1. Consider an Ising system ($N$ spins $s_i$, each of them can adopt two states, $s_i = +1$ or $s_i = -1$) in which every spin interacts with all other spins, with ferromagnetic interaction of strength $J'$.

(a) Show that coupling constant $J'$ in this system must be equal $J' = J/N$, where $J$ is independent of $N$, in order for the system energy to be properly extensive.

(b) Write down Hamiltonian of the system. Show that it can be expressed in terms of overall magnetization $S = \sum_i s_i$.

(c) Write down the partition sum of the system. Show how it can be reduced to the single summation over $S$. Show that this summation can be approximated as integration.

(d) Consider partial equilibrium of the system with fixed $S$. Find free energy of this state as a function of $S$, let us denote it $f(S)$. Sketch the plot of $f(S)$ at different values of $J$ or $T$. Do these plots suggest phase transition in the system? At which temperature?

(e) Estimate, up to numerical coefficients, the amount of fluctuations $(S^2) - (S)^2$ above the transition temperature and at the transition point. Pay special attention to how these fluctuations depend on $N$.

(f) Estimate the width of the transition range of temperature at large but finite $N$.

**Solution**

(a) Since there are $\mathcal{O}(N^2)$ interacting pairs, the energy of each should be $\mathcal{O}(1/N)$ in order for the total energy to be $\mathcal{O}(N)$.

(b) Hamiltonian of the system reads $\mathcal{H} = -(J/2N) \sum_{i\neq j} s_i s_j$. Here, factor of $1/2$ is included to avoid double counting of pairs $(i,j)$ and $(j,i)$. Given that overall magnetization is $S = \sum_i s_i$, we have $S^2 = \sum_{i,j} s_i s_j = \sum_i s_i^2 + \sum_{i\neq j} s_i s_j$ and, therefore, we can re-write Hamiltonian as

$$\mathcal{H} = -\frac{J}{2N} S^2 + \frac{J}{2}. \quad (1)$$

The last term is a constant which does not depend on anything and can be safely ignored in subsequent considerations.

(c) In general, partition sum of the system reads $Z = \sum_{\{s_i\}} e^{-\mathcal{H}/T}$, where temperature $T$ is expressed in energy units. Since $\mathcal{H}$ depends only on $S$, we can group terms corresponding to any given value of $S$, writing $Z = \sum_S \Omega(S) e^{-\mathcal{H}/T}$, where $\Omega(S)$ is the number of microstates with given value of $S$. To find $\Omega(S)$, let us denote $N_+$ and $N_-$ the numbers of spins “up” and “down”. Since $N_+ + N_- = N$ and $N_+ - N_- = S$, we can find $N_+ = (N + S)/2$ and $N_- = (N - S)/2$. At the same time, the expression of $\Omega$ in terms of $N_{\pm}$ is obvious, including the use of Stirling formula:

$$\Omega(S) = \frac{N!}{N_+!N_-!} \approx \left( \frac{N}{N_+} \right)^{N_+} \left( \frac{N}{N_-} \right)^{N_-} = \left( \frac{2N}{N + S} \right)^{N_+} \left( \frac{2N}{N - S} \right)^{N_-} \left( \frac{2N}{N + S} \right)^{N_+} \left( \frac{2N}{N - S} \right)^{N_-}. \quad (2)$$

Thus, the partition sum reads

$$Z = \sum_S \left( \frac{2N}{N - S} \right)^{N_+} \left( \frac{2N}{N + S} \right)^{N_-} e^{-\frac{J}{2T} S^2 + \frac{J}{2}}$$

$$= \sum_S \exp \left[ -\frac{N - S}{2} \ln \frac{N - S}{2N} - \frac{N + S}{2} \ln \frac{N + S}{2N} + \frac{J}{2NT} S^2 - \frac{J}{2T} \right]$$

$$= \frac{1}{2} \int dS \sum_S \exp \left[ -\frac{N - S}{2} \ln \frac{N - S}{2N} - \frac{N + S}{2} \ln \frac{N + S}{2N} + \frac{J}{2NT} S^2 - \frac{J}{2T} \right], \quad (3)$$

Full credit will be given for complete solution of any 4 of these 6 problems.
where (unimportant) factor of $1/2$ in front arises because $S$ changes with the step of 2.

(d) The expression in the exponent of the last formula is nothing but the (divided by $T$) free energy of the state of partial equilibrium at the given fixed $S$, taken per particle it reads:

$$f(S) = T \frac{N - S}{2N} \ln \frac{N - S}{2N} + T \frac{N + S}{2N} \ln \frac{N + S}{2N} - \frac{J}{2N} S^2 + \frac{J}{2N}.$$  \hfill (4)

As expected, this free energy depends on $m = S/N$ only (apart from a constant which we can drop):

$$f(m) = T \frac{1 - m}{2} \ln \frac{1 - m}{2} + T \frac{1 + m}{2} \ln \frac{1 + m}{2} - \frac{J}{2} m^2.$$  \hfill (5)

As expected, entropic part of this free energy (first two terms) favors equipartition of spins between “up” and “down” states, i.e., it has minimum at $m = 0$. By contrast, energetic part favors either positive or negative non-zero $m$, it has maximum at $m = 0$. To see this most clearly, we can expand the entropic part in powers of $m$; again dropping a constant, we have

$$f(m) \big|_{m \ll 1} \approx T \left[ \frac{m^2}{2} + \frac{m^4}{12} + \ldots \right] - \frac{J}{2} m^2 = \frac{m^2}{2} (T - J) + T \frac{m^4}{12}.$$  \hfill (6)

Clearly, $m = 0$ is the minimum if $T > J$ and it becomes a maximum at $T < J$, suggesting a phase transition at $T = J$. Importantly, at larger values of $|m|$ the free energy $f(m)$ always goes up, which means there are minima at some $m$ even at low temperature $T < J$. The sketch of $f(m)$ is shown in Figure 1.

![Figure 1: The plot of $f(m)/T$ against $m$ at three different values of $J/T$: at $J/T = 0.8$, there are two minima at non-zero $m$ and maximum at $m = 0$; at $J/T = 1.2$ there is a single minimum at $m = 0$; at $J/T = 1$, there is a very shallow minimum at $m = 0$.](image)

Note that although formula (6) looks like Landau theory, it does not involve in this case the approximation; in other words, one can say that the mean field picture is exact for this model where every spin interacts with every other spin, like in infinitely dimensional space.

(e) Above the transition, fluctuations of $m$ around zero are determined such that $Nf(m) \sim T$; therefore, dropping the numerical coefficients, $N(T - J)m^2 \sim J$, where in the right hand side $T$ can be replaced by the critical value, which is $J$. Thus, $\delta m^2 \sim m^2 \sim \frac{1}{N} \frac{J}{T - J}$; it diverges as $T$ approaches $J$. Fluctuations of $S$, accordingly, behave as $\delta S \sim \left( \frac{N}{T - J} \right)^{1/2}$.

In the transition point, by the same principle $Nf(m) \sim T$, we have $Nm^4 \sim 1$, or $\delta m \sim N^{-1/4}$. In terms of $S$, we have $\delta S \sim N^{3/4}$. Thus, fluctuations in the transition point are governed by a different power of $N$.

(f) The transition region can be determined such that growth of $\frac{J}{T - J}$ compensates for the lacking power of $N$, this happens when $\frac{J}{T - J} \sim \sqrt{N}$ which means $T - J \sim J/\sqrt{N}$.
2. For non-relativistic gases of elementary particles with either Bose or Fermi statistics, there is a simple relation between pressure \( P \) and energy per unit volume \( E/V \), namely, \( P = (\frac{2}{3}) E/V \). This relation is exact as long as gas is ideal. Derive this relation.

**Hint:** You may want to proceed as follows: start with thermodynamic potential \( \Omega \), which is natural thermodynamic potential in variables \( T, V, \mu \), write it down in terms of proper partition sum, for both Fermi and Bose statistics. Remember the relation between \( \Omega \) and pressure \( P \). Write down also the expressions for energy in terms. In both \( \Omega \) and \( E \) remember, that energy of non-relativistic elementary particles is related to momentum via \( \varepsilon_p = p^2/2m \). Performing integration by parts, establish the requisite relation.

**Solution**

For Fermi gas in general

\[
\Omega = -T \sum_k \ln \left( 1 + e^{(\mu - \varepsilon_k)/T} \right).
\] (7)

For Bose gas in general

\[
\Omega = -T \sum_k \ln \left( \frac{1}{1 - e^{(\mu - \varepsilon_k)/T}} \right).
\] (8)

Together these two are written as

\[
\Omega = \mp T \sum_k \ln \left( 1 \pm e^{(\mu - \varepsilon_k)/T} \right),
\] (9)

where upper sign is for Fermi and the lower sign is for Bose cases, respectively. Energy is also written for both cases:

\[
E = \sum_k \frac{\varepsilon_k}{e^{(\varepsilon_k - \mu)/T} \pm 1}.
\] (10)

And as regards pressure, we know that \( \Omega = -PV \).

The summation over quantum states \( k \) is written as

\[
\sum_k \ldots \rightarrow \frac{Vg}{(2\pi \hbar)^3} \int \ldots 4\pi p^2 dp,
\] (11)

where \( g = 2s + 1 \) is related to the spin degeneracy.

For non-relativistic particles, energy \( \varepsilon \) depends on momentum according to \( \varepsilon_p = p^2/2m \). This allows us to switch to integration over energies instead of integration over momenta:

\[
\sum_k \ldots \rightarrow \frac{Vg}{(2\pi \hbar)^3} \int \ldots 4\pi \cdot 2m \varepsilon \cdot d\sqrt{2m \varepsilon} = \frac{Vgm^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \int_0^\infty \ldots \sqrt{\varepsilon} d\varepsilon.
\] (12)

First we apply this to the expression for energy (10):

\[
E = \frac{Vgm^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{(\varepsilon - \mu)/T} \pm 1} d\varepsilon.
\] (13)

Second, we apply the same to \( \Omega \), formula (9), yielding

\[
\Omega = \mp \frac{Vgm^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \int_0^\infty \ln \left( 1 \pm e^{(\mu - \varepsilon)/T} \right) \varepsilon^{1/2} d\varepsilon
\]

integrate by parts

\[
= \mp \frac{Vgm^{3/2}}{\pi^2 \hbar^3 \sqrt{2}} \left[ \frac{2}{3} \varepsilon^{3/2} \ln \left( 1 \pm e^{(\mu - \varepsilon)/T} \right) \right]_0^\infty - \frac{2}{3} \int_0^\infty \varepsilon^{3/2} \frac{\pm e^{(\mu - \varepsilon)/T} (\frac{1}{T})}{1 \pm e^{(\mu - \varepsilon)/T}} d\varepsilon
\]

\[
= -2 \frac{Vgm^{3/2}}{3 \pi^2 \hbar^3 \sqrt{2}} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon - \mu)/T} \pm 1}.
\] (14)

Comparing (13) and (14), we arrive at the expected result \( PV = (2/3)E \).
3. In early Universe, temperature $T$ was very high, there was light at this temperature, there were virtually no atoms, and electron-positron pairs were born or annihilated through the "reaction"

$$e^- + e^+ \rightarrow \gamma.$$  \hfill (15)

Consider this "chemical reaction" and find equilibrium concentration of electrons at temperature $T$. Assume that all gases in question are ideal. Give an estimate of a typical distance between electrons as it depends on temperature and world constants.

**Hint:** You may follow these steps: Write down the general condition of chemical equilibrium. You should know what is chemical potential of photons; this should allow you to find chemical potential of electrons. Knowing the chemical potential of electrons, and their statistics, find their number. Do not forget that thermal speed of electrons at high temperature $T$ might be comparable to the speed of light, such that energy of an electron moving with momentum $p$ is equal to $\varepsilon_p = \sqrt{mc^2 + (pc)^2}$.

**Solution**

In the condition of equilibrium, $\mu_{e^+} + \mu_{e^-} = \mu_e$, the one thing we know right away is chemical potential of photons, which is zero: $\mu_\gamma = 0$. Next, assuming there are no electrons or positrons apart from those born in pairs, we have to have $\mu_{e^+} = \mu_{e^-}$. Therefore, in this system chemical potential of electrons must be equal to zero. Fermi distribution at zero chemical potential yields then for the number of electrons (or positrons) $N$ in volume $V$, or for their density $n = N/V$ (with factor of 2 accounting for spin degeneracy):

$$N = 2 \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\varepsilon_k/T} + 1} \quad \Rightarrow \quad n = \frac{1}{\pi^2} \int_0^\infty \frac{k^2dk}{e^{\varepsilon_k/T} + 1}. \quad (16)$$

If the temperature is not very high, then electrons born in pairs move with moderate speed much smaller than the speed of light. In this case $\varepsilon_k = mc^2 + (\hbar k)^2/2m$, and then we can neglect unity in denominator in the integral, yielding $n \approx e^{-mc^2/T}/2\pi(mT/\hbar^2)^{3/2}$. For instance, the chances to observe electron-positron pair born in the light coming to us from the Sun (temperature 5700 K) is so small that not a single pair is likely to be born in the huge volume between us and the Sun, because $mc^2$ corresponds to temperature about $6 \cdot 10^9$ K which is six orders of magnitude higher than $T_{\text{Sun}}$.

In the opposite limit, when temperature is much higher than rest energy of electrons, $T \gg mc^2$, then photons are energetic enough to give birth to electron-positron pairs in significant quantities. If $T \gg mc^2$ then electrons and positrons are ultra-relativistic, which means $\varepsilon_p \approx pc = \hbar c$ which then yields

$$n = \frac{1}{\pi^2\hbar^3c^3} \int_0^\infty \frac{\varepsilon^2d\varepsilon}{e^{\varepsilon/T} + 1} = \frac{T^3}{\pi^2\hbar^3c^3} \int_0^\infty \frac{x^2dx}{e^x + 1}. \quad (17)$$

Typical distance between electrons is $n^{-1/3} \approx \hbar c/T$. This is of the same order as de Broglie wave length of electrons at this temperature: $\lambda_T = 2\pi/\hbar = 2\pi\hbar/p = 2\pi\varepsilon_p/\hbar c \sim \hbar c/T$.

4. Consider a gas with pressure $P$ and temperature $T$ in contact with a surface on which there are some $K$ distinct adsorption sites. At most only one molecule can be adsorbed on each site at any given moment, and the adsorption free energy of one molecule is $\delta$.

(a) What physical condition determines the equilibrium fraction of occupied sites on the surface, $\phi$, as a function of gas pressure $P$? Explain why the function $\phi(P)$ is called adsorption isotherm?

(b) Show that fluctuations in the number of adsorbed particles satisfy

$$\langle (N - \langle N \rangle)^2 \rangle = T \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_T,$$

where $\mu$ is chemical potential of the gas in the bulk.

(c) Find adsorption isotherm, that is, the average number of occupied adsorption sites on the surface as it depends on the gas pressure in the bulk at constant temperature, assuming gas in the bulk is ideal (this is called Langmuir isotherm).

(d) Show that the Langmuir isotherm can be presented in the form $\langle N \rangle = K \frac{P}{\varepsilon_p + T}$, where $\langle N \rangle$ is the average number of adsorbed particles, and $P_0$ describes interaction between particles and the surface.
(e) Show that in this ideal gas case
\[
\left\langle (N - \langle N \rangle)^2 \right\rangle = K \phi (1 - \phi)
\]
where \( \phi = \langle N \rangle / K \) is the average fraction of occupied sites. Explain why the fluctuation vanishes in both \( \phi \to 0 \) and \( \phi \to 1 \) limits.

**Solution**

(a) Since particles can be exchanged between surface and bulk, the equilibrium condition demands that chemical potentials of particles in the bulk and on the surface are the same. Experimentally, one can increase the gas pressure at constant temperature and observe the increase of the adsorption fraction. Since this is done at constant temperature, the result is described in terms of isotherms.

(b) To begin with,
\[
\langle N \rangle = \sum_{N=0}^{\infty} N p(N) , \quad \langle N^2 \rangle = \sum_{N=0}^{\infty} N^2 p(N) .
\]

Now,
\[
p_{\text{state}} = \frac{e^{[N \mu - \mathcal{H}(\text{state})]/T}}{\sum_{\text{states}} e^{[N \mu - \mathcal{H}(\text{state})]/T}} = \frac{e^{[N \mu - \mathcal{H}(\text{state})]/T}}{\zeta(T, \mu)} ,
\]

where summation downstairs runs over all states, with a variety of values of \( N \), but with fixed \( \mu \). Here, we are talking about states of the adsorbed system, while \( \mu \) is fixed by the outside bulk gas. Therefore
\[
p(N) = \sum_{\text{states with given } N} p_{\text{state}} = \frac{e^{[N \mu]/T} Z(T, N)}{\zeta(T, \mu)} .
\]

Thus
\[
\frac{\partial \zeta(T, \mu)}{\partial \mu} = \sum_{\text{states}} N \frac{e^{[N \mu - \mathcal{H}(\text{state})]/T}}{T} ; \quad \frac{\partial^2 \zeta(T, \mu)}{\partial \mu^2} = \sum_{\text{states}} \left( \frac{N}{T} \right)^2 \frac{e^{[N \mu - \mathcal{H}(\text{state})]/T}}{\zeta(T, \mu)} .
\]

Therefore
\[
\left\langle \frac{N}{T} \right\rangle = \frac{1}{\zeta(T, \mu)} \frac{\partial \zeta(T, \mu)}{\partial \mu} ; \quad \left\langle \left( \frac{N}{T} \right)^2 \right\rangle = \frac{1}{\zeta(T, \mu)} \frac{\partial^2 \zeta(T, \mu)}{\partial \mu^2} .
\]

Differentiating the first of these two relations with respect to \( \mu \), one gets
\[
\frac{\partial}{\partial \mu} \left\langle \frac{N}{T} \right\rangle = - \frac{1}{\zeta^2(T, \mu)} \left( \frac{\partial \zeta(T, \mu)}{\partial \mu} \right)^2 + \frac{1}{\zeta(T, \mu)} \frac{\partial^2 \zeta(T, \mu)}{\partial \mu^2} \left( \left\langle \frac{N}{T} \right\rangle \right)^2 ,
\]

which is exactly what we had to prove.

(c) Chemical potential of the bulk is given by \( \mu = T \ln(P/P_1) \), where \( P_1 \) is a quantity with the dimension of pressure which involves chemical constant of a gas. At the same time, chemical potential of the \( N \) adsorbed particles on \( K \) sites can be determined from their free energy which is equal to
\[
F = -T \ln \frac{K!}{N!(K-N)!} - N \delta \approx -TN \ln \frac{K}{N} - T(K-N) \ln \frac{K}{K-N} - N \delta
\]
\[
\approx K \left[ T \phi \ln \phi + T(1 - \phi) \ln(1 - \phi) - \delta \phi \right] ,
\]

accordingly,
\[
\mu = \frac{\partial F}{\partial K \phi} = T \ln \frac{\phi}{1 - \phi} - \delta .
\]

Equalizing the two chemical potentials, we arrive at
\[
T \ln(P/P_1) = T \ln \frac{\phi}{1 - \phi} - \delta ,
\]

which the Langmuir isotherm.
5. Find zero field susceptibility and mean squared fluctuations of order parameter for the system in 3D described by Landau theory with single scalar order parameter. Consider both above and below the transition cases.

Solution

Landau theory is based on the Hamiltonian

\[ F = \int \left[ a(T - T_c)\eta^2 + b\eta^4 - h\eta + c(\nabla \eta)^2 \right] d^3r , \]

where \( \eta \) is an order parameter.

(a) Fluctuations above the transition, at \( T > T_c \): the average value of \( \eta \) at \( h = 0 \) is zero, fluctuations \( \delta \eta \) are determined from the condition \( V a(T - T_c)\delta \eta^2 \sim 1 \).

(b) Fluctuations below the transition, at \( T < T_c \): the average value of \( \eta \) at \( h = 0 \) is not zero, it is determined from \( 2a(T - T_c)\eta + 4b\eta^3 = 0 \), or \( \eta = \pm \sqrt[3]{a(T_c - T)/2b} \). Fluctuations \( \delta \eta \) are determined from the condition \( (1/2)F'' \delta \eta^2 \sim 1 \), where the derivative has to be evaluated at the equilibrium value of \( \eta \); this gives \( 2V a(T_c - T)\delta \eta^2 \sim 1 \). Thus, fluctuations below the transition are twice smaller than above in Landau theory:

\[ \delta \eta^2 \sim \begin{cases} 1/Va(T - T_c) & \text{when } T > T_c \\ 1/2V a(T_c - T) & \text{when } T < T_c \end{cases} . \]

(c) Susceptibility above the transition. The equilibrium average value of \( \eta \) is determined in Landau theory by the minimization, that is, by the minimum of \( a(T - T_c)\eta^2 + b\eta^4 - h\eta \); equation for average equilibrium \( \eta \) reads

\[ 2a(T - T_c)\eta + 4b\eta^3 - h = 0 . \]

In order to get to the susceptibility we can differentiate this with respect to \( h \), remembering that \( \eta \) is now not an independent quantity, but rather the solution of the above equation, and, therefore, the function of \( h \):

\[ 2a(T - T_c)\frac{\partial \eta}{\partial h} + 12b\eta^2 \frac{\partial \eta}{\partial h} - 1 = 0 . \]

Since we want the zero field susceptibility \( \chi = \frac{\partial \eta}{\partial h} \bigg|_{h=0} \), and at zero field \( \eta = 0 \), we get \( \chi = 1/2a(T - T_c) \).

(d) Susceptibility below the transition. We go the same way as above, except now we have to plug in the non-zero value of \( \eta = \pm \sqrt[3]{a(T_c - T)/2b} \) in the term with \( b \) in the final equation; the result reads \( \chi = -1/4a(T - T_c) \). To summarize,

\[ \chi = \begin{cases} \frac{1}{2a(T - T_c)} & \text{when } T > T_c \\ \frac{1}{4a(T_c - T)} & \text{when } T < T_c \end{cases} . \]
6. Consider a system of non-interacting spins in a magnetic field $B$ pointing in the $z$-direction. The work done by the field is given by $B\Delta M_z$, with a magnetization $M_z = \mu \sum_{i=1}^{N} m_i$. For each spin, $m_i$ takes only two values, $-1/2$ and $+1/2$.

(a) Calculate the Gibbs partition function $Z(T, B, N)$ (note that the ensemble corresponding to the macrostate $(T, B, N)$ includes the work by magnetic field).

(b) Calculate the Gibbs free energy $G(T, B, N)$ and find its asymptotics at small values of magnetic field $B$.

(c) Calculate the zero field susceptibility $\chi = \frac{\partial M_z}{\partial B}|_{B=0}$ and show that it satisfies the Curie law (i.e., inversely proportional to temperature).

**Solution**

(a)

$$Z = \sum_{\{m\}} e^{\sum m_i B/T} = \left( \sum_m e^{\mu m B/T} \right)^N = \left( 2 \cosh \frac{\mu B}{2T} \right)^N \tag{25}$$

(b)

$$G = -T \ln Z = -NT \ln 2 - NT \ln \cosh \frac{\mu B}{2T} \tag{26}$$

At very small $B$, $\cosh \frac{\mu B}{2T}$ approaches 1, therefore, $G$ approaches $-NT \ln 2$, which corresponds to entropy of independent choice between two possibilities for each spin. However, this is not the required asymptotics: we need to know HOW $G$ approaches this limit. This is achieved by $\cosh x \approx 1 + x^2/2 + \ldots$. then $\ln \cosh x \approx x^2/2 + \ldots$, and so

$$G \approx -NT \ln 2 - N \frac{\mu^2}{8T} B^2 \tag{27}$$

(c)

$$\langle M_z \rangle = \frac{\partial \ln Z}{\partial (B/T)} = - \frac{\partial G}{\partial B} = \frac{N\mu}{2} \tanh \frac{\mu B}{2T} \tag{28}$$

$$\chi = \frac{\partial \langle M_z \rangle}{\partial B} \tag{29}$$

In the small $B$ asymptotics, namely, when $\mu B/T \ll 1$ or $B \ll T/\mu$ we have

$$\langle M_z \rangle \approx \frac{N\mu^2}{4T} B \quad \text{and} \quad \chi \approx \frac{N\mu^2}{4T} \tag{30}$$