## Statistical Mechanics Review I with answers in footnotes

Quoted pages refer to the version Feb 26.
As a sort of 'midterm' I ask you to solve problems with $*$ marks (15 of them, numbered).


#### Abstract

Since a 400 level statistical mechanics course is a prerequisite, I did not wish to repeat the elementary explanation and practice very much, BUT it is clear that the 400 level material has not sunk into many of you. This is a review (or a checklist) of Chapters 1-3 with basic/elementary questions. If you have some trouble in answering these questions, you must carefully review the relevant topics. Chapters 1-3 are the ground-level rather-boring portion that should have been covered by any reasonable 400 level course (albeit with instructors' misunderstanding/misconception of various topics).


1. The ergodic-theoretical foundation of equilibrium statistical mechanics is only a myth. Even Boltzmann, who conceived this myth, later realized (p18 footnote 18) its irrelevance to statistical mechanics, and reached a conclusion that statistical mechanics works because almost any one of microstates compatible with an equilibrium macrostate (thermodynamic state) gives identical values for any thermodynamic observable.

The law of large numbers is believed to be behind this. You must be able to explain what the (weak) law of large numbers is (p25), why it holds (p30) and how we can use it practically (p31). How can we refine the law of large numbers (p35-)?
Q. Suppose a coin is very skewed and we expect that the H and T probabilities differ at least by $15 \%$. How many tossings of the coin is required to estimate this bias? [You must decide when you feel confident, etc.] ${ }^{1}$
2. Thermodynamic observables are either extensive or intensive (p19). You must be able to write down the Gibbs relation, and to demonstrate the Gibbs-Duhem relation (p20).
$\mathbf{Q}^{*} \mathbf{1}$. The following expression of the equation of state is obtained for 2 moles of a certain substance: $E=\sqrt{S}(1+a V)$, where $E, S, V$ are usual thermodynamic quantities and $a$ is a positive constant. Give the equation of state for $N$ moles of the same substance. ${ }^{2}$

[^0]Q. Is the above equation of state thermodynamically sound? ${ }^{3}$
3. Thermodynamic coordinates consisting of internal energy $E$ and work coordinates $\{X\}$ are the privileged set of thermodynamic variables, and span the thermodynamic space (p40). Q. What is a quasiequilibrium process? Is it reversible? ${ }^{4}$
$\mathbf{Q}^{*} \mathbf{2}$. In what sense is the thermodynamic coordinate system privileged? (p38 footnote 67$) .{ }^{5}$ Q. What is heat? [This is a hard question, but do your best.] ( $\sim \mathrm{p} 42) .{ }^{6}$
4. (-)Entropy is a convex function of thermodynamic coordinates (p55). You must understand the geometrical meaning of the Legendre transformation and why it does not lose any information about thermodynamic potentials (p95).
Q. Demonstrate that the Helmholtz free energy is convex upward (i.e., $-A$ is convex) as a function of temperature. ${ }^{7}$

[^1]5. If a system is isolated, $S=k_{B} \log w(E,\{X\})$ (Boltzmann's principle) (p43). ${ }^{8}$ You must remember that Boltzmann actually demonstrated that $d S=(1 / T) d E+(P / T) d V$ for a general particle system.

A single quantum microcanonical state corresponds to $h^{N d}$ of classical phase volume (p67).
This microcanonical ensemble/distribution is not very practical, unless the system is very simple.
Q*3. A 1D polymer consists of $N$ monomers whose length can be $a$ or $b=a(1+\theta)(a>0$, $\theta>0)$. Energy $\epsilon$ is required to change a monomer from state $a$ to state $b$. We assume that each monomer has its own kinetic energy $p^{2} / 2 m$. Study this system both under constant length $L=(N-\nu) a+\nu b$, where $\nu$ is the number of monomers in the longer state, and under constant force $F$ that stretches the chain (under constant $T$ ). That is, write down appropriate partition functions. ${ }^{9}$

[^2]${ }^{9}$ A. The system Hamiltonian is
$$
H=\sum_{i}\left(\frac{p_{i}^{2}}{2 m}+h_{i}\right)
$$
where $h_{i}=0$ or $\epsilon$, depending on the monomer conformation $a$ or $b$. To study the macrostate with internal energy $E$ and with length $L$, we need
$$
L=\sum_{i} \ell_{i}=(N-\nu) a+\nu b,
$$
where $\ell_{i}$ is the length of monomer $i$, and $\nu$ is the number of longer monomers. $\nu=(L-N a) /(b-a)$.
What we should do first is to characterize the microstates of the system. $p_{i}$ and 'long' or 'short' of the monomer characterize each monomer. The spatial location of a monomer depends on the interpretation of the system. I assumed that the ordering of the monomers along the ' $x$ '-axis does not change. Then, the set of the above mentioned variables is complete. The solution below is according to this interpretation. You could interpret that each monomer can have two lengths and the polymer is a 1 D random walk (with two different step widths). This is a possible interpretation. Why don't you redo the following solution under this interpretation; no one interpreted in this way.

The microcanonical ensemble reads

$$
\omega(E, L)=\frac{1}{h^{N}} \int_{\sum_{i} p_{i}^{2} / 2 m \in(E-\nu \epsilon, E+\delta E-\nu \epsilon]} d p_{1} \cdots d p_{N}\binom{N}{\nu} \simeq\binom{N}{\nu} \frac{1}{h^{N}} B_{N}(E-\nu \epsilon),
$$

where $B_{D}(r)$ is the volume of the $D$-sphere of radius $r$. To study the macrostate at $T$ and with length $L$, we need

$$
Z(T, L)=\left(\int d p e^{-p^{2} / 2 k_{B} T m}\right)^{N}\binom{N}{\nu} e^{-\beta \nu \epsilon}=\left(\sqrt{2 \pi k_{B} T m}\right)^{N}\binom{N}{\nu} e^{-\beta \nu \epsilon},
$$

where, properly speaking, $\nu$ must be replaced by the above formula in terms of $L$. The $T, F$ constant ensemble reads

$$
Y(T, F)=\int d L Z(T, L) e^{\beta F L}=\sum_{\nu=0}^{N} Z(T, L) e^{\beta F(N a+(b-a) \nu)}=\left(\sqrt{2 \pi k_{B} T m}\right)^{N} e^{\beta F N a}\left[1+e^{-\beta \epsilon+\beta F(b-a)}\right]^{N} .
$$

6. Gibbs paradox (explain why we need $N!$ ) (p56). Understand mixing entropy intuitively. See Problem 1.15 (or its solution).

Explain why $T>0$ (p60).
7. Understand the principle of adiabatic cooling (p77). Understand the rubber elasticity (p74). It was a good occasion to practice the so-called Jacobian technique (p75) and to learn how to use Maxwell's relations in the Jacobian form.
$\mathbf{Q}^{*} 4$. Under a constant tensile force $F$ a rubber band is cooled. What will happen? Demonstrate that your intuition is correct from the entropic elasticity point of view. ${ }^{10}$
$\mathbf{Q}^{*}$ 5. Show $T(\partial V / \partial T)_{P}=C_{P}(\partial T / \partial P)_{S} .{ }^{11}$
8. $A=-k_{B} T \log Z$ (p91), where $Z=\operatorname{Tr} e^{-\beta H}$ (and its classical counterpart).
Q. There is a classical ideal gas consisting of $N$ particles with two internal state (energy 0 and $\epsilon$ ). Find its Gibbs free energy and constant pressure specific heat $C_{P .}{ }^{12}$
Q. Why can the canonical distribution be used for small systems as well? $(\mathrm{p} 131)^{13}$

You must review elementary QM (especially, angular momentum).
Q*6. Compute the canonical partition function for the system whose (spin) Hamiltonian is $H=\sum_{i}\left(s_{i}^{2}-A s_{i z}\right)$, where $\boldsymbol{s}_{i}$ is the quantum $1 / 2$ spin of the $i$ th particle $(i=1, \cdots, N) .{ }^{14}$ $\mathbf{Q}^{*} 7$. Now, apply a magnetic field $\boldsymbol{B}$ to the above system, and compute its canonical parti-
${ }^{10} \mathbf{A}$. The rubber band lengthens.

$$
\left.\frac{\partial L}{\partial T}\right|_{F}=\frac{\partial(L, F)}{\partial(T, F)}=\frac{\partial(L, F)}{\partial(T, S)} \frac{\partial(T, S)}{\partial(T, F)}=\frac{\partial(T, S)}{\partial(T, L)} \frac{\partial(T, L)}{\partial(T, F)}=\left.\left.\frac{\partial S}{\partial L}\right|_{T} \frac{\partial L}{\partial F}\right|_{T}<0
$$

${ }^{11} \mathbf{A}$.

$$
\left.T \frac{\partial V}{\partial T}\right|_{P}=T \frac{\partial(V, P)}{\partial(T, P)}=T \frac{\partial(V, P)}{\partial(S, T)} \frac{\partial(S, T)}{\partial(T, P)}=T \frac{\partial(S, P)}{\partial(T, P)} \frac{\partial(S, T)}{\partial(S, P)}=\left.C_{P} \frac{\partial T}{\partial P}\right|_{S}
$$

$$
\begin{aligned}
& { }^{12} \mathbf{A} \text {. Its canonical partition function } Z \text { is the product of } Z_{\text {ideal }} \text { given in Section } 2.2 \text { and the canonical } \\
& \text { partition function for the internal degrees of freedom: } Z_{\text {int }}=\left(1+e^{-\beta \epsilon}\right)^{N} \text {. To obtain the Gibbs free energy, } \\
& \text { we can Laplace transform } Z \text { as } \\
& \qquad Y=Z_{\text {int }} \int Z_{\text {ideal }}(T, V) e^{-\beta P V} d V=\left(1+e^{-\beta \epsilon}\right)^{N}\left(n_{Q} k_{B} T / P\right)^{N+1}=\left(1+e^{-\beta \epsilon}\right)^{N}\left(n_{Q} / n\right)^{N+1} .
\end{aligned}
$$

Therefore,

$$
G=A+P V=-N k_{B} T \log \left(1+e^{-\beta \epsilon}\right)+N k_{B} T \log \left(n / n_{Q}\right) .
$$

Q: Is the chemical potential of this gas larger or smaller than the gas without any internal degree?
${ }^{13} \mathbf{A}$. $Z$ has a direct product structure as explained on p131. Then, the marginal distribution for a single molecule reads $\propto e^{-\beta h}$.
${ }^{14} \mathrm{~A}$.

$$
Z=\left[\operatorname{Tr} e^{-\beta \sum_{i}\left(s_{i}^{2}-A s_{i z}\right)}\right]^{N}
$$

We know $s_{i}^{2}=s(s+1)=(3 / 4) \hbar^{2}$ [remember that we are dealing with a quantum system; the magnitude of $s_{i}^{2}$ is $s(1+s)$, not $\left.s^{2}\right]$, so (note that $s=(\hbar / 2) \sigma$, where $\sigma$ is the Pauli operator)

$$
Z=\left[2 e^{-(3 / 4) \hbar^{2} \beta} \cosh (\beta A \hbar / 2)\right]^{N}
$$

tion function (i.e., add the interaction Hamiltonian $-\sum_{i} \boldsymbol{B} \cdot \boldsymbol{s}_{i}$ ). ${ }^{15}$
9. Ensemble equivalence: Classically, you must be able to choose the most convenient ensemble to compute what you want (p124).
Q. Obtain $P$ of a classical ideal gas with the aid of the grand canonical ensemble. ${ }^{16}$

Microcanonical, canonical and grand canonical results disagree only to $O[\log N]$. This implies that the thermodynamic potentials computed directly with the aid of statistical mechanics, and those computed via Legendre transformation with the aid of thermodynamics agree (ensemble equivalence) (p126-).
10. Classically, equipartition of energy may be useful (p107).
Q. What is the part of the specific heat due to the ring puckering degree of freedom? ${ }^{17}$
11. Entropy is closely related to information (Section 2.4; p109-).
$\mathbf{Q}^{*}$ 8. An intramolecular rearrangement reaction changes the molecular entropy by 11 eu . What is the (expected) required information to describe the change in a single molecule? ${ }^{18}$
12. Fluctuation-response relations and their general conclusions must be understood (p133).

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\({ }^{15}\) A. Now, we must compute
\[
Z=\left[\operatorname{Tr} e^{-\beta \sum_{i}\left(s_{i}^{2}-A s_{i z}-\boldsymbol{B} \cdot \boldsymbol{s}_{i}\right)}\right]^{N}=e^{-\left(3 N \hbar^{2} / 4\right) \beta}\left[\operatorname{Tr} e^{\beta \sum_{i}\left(A s_{i z}+\boldsymbol{B} \cdot \boldsymbol{s}_{i}\right)}\right]^{N}
\]
```

We use the usual formula: The formula we need is

$$
e^{\boldsymbol{\alpha} \cdot \boldsymbol{\sigma}}=\cosh \alpha+(\boldsymbol{n} \cdot \boldsymbol{\sigma}) \sinh \alpha
$$

Since $s=(\hbar / 2) \sigma$, in our case

$$
\boldsymbol{\alpha}=\frac{\beta \hbar}{2}\left(B_{x}, B_{y}, B_{z}+A\right),
$$

but $T r$ of $\sigma$ is zero, so

$$
Z=e^{-\left(3 N \hbar^{2} / 4\right) \beta}\left[2 \cos \left\{(\beta \hbar / 2) \sqrt{B_{x}^{2}+B_{y}^{2}+\left(A+B_{z}\right)^{2}}\right\}\right]^{N}
$$

${ }^{16} \mathbf{A}$.

$$
\Xi(T, V, \mu)=\sum_{N=0}^{\infty} Z(T, V, N) e^{\beta \mu N}=\sum_{N=0}^{\infty} \frac{\left(n_{Q} V\right)^{N}}{N!} e^{\beta \mu N}=\exp \left(n_{Q} V e^{\beta \mu}\right) .
$$

We must determine $\mu$ with the condition

$$
\frac{\partial \log \Xi}{\partial \beta \mu}=N \Rightarrow N=n_{Q} V e^{\beta \mu} .
$$

Therefore, $\Xi=e^{N} \cdot \log \Xi=P V / k_{B} T$, but this is indeed $N$.
${ }^{17} \mathbf{A}$. This is directly related to Problem 2.7. The equipartition of energy implies $\left\langle A x^{4}\right\rangle=k_{B} T / 4$. Therefore, $C_{V}=k_{B} / 4$ is the contribution. [the answer corrected]
${ }^{18} \mathbf{A} .1$ eu $=0.72$ bit, so $11 \times 0.72=8$ bits $/$ molecules. In any case, the point is that 1 eu and $1 \mathrm{bit} / \mathrm{molecule}$ are the same order
Q. What is the volume fluctuation related to? ${ }^{19}$

Q*9. The constant pressure specific heat $C_{P}$ should be written in terms of the fluctuation of some extensive quantity. Find the expression. ${ }^{20}$
Q. Explain how to measure the (effective) spring constant that governs the opening of a gate of some molecular pore. ${ }^{21}$
Do not forget that the quantum version is complicated due to the noncommutativity of the original Hamiltonian and the perturbation Hamiltonian (p134). It is a good occasion to learn the Trotter formula.
13. Thermodynamic fluctuation theory (Einstein theory). Notice that the general formula can be written down easily if you know the Gibbs relation, but you must understand how to compute the multivariate Gaussian distribution (p138). Recall also the relation to the minimum reversible work and fluctuation probability (p139).
Q. Show that $\langle\delta X \delta y\rangle=0 .{ }^{22}$

Fluctuations are closely related to the stability criterion and evolution criterion (p141). It is basically a result of convex analysis, so no differentiability is required to apply the basic theory ( p 142 ).
$\mathbf{Q}^{*} \mathbf{1 0}$. What can you say about the magnetization in the $z$ direction of the phases, if a magnetic field in the $z$ direction causes a phase transition from phase I to phase II. ${ }^{23}$
Le Chatelier-Braun's principle: if you remember $C_{P}>C_{V}$, it is easy to guess the general relations $(\Delta X)_{y}>(\Delta X)_{Y}$ and $(\Delta x)_{Y}>(\Delta X)_{y}(\mathrm{p} 143)$.
14. The second law and equilibrium statistical mechanics have some tantalizing relations (p115-).
Q. Write down Jarzynski's equality, and then explain how to use it experimentally to esti-
${ }^{19} \mathbf{A}$.

$$
\left\langle\delta V^{2}\right\rangle=-\left.k_{B} T \frac{\partial V}{\partial P}\right|_{T}=k_{B} T V \kappa
$$

where $\kappa$ is the isothermal compressibility.
${ }^{20} \mathbf{A}$. $C_{P}=T(\partial S / \partial T)_{P}$. One hint is $\left\langle\delta X^{2}\right\rangle=\left.k_{B} T \frac{\partial X}{\partial x}\right|_{y}$

$$
\left.k_{B} T \frac{\partial S}{\partial T}\right|_{P}=\left\langle\delta S^{2}\right\rangle
$$

That is, $k_{B} C_{P}=\left\langle\delta S^{2}\right\rangle$.
(In this paragraph $H$ is enthalpy) If we use the pressure ensemble $Y(T, P), H=-(\partial \log Y / \partial \beta)_{P}$. Therefore, $\left(\partial^{2} \log Y / \partial \beta^{2}\right)_{P}=-(\partial H / \partial \beta)_{P}=k_{B} T^{2}(\partial H / \partial T)_{P}=\left\langle\delta H^{2}\right\rangle$. Since $d H=T d S+V d P$, $(\partial H / \partial T)_{P}=C_{P}$. Therefore, $k_{B} T^{2} C_{P}=\left\langle\delta H^{2}\right\rangle$. If you know $k_{B} T^{2} C_{V}=\left\langle\delta E^{2}\right\rangle$, the second answer may be more natural than the first.
${ }^{21} \mathbf{A}$. The potential energy is $k x^{2} / 2$, where $x$ is the displacement and $k$ is Hooke's constant. The equipartition implies $\left\langle x^{2}\right\rangle=k_{B} T / k$. Sometimes the force $F=k x$ is measured, so the force fluctuation is of interest $\left\langle\delta F^{2}\right\rangle=k^{2}\left\langle x^{2}\right\rangle=k_{B} T k$.
${ }^{22} \mathbf{A}$.

$$
\langle\delta X \delta y\rangle=\left.\sum_{Z}\langle\delta X \delta Z\rangle \frac{\partial y}{\partial Z}\right|_{\ldots}=\left.\left.\sum_{Z} \frac{\partial Z}{\partial x}\right|_{\ldots} \frac{\partial y}{\partial Z}\right|_{\ldots}=\delta_{x y}=0
$$

${ }^{23} \mathbf{A}$. The stability (this is from convexity of $E$ ) implies $\Delta B_{z} \Delta M_{z}>0$, so phase II must have larger $z$-component magnetization than phase I.
mate the free energy change. However, it is not equivalent to the second law. [This answer will not be given. You should reread the relevant pages.]
15. Grand canonical formalism $\log \Xi=\beta P V$, where $\mu$ is fixed implicitly from the expression of $N$. Use $A=G-P V=N \mu-P V$ (p179, p187). The sum over 1P (= one-particle) states may be replaced with the corresponding integral for $P V$ and $E$ (p168), but not always for $N$ in the case of bosons (p189).
16. At least one charged species (+ or - ) must be fermions for a matter to be stable (p164 footnote 2). Fermions tend to avoid each other and bosons to do the opposite (Fig. 3.1.1). This can be illustrated by the variation of the occupation number of a single 1P state: $\left\langle\delta n^{2}\right\rangle$. incidentally, recall the Poisson distribution and the law of small numbers.
$\mathbf{Q}^{*} 11$. Compute this directly from the grand canonical partition function (i.e., $\left.\partial^{2} \log \Xi / \partial\left(\beta \epsilon_{i}\right)^{2}\right){ }^{24}$
17. You should remember when thermodynamic quantities are easy to calculate: at $T=0$ for fermions (p181-2), and $T<T_{c}$ for bosons (p189-90).
$\mathrm{Q}^{*} 12$. Suppose $N$ bosons (without spin) are confined in a 2 D harmonic potential. After showing that the BEC is possible, determine the exponents for $E$ and $P V$ as functions of $T$

[^3]$$
\log \Xi=\mp \sum \log \left(1 \mp e^{-\beta(\epsilon-\mu)}\right) .
$$

From this we know

$$
-\frac{\partial \log \Xi}{\partial \beta \epsilon_{i}}=\frac{1}{e^{\beta\left(\epsilon_{i}-\mu\right)} \mp 1} .
$$

Therefore, the fluctuation can be computed as

$$
\frac{\partial^{2} \log \Xi}{\partial\left(\beta \epsilon_{i}\right)^{2}}=-\frac{\partial}{\partial \beta \epsilon_{i}} \frac{1}{e^{\beta\left(\epsilon_{i}-\mu\right)} \mp 1}=\frac{e^{\beta\left(\epsilon_{i}-\mu\right)}}{\left(e^{\beta\left(\epsilon_{i}-\mu\right)} \mp 1\right)^{2}}=n_{i}^{2} e^{\beta\left(\epsilon_{i}-\mu\right)}
$$

(There were not a few people who stopped just before the last equality. As you know the answer is $\left\langle\delta n^{2}\right\rangle=$ $n \pm n^{2}$. Could you immediately see these two answers were identical? If not, I cannot believe why you stop there.) We can calculate $e^{\beta\left(\epsilon_{i}-\mu\right)}=\left(1 / n_{i}\right) \pm 1$. Therefore,

$$
n_{i}^{2} e^{\beta\left(\epsilon_{i}-\mu\right)}=n_{i}^{2}\left(\frac{1}{n_{i}} \pm 1\right)=n_{i} \pm n_{i}^{2} .
$$

$\left(<T_{c}\right) .{ }^{25}$
18. For fermions thermodynamic quantities for small $T$ may be understood qualitatively with the aid or thermodynamics (p184). For example, we see at once that $E(T)-E(0)=O\left[T^{2}\right]$. This implies $C_{V}=O[T]$ and $S(T) \simeq C_{V}$ for sufficiently small $T$.
$\mathbf{Q}^{*}$ 13. Show $\mu(0)-\mu(T)=o[T]>0$. Is this true for bosons in 2-space as well? (Obviously wrong in 3 -space $)^{26}$
19. It is a good occasion to learn/review the second quantization formalism (p172, i.e., creation-annihilation operators) and Bloch-De Dominicis theorem (p174).
$Q^{*}$ 14. Compute $\left\langle a^{+} a^{+} a a\right\rangle$ for fermions and bosons. ${ }^{27}$
$\mathbf{Q}^{*}$ 15. Compute $\left\langle e^{a^{+}} e^{a}\right\rangle$ for bosons and for fermions. ${ }^{28}$
${ }^{25}$ A. $E=\left(n_{x}+n_{y}\right) \hbar \omega$ (here the ground state is zero according to the usual boson formulas):

$$
N=\sum_{n_{x}, n_{y}} \frac{1}{e^{\beta\left[\hbar \omega\left(n_{x}+n_{y}\right)-\mu\right]}-1} .
$$

The integral version of this formula reads as follows, and we wish to who it is bounded from above as

$$
N_{1}=\int d x d y \frac{1}{e^{\beta[\hbar \omega(x+y)-\mu]}-1}<C T^{2}
$$

where $C$ is a positive constant; Its convergence on the large variables is OK. What happens near the ground state, if $\mu=0$ ? Basically, we must consider

$$
\int_{[0,1]^{2}} d x d y \frac{1}{x+y}=\int_{0}^{1} d x[\log (x+1)-\log x]<+\infty
$$

Therefore, $N_{1}$ is bounded from above. We must conclude that there is BEC.
Since $\mu=0$, we can write

$$
\begin{gathered}
E=\sum_{n_{x}, n_{y}} \frac{\hbar \omega\left(n_{x}+n_{y}\right)}{e^{\beta \hbar \omega\left(n_{x}+n_{y}\right)}-1} \propto T^{3} . \\
P V=-k_{B} T \sum_{n_{x}, n_{y}} \log \left(1-e^{-\beta \hbar \omega\left(n_{x}+n_{y}\right)}\right) \propto T^{3} .
\end{gathered}
$$

Q. Is there any clean relation between $P V$ and $E$ ?
${ }^{26} \mathbf{A}$. Let us compute

$$
\left.\frac{\partial \mu}{\partial T}\right|_{N, V}=\left.\frac{\partial(\mu, N)}{\partial(T, N)}\right|_{V}=\left.\left.\frac{\partial(\mu, N)}{\partial(S, T)}\right|_{V} \frac{\partial(S, T)}{\partial(T, N)}\right|_{V}=-\left.\frac{\partial S}{\partial N}\right|_{T, V}<0
$$

This goes to zero in the $T \rightarrow 0$ limit, so the first order term should not exist. The sign was discussed long ago for ideal gasses.
You cannot show thermodynamically that $\mu(0)-\mu(T)>0$ around $T=0$. Actually, if BEC occurs, this is false!. Sorry.
${ }^{27}$ A. For fermions this must be zero; you do not need Bloch-De Dominicis, since $a^{2}=0$ (such relations are operator-algebraic, so use them before any calculation). For bosons

$$
\left\langle a^{+} a^{+} a a\right\rangle=2\left\langle a^{+} a\right\rangle\left\langle a^{+} a\right\rangle=2\langle\hat{n}\rangle^{2} .
$$

Do not forget that $a$ and $a^{*}$ are operators. Do not equate them sixth, e.g., $\sqrt{n}$.
${ }^{28} \mathbf{A}$. For fermions obviously, $1+n$, because $e^{a^{+}}=1+a^{+}$.
20. Detailed balance is a very important concept (p177).
21. Photons and phonons may be treated as bosons with zero chemical potential formally (p192). ${ }^{29}$ Therefore, they are treated as bosons below $T_{c}$. From this point of view, it is easy to determine $E$ and $P V$ as a function of $T$ (p194-).

For bosons, we have

$$
\left\langle e^{a^{+}} e^{a}\right\rangle=1+\left\langle a^{+} a\right\rangle+(2!)^{-2}\left\langle\left(a^{+}\right)^{2} a^{2}\right\rangle+\cdots+(n!)^{-2}\left\langle\left(a^{+}\right)^{n} a^{n}\right\rangle+\cdots .
$$

We need

$$
\left\langle\left(a^{+}\right)^{n} a^{n}\right\rangle=n\left\langle a^{+} a\right\rangle\left\langle\left(a^{+}\right)^{n-1} a^{n-1}\right\rangle=\cdots=n!\langle\hat{n}\rangle^{n}
$$

Therefore,

$$
\left\langle e^{a^{+}} e^{a}\right\rangle=1+\langle\hat{n}\rangle+(2!)^{-1}\langle\hat{n}\rangle^{2}+\cdots+(n!)^{-1}\langle\hat{n}\rangle^{n}+\cdots=e^{\langle\hat{n}\rangle} .
$$

${ }^{29}$ Do not misunderstand that their chemical potentials are indeed 0 ; chemical potentials are well defined only for particles with definite conservation laws such as baryon number or charge conservation.


[^0]:    ${ }^{1} \mathbf{A}$. Let $X_{i}$ be a stochastic variable for the $i$-th tossing of the coin such that $X_{i}=1$ if it is head, and 0 , otherwise. Chebyshev tells us (the equality signs may be included or omitted)

    $$
    \begin{equation*}
    P\left(\left|\frac{1}{N} \sum_{i=1}^{N} X_{i}-P\right|>\epsilon\right)<\frac{V / N}{\epsilon^{2}} \tag{1}
    \end{equation*}
    $$

    where $P$ is the probability for $\mathrm{H}, V$ is the variation, which is equal to $V=P(1-P) \leq 1 / 4$ (a binomial distribution!). The question is how big $\epsilon$ we should allow. $|E-0.5|>0.0375$ ( $15 \%$ of 0.5 is 0.075 ), so $E$ should be estimated at least within the error of ca. 0.005 . Now, how often can we tolerate a big error when we perform experiments of $N$-coin-tossing runs? Perhaps once in 100 times? Then, $\frac{V / N}{\epsilon^{2}}<1 /\left(4 \times 0.005^{2} N\right)$ should be 0.01 or smaller. Therefore, $N$ must be at least $25 / 0.005^{2}=10^{6}$. You have just seen how difficult to estimate the probability accurately.
    ${ }^{2} \mathbf{A}$. If we regard $E, S$ and $V$ are the quantities for $N$ moles. $2 E / N=\sqrt{2 S / N}(1+a 2 V / N)$. Therefore,

    $$
    \begin{equation*}
    E=\sqrt{\frac{N S}{2}}\left(1+a \frac{2 V}{N}\right) \tag{2}
    \end{equation*}
    $$

    [The above might look cryptic: Let $X_{m}$ be $X$ for the $m$-mole system. $E_{2}=2 E_{N} / N, S_{2}=2 S_{N} / N$ and $V_{2}=V_{N} / N$. The problem gives $E_{2}=\sqrt{S_{2}\left(1+a V_{2}\right)}$. Combining all of them solves the problem.]

[^1]:    ${ }^{3} \mathbf{A}$. While $T>0, P$ is not positive. Therefore, it is not a normal system. Further worse, $C_{V}$ is negative.
    ${ }^{4}$ A quasiequilibrium process is a process whose path may be drawn in the thermodynamic space, because at any time the state is infinitesimally close to equilibrium. For this to be true changes have only to be sufficiently slow. However, as can be exemplified by a hot coffee in a good thermos, even if the change is very slow, the process need not be reversible.
    ${ }^{5} \mathbf{A}$. A thermodynamic state is an equivalence class of equilibrium macrostates according to the values of the thermodynamic coordinates, so a thermodynamic state and a set of thermodynamic coordinates are one-to-one correspondent. This is the privilege. However, you might say it is unfair, because thermodynamic states are so defined to make thermodynamic coordinates special. That is true, but you must think why this definition is unanimously accepted. We must pay attention to the following two points:
    (i) These variables are all non-thermal quantities. That is, only (macroscopic) mechanics and electromagnetism are required to define/measure [i.e., these quantities are operationally definable clearly].
    (ii) Phase coexistence can be described 'in detail.' That is, a coexistence phase composition (say, liquid $20 \%$, solid $80 \%$ ) can be described for any phase coexistence. [In contrast, in terms of $T$ and other variables, as you know well, the melting temperature remains the same for any composition of the phases.]
    ${ }^{6}$ A. Clausius wrote a paper entitled "Über die Art der Bewegung, die wir Wärme nennen," Annalen der Physik, 100: 353-379 (1857) [in English (not available at UIUC) "On the Nature of the Motion which we call Heat," Phil Mag 14, 108-27 (1857)]. Thus, heat is a kind of 'motion,' but I do not think anyone has given a respectable definition of heat in terms of microscopically meaningful quantities. We all know it is a part of motion, and, for example, Einstein formally introduced the expression of work in his derivation of statistical mechanics as outlined in Chapter 2, so conservation of energy (the first law) allows us to define heat as well. However, his definition of work does not contain any macroscopic feature of work in thermodynamics. Thus, if you wish to be theoretically conscientious, we must recognize that heat is defined only thermodynamically. This is outlined in footnote 77 on p42: Suppose a system can be changed from a state A to state B under isolation solely with the mechanical changes of work coordinates. If we can bring the state A to B by a process with exactly the same mechanical changes of work coordinates, the process is called an adiabatic process. Now, we go from A to B using thus defined adiabatic process, we can define heat unambiguously." Suppose we can go from A to B adiabatically only doing work $W$; notice that the process may be irreversible, so state B is with a larger entropy, generally speaking. We know $\Delta E=E_{B}-E_{A}=W$. Next, we use a different process and go from A to B . If the work needed is $W^{\prime}$, then $Q=\Delta E-W^{\prime}$ is called the heat supplied during this process.
    ${ }^{7}$ A. $A=\inf _{S}(E-S T)$ or $-A=\sup _{S}(S T-E)$ (inf may be understood as 'min,' and sup as 'max.' $E$ is a convex function of $S$, and this formula is a legitimate Legendre transformation. Therefore, $-A$ is a convex function of $T$. [Warning: any exposition of Legendre transformation that does not mention 'complex analysis' may be questionable. You must clearly understand that differentiation has nothing to do with complex analysis itself (let alone Legendre transformation). That is why we can discuss phase coexistence without any difficulty.]

[^2]:    ${ }^{8}$ If an isolated system is under the influence of an external field $x$ conjugate to $X$, we can apply Boltzmann's principle as if the system Hamiltonian is $H^{\prime}=H-x \hat{X}$. Do not forget, however, that, precisely speaking, the $\left\langle H^{\prime}\right\rangle$ is not the internal energy, but $J=E-x X$ (a generalized enthalpy). See, e.g., a system under constant magnetic field $B . S=k_{B} \log w(J, x,\{Y\})$ and $d J=T d S-M d B($ cf p94).

[^3]:    ${ }^{24}$ A. We know

