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Exercise Sheet 13

(1) Grandcanonical ensemble

We consider a quantum many-body system for particles, discribed by a Hamiltonian $\mathbf{H}$, which is bounded from below, i.e., the with energy eigenvalues $E \geq 0$. In addition there is a conserved charge Q. The grandcanonical ensemble is defined by a (large) subsystem in (an even larger) closed system of particles, which can exchange energy as well as particles/charges with its environment.

The equilibrium statistical operator $\mathbf{R}$ is determined by giving the average internal energy $U = \langle \mathbf{H} \rangle$ and average charge $q = \langle \mathbf{Q} \rangle$ and fulfilling the normalization condition $\mathrm{Tr}\,\mathbf{R} = 1$, which is fixed due to the conservation laws and maximizing the entropy

$$S = -\mathrm{Tr}(\mathbf{R} \ln \mathbf{R}) = -\langle \ln \mathbf{R} \rangle. \tag{1}$$

Show that with appropriate Lagrange multipliers to fulfill the above given constraints this statistical operator reads

$$\mathbf{R} = \exp(-\beta \mathbf{H} - \alpha \mathbf{Q} - \Omega). \tag{2}$$

The normalization condition gives

$$\mathrm{Tr}\,\rho = 1 \Rightarrow \Omega(\beta, \alpha) = \ln Z(\beta, \alpha), \quad Z = \mathrm{Tr} \exp(-\beta \mathbf{H} - \alpha \mathbf{Q}). \tag{3}$$

Show that the internal energy and mean total charge are given by

$$U = -\partial_\beta \Omega, \quad q = -\partial_\alpha \Omega. \tag{4}$$

Then calculate the entropy, using Eq. (1). Finally show, calculating $\mathrm{d}S$, with help of the thermodynamic relation

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu \mathrm{d}q \tag{5}$$

the relation of β and α to T and μ.

Hint: to get the pressure, note that Ω also depends implicitly on $L = V^{1/3}$, when introducing a cube of length L as a finite volume with imposing periodic bounddary conditions on the (quantum) fields, describing the particles. Then, due to the periodic boundary conditions, the momenta take the discrete values $\vec{p} \in (2\pi/L)\mathbb{Z}^3$.

$$\mathrm{d}\Omega = \mathrm{d}\beta \partial_\beta \Omega + \mathrm{d}\alpha \partial_\alpha \Omega + \mathrm{d}V \partial_V \Omega. \tag{6}$$

Solutions: to find the maximum-entropy statistical operator under the given constraints we introduce Lagrange mutlipliers for the variation of S:

$$\begin{split}\delta S + \lambda_U \delta U + \lambda_q \delta U + \lambda_{\text{norm}} \delta \langle 1 \rangle &= \delta\, \mathrm{Tr}[\mathbf{R}(-\ln \mathbf{R} + \lambda_U \mathbf{H} + \lambda_q \mathbf{Q} + \lambda_{\text{norm}})] \\ &= \mathrm{Tr}[\delta \mathbf{R}(-1 - \ln \mathbf{R} + \lambda_U \mathbf{H} + \lambda_q \mathbf{Q}) + \lambda_{\text{norm}}] = 0.\end{split} \tag{7}$$

Since now thanks to the Lagrange multipliers this has to hold for all $\delta \mathbf{R}$ we must set

$$\ln \mathbf{R} = \lambda_U \mathbf{H} + \lambda_q \mathbf{Q} + \lambda_{\text{norm}} - 1, \tag{8}$$

i.e., we get indeed (2) by renaming the Lagrange multipliers to $\lambda_U = -\beta$, $\lambda_1 = -\alpha$, and $\lambda_{\text{norm}} = 1 - \Omega$.

From (2) we find

$$\begin{split}\partial_\beta \Omega = \partial_\beta \ln Z = \frac{1}{Z} \partial_\beta Z = \mathrm{Tr}(-\mathbf{R}\mathbf{H}) = -U, \\ \partial_\alpha \Omega = \partial_\alpha \ln Z = \frac{1}{Z} \partial_\alpha Z = \mathrm{Tr}(-\mathbf{R}\mathbf{Q}) = -q,\end{split} \tag{9}$$

proving (4).
Using (2) in (1) we get

$$S = -\operatorname{Tr}(\mathbf{R}\ln\mathbf{R}) = \operatorname{Tr}[\mathbf{R}(\beta\mathbf{H}+\alpha\mathbf{Q}+\Omega)] = \beta U + \alpha q + \Omega. \tag{10}$$

The differential is

$$\mathrm{d}S = \mathrm{d}U\beta + \mathrm{d}\beta U + \mathrm{d}\alpha q + \mathrm{d}q\alpha + \mathrm{d}\beta\partial_\beta\Omega + \mathrm{d}V\partial_V\Omega. \tag{11}$$

With (4) this simplifies to

$$\mathrm{d}S = \mathrm{d}U\beta + \mathrm{d}q\alpha + \mathrm{d}V\partial_V\Omega. \tag{12}$$

This implies

$$\mathrm{d}U = \mathrm{d}S\frac{1}{\beta} - \frac{\alpha}{\beta}\mathrm{d}q - \mathrm{d}V\frac{1}{\beta}\partial_V\Omega. \tag{13}$$

Comparing with (5) gives

$$\beta = \frac{1}{T}, \quad P = \frac{1}{\beta}\partial_V\Omega, \quad \mu = -\frac{\alpha}{\beta}. \tag{14}$$

In the following we consider Ω as a function $\Omega(\beta,\alpha,V)$.

(2) Thermodynamics of a charged Bose gas

We consider the ideal gas of a charged relativistic Bose gas considering the scalar particles described by a Klein-Gordon field (see Lecture 6 of "Kerne und Teilchen 1"[1]), describing charged particles and their antiparticles. We start with the "box regularized version", i.e., take a cube of length L as a finite volume with the fields obeying periodic boundary conditions. Then the Hamiltonian and total charge is given by the occupation numbers $\mathbf{N} = \mathbf{a}^\dagger(\vec{p})\mathbf{a}(\vec{p})$ and $\overline{\mathbf{N}} = \mathbf{b}^\dagger(\vec{p})\mathbf{b}(\vec{p})$ with momenta $\vec{p} \in (2\pi/L)\mathbb{Z}^3$ and creation and annihilation operators $\mathbf{a}^\dagger(\vec{p})$ and $\mathbf{a}(\vec{p})$ for a particle with momentum $\vec{p}$ and $\mathbf{b}^\dagger(\vec{p})$ and $\mathbf{b}(\vec{p})$ for an antiparticle, obeying bosonic commutation relations

$$\left[\mathbf{a}(\vec{p}),\mathbf{a}^\dagger(\vec{q})\right] = \left[\mathbf{b}(\vec{p}),\mathbf{b}^\dagger(\vec{p})\right] = \delta_{\vec{p},\vec{q}} \tag{15}$$

and all other commutators of creation and annihilation operators vanishing.
The Hamiltonian and charge operator are given by

$$\begin{aligned} \mathbf{H} &= \sum_{\vec{p}} E_p[\mathbf{N}(\vec{p}) + \bar{\mathbf{N}}(\vec{p})], \quad E_p = \sqrt{m^2+\vec{p}^2}, \\ \mathbf{Q} &= \sum_{\vec{p}}[\mathbf{N}(\vec{p}) - \overline{\mathbf{N}}(\vec{p})] \end{aligned} \tag{16}$$

Use the occupation-number basis (Fock basis), i.e., the common eigenvectors $\left|\{N(\vec{p}),\overline{N}(\vec{p})\}_{\vec{p}}\right\rangle$ with $N(\vec{p}),\overline{N}(\vec{p}) \in \mathbb{N}_0 = \{0,1,2,\ldots\}$ of the particle and antiparticle number operators to evaluate the partition sum. Then show that the internal energy and mean total charge are given by

$$U = -\partial_\beta\Omega, \quad q = -\partial_\alpha\Omega. \tag{17}$$

Then calculate the entropy, using Eq. (1). Finally show, calculating $\mathrm{d}S$, with help of the thermodynamic relation

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}q \tag{18}$$

the relation of β and α to T and μ.

[1] https://itp.uni-frankfurt.de/ ~ hees/old-teilchen-kerne-1-WS2526/index.html

Hint: to get the pressure, note that Ω also depends implicitly on $L = V^{1/3}$, i.e., you need to evaluate

$$\mathrm{d}\Omega = \mathrm{d}\beta \partial_\beta \Omega + \mathrm{d}\alpha \partial_\alpha \Omega + \mathrm{d}V \partial_V \Omega. \tag{19}$$

Also discuss the physical range of values for temperature, T and chemical potential, μ.
Solutions: The partition sum is given by

$$\begin{aligned} Z = \prod_{\vec{p}} Z(\vec{p}), \quad Z(\vec{p}) &= \sum_{N(\vec{p})} \exp[-\beta(E_p - \mu) N(\vec{p})] \sum_{\overline{N}(\vec{p})} \exp[-\beta(E_p + \mu)\overline{N}(\vec{p})] \\ &= \frac{1}{1-\exp[-\beta(E_p-\mu)]} \frac{1}{1-\exp[-\beta(E_p-\mu)]} \\ &= Z_{\text{part}}(\vec{p}) Z_{\text{anti}}(\vec{p}) \end{aligned} \tag{20}$$

For the sums to exist we must have $\beta(E_p + \mu) > 0$ as well as $\beta(E_p - \mu) > 0$ for all $\vec{p}$. Since $E_p \geq m$ this implies that we must have $\beta > 0$ and $|\mu| < m$.
From this we get

$$\Omega = \ln Z = -\sum_{\vec{p}} \{\ln[1 - \exp[-\beta E_p - \alpha]] + \ln[1 - \exp[-\beta E_p + \alpha)]]\}. \tag{21}$$

We note in passing that from the $Z(\vec{p})$ one can get the mean occupation number for particles and antiparticles with momentum $\vec{p}$ by

$$\begin{aligned} \left\langle N(\vec{p}) \right\rangle &= q_{\text{part}} = -\partial_\alpha \ln Z_{\text{part}} = \frac{1}{\exp[\beta(E_p - \mu)] - 1} = f_{\text{B}}(E_p - \mu), \\ \left\langle \overline{N}(\vec{p}) \right\rangle &= -q_{\text{anti}} = +\partial_\alpha \ln Z_{\text{anti}} = \frac{1}{\exp[\beta(E_p + \mu)] - 1} = f_{\text{B}}(E_p + \mu) \end{aligned} \tag{22}$$

with the Bose-Einstein distribution

$$f_{\text{B}}(E) = \frac{1}{\exp(\beta E) - 1}. \tag{23}$$

For the internal energy and total charge we get

$$\begin{aligned} U &= -\partial_\beta \Omega = \sum_{\vec{p}} E_p [f_{\text{B}}(E_p - \mu) + f_{\text{B}}(E_p + \mu)], \\ q &= -\partial_\alpha \Omega = \sum_{\vec{p}} [f_{\text{B}}(E_p - \mu) - f_{\text{B}}(E_p + \mu)], \end{aligned} \tag{24}$$

where we have substuted again $\alpha = -\beta\mu$. For the calculation of the pressure we must use that

$$\vec{p} = \frac{2\pi}{L} \vec{n} = \frac{2\pi}{V^{1/3}} \vec{n}. \tag{25}$$

Then we get

$$P = \frac{1}{\beta} \partial_V \Omega = \sum_{\vec{p}} \frac{p^2}{3 V E_p} \left[f_{\text{B}}(E_p - \mu) + f_{\text{B}}(E_p + \mu) \right]. \tag{26}$$

The thermodynamic quantities (24) and (26) take more familiar forms by taking the thermodynamic limit "$L \to \infty$", where this limes has to be understood such that the intensive quantities U/V, q/V, p, and Ω have to be kept constant. Then one uses that for $L \to \infty$ we have in a momentum-volume element

$$\mathrm{d}^3 n = \frac{V}{(2\pi)^3} \mathrm{d}^3 \vec{p} \tag{27}$$

states. Thus we must make the substitution

$$\sum_{\vec{p}} \rightarrow V \int \mathrm{d}^3 \vec{p}. \tag{28}$$

It is most simple to do this first for Ω, using (21):

$$\Omega = -V \int_{\mathbb{R}^3} \frac{\mathrm{d}^3 \vec{p}}{(2\pi)^3} \{\ln[1-\exp[-\beta E_p - \alpha]] + \ln[1-\exp[-\beta E_p + \alpha)]]\}. \tag{29}$$

Then one finds

$$\begin{aligned}
U &= -\partial_\beta \Omega = V \int_{\mathbb{R}^3} \frac{\mathrm{d}^3 \vec{p}}{(2\pi)^3} E_p [f_{\mathrm{B}}(E_p - \mu) + f_{\mathrm{B}}(E_p + \mu)], \\
q &= -\partial_\alpha \Omega = V \int_{\mathbb{R}^3} \frac{\mathrm{d}^3 \vec{p}}{(2\pi)^3} [f_{\mathrm{B}}(E_p - \mu) - f_{\mathrm{B}}(E_p + \mu)], \\
P &= \beta \partial_V \Omega = -\beta \int_{\mathbb{R}^3} \frac{\mathrm{d}^3 \vec{p}}{(2\pi)^3} \{\ln[1-\exp[-\beta E_p - \alpha]] + \ln[1-\exp[-\beta E_p + \alpha)]]\}.
\end{aligned} \tag{30}$$

To get the pressure in the form of (26) with the substitution rule (28) we must do an integration by parts using $\mathrm{d}^3 \vec{p} = 4\pi p^2 \mathrm{d}p$ (when integrating over functions which depend only on $p = |\vec{p}|$), finally leading indeed to

$$P = \int_{\mathbb{R}^3} \frac{\mathrm{d}^3 \vec{p}}{(2\pi)^3} \frac{p^2}{3E_p} \left[f_{\mathrm{B}}(E_p - \mu) + f_{\mathrm{B}}(E_p + \mu) \right]. \tag{31}$$

Note: Here we have ignored a subtlety in the case of the Bose gas, namely Bose-Einstein condensation when taking the thermodynamic limit $L \rightarrow \infty$. This happens when at low temperatures the given charge q cannot be reached even in the limit $\mu \rightarrow \pm m$. This occurs, because by the substitution (28) the contribution from the "zero mode" at $\vec{p} = 0$, where $E_0 = m$, which one has to carefully add again, leading to the conclusion that the "missing charge" is in the Bose-Einstein condensate, i.e., a "macroscopic number" of particles N_0 (if $q > 0$ and $\mu = +m$) or antiparticles $\overline{N}_0$ (if $q < 0$ and $\mu = -m$) occupies the ground state at $\vec{p} = 0$. This subtlety does not occur when keeping the sums instead of the integrals, because then for $\mu \rightarrow \pm m$ the occupation numbers of the zero mode diverge, i.e., one can accomodate any q without special treatment of the zero mode as in the thermodynamic limit. For a more thorough discussion of this somewhat subtle point, see the solution of Exercise 6 of the "Kerne und Teilchen 1" lecture.

(3) Thermodynamics of a charged Fermi gas

Repeat the steps for an ideal gas of Dirac fermions and antifermions. Here we have anticommutators instead of commutators for the annihilation and creation operators and in addition two spin/ polarization-degrees of freedom $\sigma = \pm 1/2$. Note that the only difference is that one has a sum over momenta and spins and the possible occupation numbers can only take the eigenvalues $N(\vec{p}, \sigma), \overline{N}(\vec{p}, \sigma) \in \{0, 1\}$.

Solutions: Everything is identical with the case of the Bose gas above, except that in the sums over the occupation numbers in (20) are only running over the values 0 and 1 and the product goes in addition over $\sigma = \pm 1$ for each $\vec{p}$:

$$Z = \prod_{\vec{p}, \sigma} Z(\vec{p}), \quad Z(\vec{p}) = [1 + \exp(-\beta(E_p - \mu))][1 + \exp(-\beta(E_p + \mu))], \tag{32}$$

leading to

$$\Omega = 2V \int_{\mathbb{R}^3} \frac{\mathrm{d}^3 \vec{p}}{(2\pi)^3} \{\ln[1 + \exp(-\beta(E_p - \mu))] + \ln[1 + \exp(-\beta(E_p + \mu))]\}, \tag{33}$$

where we used the $L \to \infty$ limit. The factor $2 = (2s+1)$ (with the spin $s = 1/2$ of Dirac particles) originates from the two spin-degrees of freedom $\sigma = \pm 1$ for each $\vec{p}$.

The thermodynamic quantities are given again analogously to the Bose case but now with Fermi distribution functions,

$$\begin{aligned} U &= -\partial_\beta \Omega = (2s+1)V \int_{\mathbb{R}^3} \frac{\mathrm{d}^3\vec{p}}{(2\pi)^3} E_p [f_{\mathrm{F}}(E_p - \mu) + f_{\mathrm{F}}(E_p + \mu)], \\ q &= -\partial_\alpha \Omega = (2s+1)V \int_{\mathbb{R}^3} \frac{\mathrm{d}^3\vec{p}}{(2\pi)^3} [f_{\mathrm{F}}(E_p - \mu) - f_{\mathrm{F}}(E_p + \mu)], \\ P &= (2s+1) \int_{\mathbb{R}^3} \frac{\mathrm{d}^3\vec{p}}{(2\pi)^3} \frac{p^2}{3E_p} \left[f_{\mathrm{F}}(E_p - \mu) + f_{\mathrm{F}}(E_p + \mu) \right] \end{aligned} \tag{34}$$

with

$$f_{\mathrm{F}}(E) = \frac{1}{\exp(\beta E) + 1}. \tag{35}$$

Of course for fermions there's no condensation phenomenon, because each state $(\vec{p}, \sigma)$ can be occupied with at most one particle and/or one antiparticle. Of course we still must have $\beta > 0$ for the sums (integrals) over $\vec{p}$ to be convergent, but there's no restriction on the chemical potential, i.e., one can have $\mu \in \mathbb{R}$ and thus accomodate for any temperature any given charge q.