial S}{\partial x}\right)_E$$

$$0 = \left(\frac{\partial S}{\partial E}\right)_x \frac{dE}{dx} + \left(\frac{\partial S}{\partial x}\right)_E$$

$$\frac{dE}{dx} = -\frac{\left(\frac{\partial S}{\partial x}\right)_E}{\left(\frac{\partial S}{\partial E}\right)_x} = -T\left(\frac{\partial S}{\partial x}\right)_E$$

$$-\langle X\rangle = -T\left(\frac{\partial S}{\partial x}\right)_E$$

$$\langle X\rangle = T\left(\frac{\partial S}{\partial x}\right)_E \qquad \left(\text{Primer } P = T\left(\frac{\partial S}{\partial V}\right)_{E,N}\right)$$

Generalisana sila napona

Da bi zadržali dopustivu dužinu lanca na x, treba primeniti silu napona jednaku

$$-T\,\frac{\partial S(x,N)}{\partial x} = \ldots = \frac{kT}{2a}\ln\frac{1+\frac{x}{Na}}{1-\frac{x}{Na}}$$

Domaći: Reprodukovati iz poslednjeg izraza klasični Hooke-ov zakon $(\vec{F} = -k\vec{x})$

Sistem se sastoji od N nezavisnih čestica. Svaka čestica može da se nalazi samo na jednom od dva energetska nivoa $-\varepsilon_0, \varepsilon_0$.

a) ~~Naći entropiju S i temperaturu T sistema u f-ji energije E.~~ proveriti formulaciju

b) Ispitati u kojoj je oblasti energije sistem normalan u statistično-termodinamičkom smislu i u toj oblasti naći vezu između E i T, kao i toplotni kapacitet C.

N_+ ———— ε_0

N_- ———— $-\varepsilon_0$

$$E = N_+\varepsilon_0 - N_-\varepsilon_0$$
$$= (N_+ - N_-)\varepsilon_0$$
$$= n\varepsilon_0$$

$$\underbrace{N_+ + N_- = N \qquad N_+ - N_- = n}$$

$$\downarrow$$

$$N_+ = \frac{n+N}{2}, \quad N_- = \frac{N-n}{2}$$

$$\Gamma^*(E) = \frac{N!}{N_+!\,N_-!} \qquad \longrightarrow$$

$$\Gamma^*(E) = \frac{N!}{\left(\frac{n+N}{2}\right)!\left(\frac{N-n}{2}\right)!}$$

$$S = k \ln \Gamma^*(E)$$

$$\vdots \longrightarrow \text{Domaći}$$

$$S = k\left\{N\ln N - 2N - \frac{n+N}{2}\ln\left(\frac{n+N}{2}\right) - \left(\frac{N-n}{2}\right)\ln\left(\frac{N-n}{2}\right)\right\}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

$$\frac{1}{T} = \frac{\partial S}{\partial n}\frac{\partial n}{\partial E} \quad ; \quad \frac{\partial E}{\partial n} = \varepsilon_0 \Rightarrow \frac{\partial n}{\partial E} = \frac{1}{\varepsilon_0}$$

$$\vdots \longrightarrow \text{Domaći}$$

$$\boxed{\frac{1}{T} = \frac{1}{2\varepsilon_0} k \ln\frac{N-n}{N+n}}$$

U teoriji se pokazuje da su normalni sistemi oni za koje je ispunjeno $T>0$

Ovde će to biti ispunjeno ako je $n<0 \Rightarrow E<0$ tj $N_- > N_+$

$$\frac{2\varepsilon_0}{kT} = \ln\frac{N-n}{N+n}$$

$$e^{\frac{2\varepsilon_0}{kT}} = \frac{N-n}{N+n}$$

$$\vdots \longrightarrow \text{Domaći}$$

$$n = N\,\frac{1-e^{\frac{2\varepsilon_0}{kT}}}{1+e^{\frac{2\varepsilon_0}{kT}}}$$

$$E = N\varepsilon_0 \, \frac{1 - e^{\frac{2\varepsilon_0}{kT}}}{1 + e^{\frac{2\varepsilon_0}{kT}}}$$

Domaći: Naći c_V

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V$$

7. Sistem od N čestica nalazi se u magnetnom polju $\vec{H}$. Ako je magnetni moment svake čestice $\vec{\mu}$ takav da se može orijentisati samo u dva pravca (paralelno i antiparalelno polju $\vec{H}$), onda su odgovarajući energijski nivoi svake čestice $-\mu H$ i $+\mu H$.
Pretpostavljajući da se sistem magnetnih momenata nalazi u toplotnoj ravnoteži sa okolinom, kao i da magnetni momenti međusobno ne interaguju, naći srednju vrednost ukupnog magnetnog momenta, njegovu disperziju, statističku sumu sistema i kaloričku f-ju sistema.

Verovatnoća nalaženja u stanju kome odgovara energija E_n

$$w_n = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

Magnetni momenti imaju zanemarljivu kinetičku energiju, pa sistem možemo smatrati približno lokalizovanom

$$Z = Z_1^N$$

$$Z_1 = e^{-\beta E_1} + e^{-\beta E_2} \, ; \quad \boxed{\begin{aligned} E_1 &= -\mu H \\ E_2 &= \mu H \end{aligned}}$$

$$Z_1 = e^{\beta \mu H} + e^{-\beta \mu H}$$

$$Z_1 = 2\,\mathrm{ch}(\beta\mu H)$$

$$\boxed{Z = Z_1^N = 2^N \mathrm{ch}^N(\beta\mu H)}$$

$$F = -kT \ln Z = \ldots = -NkT \ln(2\,\mathrm{ch}(\beta\mu H))$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \ldots = -Nk\{\ln(2\,\mathrm{ch}(\beta\mu H)) - \beta\mu H\,\mathrm{th}(\beta\mu H)\}$$

Magnetni moment sistema

$$\vec{M} = \sum_{i=1}^{N} \vec{\mu_i}$$

$$\langle\vec{M}\rangle = \frac{1}{Z}\sum_s \vec{M_s}\, e^{-\beta E_s}$$

$$E_s = -\vec{M_s}\cdot\vec{H}$$

$$Z = \sum_s e^{+\beta \vec{M_s}\cdot\vec{H}}$$

$$\frac{\partial Z}{\partial \vec{H}} = \sum_s \beta\vec{M_s}\, e^{\beta\vec{M_s}\cdot\vec{H}}$$

$$= \beta Z\langle\vec{M}\rangle \Rightarrow \qquad \langle\vec{M}\rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \vec{H}}$$

$$\langle\vec{M}\rangle = \frac{1}{\beta} N \frac{\mathrm{sh}(\beta\mu H)}{\mathrm{ch}(\beta\mu H)}\beta\mu$$

$$\langle \vec{M} \rangle = N\mu \, th(\beta \mu H)$$

$\to$ Termička jednačina stanja (nelinearna)

$$\frac{\partial \langle \vec{M} \rangle}{\partial \vec{H}} = \frac{\beta Z \sum_s \vec{M}_s^{\,2} e^{\beta \vec{M}_s \cdot \vec{H}} - \beta \sum_s \vec{M}_s e^{\beta \vec{M}_s \cdot \vec{H}} \sum_s \vec{M}_s e^{-\beta \vec{M}_s \cdot \vec{H}}}{Z^2}$$

$$= \frac{\beta Z^2 \langle \vec{M}^2 \rangle - \beta Z^2 \langle \vec{M} \rangle^2}{Z^2}$$

$$\frac{\partial \langle \vec{M} \rangle}{\partial \vec{H}} = \beta D(\vec{M}) = \chi_M$$

$\to$ Magnetska susceptibilnost

$$D(\vec{M}) = \frac{1}{\beta} \frac{\partial \langle \vec{M} \rangle}{\partial \vec{H}} = \frac{N\mu}{\beta} \left[th \beta \mu H \right]'_H$$

$$= \frac{N\mu}{\beta} \frac{1}{ch^2(\beta \mu H)} \beta \mu$$

$$D(\vec{M}) = N\mu^2 \frac{1}{ch^2(\beta \mu H)}$$

Kalorička j-na stanja

$$U = F + TS = \dots = -\langle \vec{M} \rangle \cdot \vec{H}$$

Za alternativno rešavanje, videti zbirku Kubo et al, str. 93,

8 Sistem ima nedegenerisani spektar vrednosti energija $\epsilon_k = k\epsilon$ $(k=0,1,2,\ldots)$. Odrediti srednju energiju sistema. Raditi u formalizmu kanonskog ansambla.

$$\langle E\rangle = \frac{\sum_k \epsilon_k e^{-\beta\epsilon_k}}{\sum_k e^{-\beta\epsilon_k}}$$

$$Z = \sum_k e^{-\beta\epsilon_k}$$

$$\frac{\partial Z}{\partial\beta} = -\sum_k \epsilon_k e^{-\beta\epsilon_k}$$

$$\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{1}{Z}\sum_k \epsilon_k e^{-\beta\epsilon_k}$$

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

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

Zadato je $\epsilon_k = k\epsilon$

$$Z = \sum_{k=0}^{\infty} e^{-\beta k\epsilon} = \sum_{k=0}^{\infty}\left(e^{-\beta\epsilon}\right)^k = \frac{1}{1-e^{-\beta\epsilon}}$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln\frac{1}{1-e^{-\beta\epsilon}} = \frac{\partial}{\partial\beta}\ln\left(1-e^{-\beta\epsilon}\right)$$

$$= \frac{1}{1-e^{-\beta\epsilon}} \cdot \epsilon e^{-\beta\epsilon} = \frac{\epsilon}{e^{\beta\epsilon}-1}$$

Domaći 1: Naći C_V za ovaj fizički sistem

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2} \frac{\partial \langle E \rangle}{\partial \beta}$$

$$= -k\beta^2 \frac{\partial \langle E \rangle}{\partial \beta} = -k\beta^2 \epsilon \frac{(-1)\epsilon}{(e^{\beta\epsilon}-1)^2}$$

$$= k\beta^2 \frac{\epsilon^2}{(e^{\beta\epsilon}-1)^2}$$

Domaći 2: Naći izraz za entropiju ovog fizičkog sistema.

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

$$S = k\beta^2 \frac{\partial F}{\partial \beta}$$

$$F = -\frac{1}{\beta} \ln Z$$

$$\frac{\partial F}{\partial \beta} = -\frac{\beta \frac{\partial \ln Z}{\partial \beta} - \ln Z}{\beta^2} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \beta} + \frac{\ln Z}{\beta^2} =$$

$$= \frac{\langle E \rangle}{\beta} + \frac{\ln Z}{\beta^2}$$

$$\frac{\partial F}{\partial \beta} = \frac{\epsilon}{\beta}\frac{1}{e^{\beta\epsilon}-1} + \frac{1}{\beta^2}\ln\left(\frac{1}{1-e^{-\beta\epsilon}}\right)$$

$$= \frac{\epsilon}{\beta}\frac{1}{e^{\beta\epsilon}-1} - \frac{1}{\beta^2}\ln\left(1-e^{-\beta\epsilon}\right)$$

$$S = \frac{k\beta\epsilon}{e^{\beta\epsilon}-1} - k\ln\left(1-e^{-\beta\epsilon}\right)$$

(4) Za kolokvijum

$$\epsilon_K = K\epsilon^2$$

$$Z = g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2}$$

$$\langle E \rangle = \frac{g_1 E_1 e^{-\beta E_1} + g_2 E_2 e^{-\beta E_2}}{Z}$$

$$\langle E^2 \rangle = \frac{g_1 E_1^2 e^{-\beta E_1} + g_2 E_2^2 e^{-\beta E_2}}{Z}$$

9

Domaći

Naći fluktuaciju energije za sistem ~~sa~~ koji ima samo dva energijska nivoa E_1 i E_2 ($E_1 - E_2 = a$), a čije su degeneracije g_1 i g_2, respektivno

$$\left.\begin{aligned} E_1 + E_2 &= a \\ E_1 - E_2 &= b \end{aligned}\right\} \qquad E_1 = \frac{a+b}{2} \qquad E_2 = \frac{a-b}{2}$$

$$D(E) = \langle E^2 \rangle - \langle E \rangle^2 = \frac{g_1 E_1^2 e^{-\beta E_1} + g_2 E_2^2 e^{-\beta E_2}}{Z} - \frac{g_1^2 E_1^2 e^{-2\beta E_1} + 2 g_1 g_2 E_1 E_2 e^{-\beta(E_1+E_2)} + g_2^2 E_2^2 e^{-2\beta E_2}}{Z^2}$$

$$D(E) = \frac{\left(g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2}\right)\left(g_1 E_1^2 e^{-\beta E_1} + g_2 E_2^2 e^{-\beta E_2}\right) - g_1^2 E_1^2 e^{-2\beta E_1} - 2 g_1 g_2 E_1 E_2 e^{-\beta(E_1+E_2)} - g_2^2 E_2^2 e^{-2\beta E_2}}{Z^2}$$

$$D(E) = \frac{\cancel{g_1^2 E_1^2 e^{-2\beta E_1}} + g_1 g_2 E_2^2 e^{-\beta(E_1+E_2)} + g_1 g_2 E_1^2 e^{-\beta(E_1+E_2)} + \cancel{g_2^2 E_2^2 e^{-2\beta E_2}} - \cancel{g_1^2 E_1^2 e^{-2\beta E_1}} - 2 g_1 g_2 E_1 E_2 e^{-\beta(E_1+E_2)} - \cancel{g_2^2 E_2^2 e^{-2\beta E_2}}}{Z^2}$$

$$\frac{g_1 g_2 e^{-\beta(E_1+E_2)}\left(E_2^2 + E_1^2 - 2E_1E_2\right)}{g_1^2 e^{-2\beta E_1} + 2 g_1 g_2 e^{-\beta(E_1+E_2)} + g_2^2 e^{-2\beta E_2}} = \frac{g_1 g_2 (E_1 - E_2)^2 e^{-\beta(E_1+E_2)}}{g_1^2 e^{-2\beta E_1} + 2 g_1 g_2 e^{-\beta(E_1+E_2)} + g_2^2 e^{-2\beta E_2}}; \quad E_1 - E_2 = a$$

$$= \frac{g_1 g_2 a^2 e^{-\beta(E_1+E_2)}}{e^{-2\beta E_2}\left(g_1^2 e^{-2\beta(E_1-E_2)} + 2 g_1 g_2 e^{-\beta(E_1-E_2)} + g_2^2\right)} = \frac{g_1 g_2 a^2 e^{-\beta a}}{\left(g_2 + g_1 e^{-\beta a}\right)^2}$$

Stauffer, Chowdhury

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3.7.2 Canonical Ensemble

The partition function for ideal Bose gas and ideal Fermi gas can be written as

$$Z = \sum_{\{n_i\}} \exp[-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots)] \tag{3.135}$$

So, the average number of particles in a state r is

$$< n_r >= \frac{\sum_{n_1,n_2,\ldots} n_r e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\ldots+n_r\epsilon_r+\ldots}}{\sum_{n_1,n_2,\ldots} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\ldots+n_r\epsilon_r+\ldots}} \tag{3.136}$$

or,

$$< n_r >= -\{1/(\beta Z)\}(\partial Z/\partial\epsilon_r) = -(1/\beta)[\partial(\ln Z)/\partial\epsilon_r] \tag{3.137}$$

The formula (3.136) can be used to derive the mean occupation of the levels in a quantum gas. But, in order to emphasize the crucial differences between the Fermi gas, Bose gas (and photon gas) we shall calculate $< n_r >$ directly from its fundamental definition (3.135) which can be reexpressed as

$$< n_r >= \frac{[\{\sum_{n_r} n_r e^{-\beta n_r\epsilon_r}\}\{\sum^{(r)}_{n_1,n_2,\ldots} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\ldots+n_r\epsilon_r+\ldots)}\}]}{[\{\sum_{n_r} e^{-\beta n_r\epsilon_r}\}\{\sum^{(r)}_{n_1,n_2,\ldots} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\ldots+n_r\epsilon_r+\ldots)}\}]}$$

where the symbol $\sum^{(r)}_{n_1,n_2,..}$ denotes sum over all states except the r-th. Note that, the allowed values of n_r depend on the nature of the particles, i.e., whether these are Fermions or Bosons. Moreover, the upper limits of the n's in the summations are, in general, correlated because of the condition $\sum_i n_i = N$.

However, the formula (3.135) gets simplified in the case of the *photon gas* where each level can accomodate any number of particles and total number of particles need not be conserved. Then, each of the sums in (3.135) extends from 0 to ∞, independent of each other. Consequently, the second factors within the brackets in the numerator and denominator cancel each other and we are left with the simpler expression

$$< n_r >= \left[\sum_{n_r} n_r e^{-\beta n_r\epsilon_r}\right] / \left[\sum_{n_r} e^{-\beta n_r\epsilon_r}\right]$$

$$= -(1/\beta)(\partial/\partial\epsilon_r)\left[\ln\left\{\sum_{n_r=0}^{\infty}\left(e^{-\beta\epsilon_r}\right)^{n_r}\right\}\right] = (1/\beta)(\partial/\partial\epsilon_r)[\ln(1-e^{-\beta\epsilon_r})]$$

i.e.,

$$< n_r >= [e^{\beta\epsilon_r} - 1]^{-1} \tag{3.138}$$

which is the Planck distribution for the photon gas.

As we shall demonstrate now, one has to proceed more carefully in the case of ideal quantum gases where the total number of particles is conserved. The symbol

$$Z_r(N) = \sum_{n_1,n_2,\ldots}^{(r)} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots)} \tag{3.139}$$

denotes the partition function of a system of N particles which are distributed over all the states except the r-th, i.e., N particles are accounted for before the remaining sum over the states of the r-th cells are carried out.

•Ideal Fermi Gas

Since for Fermions, 0 and 1 are the only two allowed values of n_r

$$< n_r >= \frac{0 + e^{-\beta\epsilon_r} Z_r(N-1)}{Z_r(N) + e^{-\beta\epsilon_r} Z_r(N-1)} = [\frac{Z_r(N)}{Z_r(N-1)} e^{\beta\epsilon_r} + 1]^{-1}$$

But, for $\Delta N \ll N$,

$$\ln Z_r(N - \Delta N) \simeq \ln Z_r(N) - \alpha\Delta N \tag{3.140}$$

where $\alpha = \partial(\ln Z_r)/\partial N = -\mu/(k_B T)$. Taking $\Delta N = 1$, we have

$$Z_r(N-1) \simeq e^{-\alpha} Z_r(N) \tag{3.141}$$

and, hence,

$$< n_r >= [e^{\alpha + \beta\epsilon_r} + 1]^{-1} \tag{3.142}$$

which is identical to the equation (3.123).

In the above derivation we have made two assumptions, (i) that $\alpha_r = \partial(\ln Z_r)/\partial N = \alpha$, independent of r; and (ii) one can truncate the series in (3.139) after the second term even when $\Delta N = 1$. We can now derive conditions required to be satisfied for the validity of these two assumptions. Since,

$$Z(N) = Z_r(N)[1 + e^{-\alpha - \beta\epsilon_r}]$$

taking derivatives of the logarithms of both sides with respect to N

$$\alpha = \alpha_r - < n_r > (\partial\alpha/\partial N)$$

Therefore, in order that $\alpha = \alpha_r$, we must have $(\partial\alpha/\partial N) < n_r > \ll \alpha$ and since $< n_r > \leq 1$, the required condition to be satisfied is $(\partial\alpha/\partial N) \ll \alpha$, i.e., if the chemical potential does not change significantly on additing a particle. This condition is normally satisfied by a macroscopically large system of ideal Fermi gas. The justification for the assumption (ii) can be given along the same line as some of the arguments presented in sections 3.3 and 3.4 in the context of classical systems.

•Ideal Bose Gas

Since, for Bosons, all the integers $0, 1, 2, 3, ...$ are allowed values of n_r, with the abbreviation $y = \exp(-\beta\epsilon_r)$,

$$< n_r >= \frac{0 + yZ_r(N-1) + 2y^2 Z_r(N-2) + 3y^3 Z_r(N-3) + ...}{Z_r(N) + yZ_r(N-1) + y^2 Z_r(N-2) + y^3 Z_r(N-3) + ...}$$

$$= \frac{e^{-(\alpha+\beta\epsilon_r)} + 2e^{-2(\alpha+\beta\epsilon_r)} + 3e^{-3(\alpha+\beta\epsilon_r)} + ...}{1 + e^{-(\alpha+\beta\epsilon_r)} + e^{-2(\alpha+\beta\epsilon_r)} + e^{-3(\alpha+\beta\epsilon_r)} + ...},$$

or,

$$< n_r >= [e^{\alpha+\beta\epsilon_r} - 1]^{-1} \tag{3.143}$$

•Ideal Boltzmann Gas

For a given set $\{n_1, n_2, ...\}$, there are $N!/(n_1!n_2!...)$ possible ways in which the N particles can be put into the given single-particle states. So, in contrast to the equation (3.134) for the partition function for ideal Bose and fermi gases, the partition function for ideal Boltzmann gas is obtained from

$$Z = \sum_{n_1, n_2, ..} [N!/(n_1!n_2!...)] e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + ...)}$$

$$= \sum_{n_1, n_2, ..} [N!/(n_1!n_2!...)] (e^{-\beta\epsilon_1})^{n_1} (e^{-\beta\epsilon_2})^{n_2} ...$$

i.e.,

$$Z = (e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + ...)^N$$

Therefore, $\ln\ Z = N\ \ln(\sum_r e^{-\beta\epsilon_r})$ which leads to

$$< n_r >= Ne^{-\beta\epsilon_r} / (\sum_r e^{-\beta\epsilon_r}) \tag{3.144}$$

which is identical to classical Maxwell-Boltzmann distribution.

Solve problem 3.23.

3.7.3 Grand-Canonical Ensemble

Just as in case of canonical ensemble, we can now show that in case of the grand canonical ensemble,

$$< n_r >= -(1/\beta)[\partial(\ln Z_G)/\partial\epsilon_r]$$

In this ensemble, the derivation of $< n_r >$ is the simplest.

•Ideal Fermi Gas

The grand partition function is given by

$$Z_G = \Pi_i[\sum_{n_r=0}^{1} e^{-\beta(\epsilon_r-\mu)n_r}]$$

or, $\ln\ Z_G = \sum_r \ln[1 + e^{\beta(\mu-\epsilon_r)}]$ and, hence,

$$< n_r >= [e^{\beta(\epsilon_r-\mu)} + 1]^{-1} \quad (3.145)$$

•Ideal Bose Gas

In this case

$$Z_G = \Pi_i[\sum_{n_r=0}^{\infty} e^{-\beta(\epsilon_r-\mu)n_r}]$$

i.e., $\ln\ Z_G = -\sum_r \ln[1 - e^{\beta(\mu-\epsilon_r)}]$ and, hence,

$$< n_r >= [e^{\beta(\epsilon_r-\mu)} - 1]^{-1} \quad (3.146)$$

Solve problem 3.24 - 3.26.

3.8 Quantum Systems; Density Operator

In quantum mechanics, say, in the Dirac formulation, the completely prepared states are represented by their "ket" vectors $|\lambda >$. But, in quantum statistical mechanics, the preparations are always incomplete and, hence, a system is not described by a well-defined ket. This situation is the quantum counterpart of the incomplete knowledge about the micro-states in classical statistical mechanics, where we do not know in which micro-state the system has been prepared. Naturally, just as we assign a probability P_r with each micro-state r in classical statistical mechanics, we assign a probability

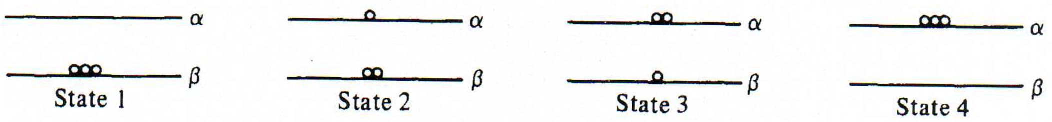

Fig. 4.1. The four states of a three-particle system with two single particle states.

large collection of particles. An example is the small amplitude vibrational modes of a solid. These modes are called *phonons*. Another example is the *occupation numbers* for quantum mechanical systems composed of non-interacting particles.

In this chapter, we will consider phonons, occupation numbers, classical ideal gases, and a number of other examples to illustrate how the factorization method is applied.

Chandler : Introduction to modern statistical physics

4.1 Occupation Numbers

The first step in analyzing any model involves the classification of microstates. The state of a quantum system can be specified by the wavefunction for that state, $\Psi_\nu(r_1, r_2, \ldots, r_N)$. Here, Ψ_ν is the νth eigensolution to Schrödinger's equation for an N-particle system. If the particles are non-interacting (i.e., ideal), then the wavefunction can be expressed as a symmetrized* product of single particle wavefunctions. Let us denote these single particle wavefunctions as $\phi_1(r), \phi_2(r), \ldots, \phi_j(r), \ldots$. For a particular state, say ν, $\Psi_\nu(r_1, \ldots, r_N)$ will be a symmetrized product containing n_1 particles with the single particle wavefunction ϕ_1, n_2 particles with the single particle wavefunction ϕ_2, and so on. These numbers, $n_1, n_2, \ldots, n_j, \ldots$ are called the *occupation numbers* of the first, second, $\ldots j$th, $\ldots$ single particle states. If the N particles are indistinguishable—as quantum particles are—then *a state, ν, is completely specified by the set of occupation numbers* $(n_1, n_2, \ldots, n_j, \ldots)$ since any more detail would distinguish between the n_j particles in the jth single particle state.

For example, consider three particles (denoted in Fig. 4.1 by circles) which can exist in one of two single particle states, α and β. All the possible states for this three-particle system are exhibited in Fig. 4.1. In terms of occupation numbers, state 1 has $n_\alpha = 0$, $n_\beta = 3$; state 2 has $n_\alpha = 1$, $n_\beta = 2$; and so on. Notice that an occupation number is a collective variable in the sense that its value depends upon the instantaneous state of all the particles.

Let us now express the total number of particles and the total

* For Fermi particles, the product is antisymmetric; for Bose particles the product is symmetric.

energy in terms of the occupation numbers. Let

$$\nu = (n_1, n_2, \ldots, n_j, \ldots) = \nu\text{th state}.$$

Then

$$N_\nu = \sum_j n_j = \text{total number of particles in the } \nu\text{th state}.$$

Let ε_j be the energy of the jth single particle state. Then,

$$E_\nu = \sum_j \varepsilon_j n_j = \text{energy in the } \nu\text{th state}.$$

Particles with half-integer spin obey an exclusion principle*: $n_j = 0$ or 1, only. Such particles are called *fermions* and the statistics associated with $n_j = 0$ or 1 is called *Fermi–Dirac* statistics.

Particles with integer spin obey Bose–Einstein statistics: $n_j = 0, 1, 2, 3, \ldots$. These particles are called *bosons*.

4.2 Photon Gas

As an example of how we use occupation numbers, consider the photon gas—an electromagnetic field in thermal equilibrium with its container. We want to describe the thermodynamics of this system. From the quantum theory of the electromagnetic field, it is found that the Hamiltonian can be written as a sum of terms, each having the form of a Hamiltonian for a harmonic oscillator of some frequency. The energy of a harmonic oscillator is $n\hbar\omega$ (zero point energy omitted), where $n = 0, 1, 2, \ldots$. Thus, we are led to the concept of photons with energy $\hbar\omega$. A state of the free electromagnetic field is specified by the number n for each of the "oscillators," and n can be thought of as the number of photons in a state with single "particle" energy $\hbar\omega$.

Photons obey Bose–Einstein statistics: $n = 0, 1, 2, \ldots$. The canonical partition function is thus

$$e^{-\beta A} = Q = \sum_\nu e^{-\beta E_\nu} = \sum_{\substack{n_1, n_2, \ldots, n_j, \ldots \\ =0}}^{\infty} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots + n_j\varepsilon_j + \cdots)},$$

where we have used the occupation number representation of E_ν, and denoted $\hbar\omega_j$ by ε_j. Since the exponential factors into independ-

* The requirement that the N-particle wavefunction be an antisymmetric product implies the exclusion principle.

ent portions, we have

$$Q = \prod_j \left[\sum_{n_j=0}^{\infty} e^{-\beta n_j \varepsilon_j} \right].$$

The term in brackets is just a geometric series, thus

$$Q(\text{photon gas}) = \prod_j \left[\frac{1}{1 - e^{-\beta \varepsilon_j}} \right].$$

From this formula, we can obtain all the properties we want since $Q = e^{-\beta A}$. One quantity that is particularly interesting is the average value of the occupation number of the jth state, $\langle n_j \rangle$. In the canonical ensemble

$$\langle n_j \rangle = \frac{\sum_\nu n_j e^{-\beta E_\nu}}{\sum_\nu e^{-\beta E_\nu}} = \frac{\sum_{n_1, n_2, \ldots} n_j e^{-\beta(n_1\varepsilon_1 + \cdots + n_j\varepsilon_j + \cdots)}}{Q}$$

$$= \left[\frac{\partial}{\partial(-\beta\varepsilon_j)} \sum_{n_1, n_2, \ldots} e^{-\beta(n_1\varepsilon_1 + \cdots + n_j\varepsilon_j + \cdots)} \right] \Big/ Q$$

$$= \frac{\partial \ln Q}{\partial(-\beta\varepsilon_j)}.$$

Returning to our formula for Q we thus have

$$\langle n_j \rangle = + \frac{\partial}{\partial(-\beta\varepsilon_j)} \left\{ \sum_j - \ln(1 - e^{-\beta\varepsilon_j}) \right\}$$

$$= e^{-\beta\varepsilon_j} / [1 - e^{-\beta\varepsilon_j}]$$

or

$$\langle n_j \rangle = [e^{\beta\varepsilon_j} - 1]^{-1},$$

which is called the Planck distribution.

Exercise 4.1 For the photon gas derive a formula for the *correlation function* $\langle \delta n_i \, \delta n_j \rangle$ where $\delta n_i = n_i - \langle n_i \rangle$.

Exercise 4.2* Use the formula for $\langle n_j \rangle$ to show that the energy density of a photon gas is σT^4, where σ is a constant, $(\pi^2 k_B^4 / 15\hbar^3 c^3)$. [*Hint*: You will need to construct a formula for the number of standing wave solutions to use the wave equation for waves in a three-dimensional cavity and with frequency between ω and $\omega + d\omega$.]
