Thermodynamics cont'd

1 Mean-field approximations

We begin by recapitulating the thermodynamics that was discussed in the last section. In the Grand-Canonical Ensemble, which we will use almost exclusively from now on, the partition function is of the form

$$Z(T, \mu, V) = \sum_n e^{-\beta(E_n - \mu N_n)} . \tag{1}$$

The sum goes over microstates n, with energy E_n and particle number N_n, and $\beta = 1/k_B T$, where k_B is the Boltzmann constant. The probability that the microstate n is occupied is

$$p_n = \frac{1}{Z(T, \mu, V)} e^{-\beta(E_n - \mu N_n)} . \tag{2}$$

The mean energy and particle number are then given by

$$\begin{aligned} \langle E \rangle &= \sum_n E_n p_n \\ \langle N \rangle &= \sum_n N_n p_n . \end{aligned} \tag{3}$$

The thermodynamic potential is

$$\Omega(T, \mu, V) = -k_B T \log Z(T, \mu, V) = E - TS - \mu N , \tag{4}$$

where $E = \langle E \rangle$ and $N = \langle N \rangle$ is the mean energy and mean particle number, respectively. The differentials of the thermodynamic potential are given by

$$d\Omega = -S dT - N d\mu - p dV \tag{5}$$

where p is the pressure. In a homogeneous system, the thermodynamic potential is given by

$$\Omega = -pV . \tag{6}$$

In a non-interacting system, the partition sum can be performed. The energy and particle number that enter the partition function (1) are given by

$$E_n = \sum_\ell \varepsilon_\ell \hat{n}_\ell^{(n)} \tag{7}$$

and

$$N_n = \sum_\ell \hat{n}_\ell^{(n)} \,, \tag{8}$$

where $\hat{n}_\ell^{(n)} = 0, 1, 2, 3, 4, \ldots$ for bosons and $\hat{n}_\ell^{(n)} = 0, 1$ for fermions, is the occupation number of the single-particle state ℓ in the microstate n.

One finds

$$Z_0(T, \mu, V) = \prod_\ell \frac{1}{1 - e^{-\beta(\varepsilon_\ell - \mu)}} \tag{9}$$

for bosons, and

$$Z_0(T, \mu, V) = \prod_\ell \left(1 + e^{-\beta(\varepsilon_\ell - \mu)}\right) \tag{10}$$

for fermions. Thus, the thermodynamic potential of the non-interacting quantum gas is given by

$$\Omega_0(T, \mu, V) = \mp k_B T \sum_\ell \ln(1 \pm e^{-\beta(\varepsilon_\ell - \mu)}) \,, \tag{11}$$

where the upper sign is for fermions and lower one for bosons. For a uniform system, the thermodynamic potential is proportional to the pressure, i.e., $\Omega = -pV$. Consequently, the so called thermodynamic pressure of a non-interacting gas is

$$p_0 = \pm \frac{k_B T}{V} \sum_\ell \ln(1 \pm e^{-\beta(\varepsilon_\ell - \mu)}) \,, \tag{12}$$

In such a system, we can use plane-wave states, labeled by the momentum $\vec{k}$. Setting $\vec{k}_\ell = \vec{k}$, we can convert the sum into an integral using $\sum_\ell = (V/(2\pi)^3) \int d^3k$. One then recovers the expression for the kinetic pressure by partial integration

$$p_0 = k_B T \int \frac{d^3k}{(2\pi)^3} \frac{1}{3} \vec{k} \cdot \vec{v}_k \, n_k \,, \tag{13}$$

where $n_k = 1/(e^{\beta(\varepsilon_k - \mu)} \pm 1)$.

2 Second quantization

In this section we give a very brief, and necessarily incomplete introduction to second quantization. The reader who feels uncomfortable with this admittedly sketchy treatment is referred to one of the standard textbooks on the subject [1].

[1] e.g. Fetter & Walecka, Bjorken & Drell, Itzykson & Zuber

Consider a state in many-body Hilbert space

$$|\hat{n}_1, \hat{n}_2, \ldots, \hat{n}_\infty\rangle \tag{14}$$

with $\hat{n}_1$ particles in state 1, $\hat{n}_2$ particles in state 2 etc.. We define an annihilation operator, which annihilates a particle in state k

$$\underset{\sim}{a}_k |\ldots, \hat{n}_k, \ldots\rangle = \sqrt{\hat{n}_k}\, |\ldots, \hat{n}_k - 1, \ldots\rangle \tag{15}$$

and a creation operator, which creates a particle in the state k

$$\underset{\sim}{a}_k^\dagger |\ldots, \hat{n}_k, \ldots\rangle = \sqrt{\hat{n}_k + 1}\, |\ldots, \hat{n}_k + 1, \ldots\rangle \,. \tag{16}$$

It is straightforward to verify that the operator $\underset{\sim}{n}_k = \underset{\sim}{a}_k^\dagger \, \underset{\sim}{a}_k$ counts the number of particles, i.e.,

$$\underset{\sim}{n}_k |\ldots, \hat{n}_k, \ldots\rangle = \hat{n}_k |\ldots, \hat{n}_k, \ldots\rangle \,, \tag{17}$$

where $\hat{n}_k$ denotes the number of particles in the state k. In terms of this operator, the number operator, which counts the total number of particles is $\underset{\sim}{N} = \sum_k \underset{\sim}{n}_k$ while the free Hamiltonian is

$$\underset{\sim}{H} = \sum_k \varepsilon_k \, \underset{\sim}{a}_k^\dagger \, \underset{\sim}{a}_k \,. \tag{18}$$

Thus,

$$\underset{\sim}{H}\, |\hat{n}_1, \hat{n}_2, \ldots, \hat{n}_\infty\rangle = \sum_k \varepsilon_k \, \hat{n}_k \, |\hat{n}_1, \hat{n}_2, \ldots, \hat{n}_\infty\rangle \,. \tag{19}$$

For completeness we give the commutation relations for bosons

$$\begin{aligned} \left[\underset{\sim}{a}_k, \underset{\sim}{a}_{k'}^\dagger\right] &= \underset{\sim}{a}_k \, \underset{\sim}{a}_{k'}^\dagger - \underset{\sim}{a}_k^\dagger \, \underset{\sim}{a}_{k'} = \delta_{k,k'} \\ \left[\underset{\sim}{a}_k, \underset{\sim}{a}_{k'}\right] &= \left[\underset{\sim}{a}_k^\dagger, \underset{\sim}{a}_{k'}^\dagger\right] = 0 \end{aligned} \tag{20}$$

and for fermions

$$\begin{aligned} \left\{\underset{\sim}{a}_k, \underset{\sim}{a}_{k'}^\dagger\right\} &= \underset{\sim}{a}_k \, \underset{\sim}{a}_{k'}^\dagger + \underset{\sim}{a}_k^\dagger \, \underset{\sim}{a}_{k'} = \delta_{k,k'} \\ \left\{\underset{\sim}{a}_k, \underset{\sim}{a}_{k'}\right\} &= \left\{\underset{\sim}{a}_k^\dagger, \underset{\sim}{a}_{k'}^\dagger\right\} = 0 \,. \end{aligned} \tag{21}$$

We introduce the compact notation

$$|m\rangle = |\hat{n}_1^{(m)}, \hat{n}_2^{(m)}, \ldots, \hat{n}_\infty^{(m)}\rangle \tag{22}$$

for a many-body state, where the one-body state k is occupied by $\hat{n}_k^{(m)}$ particles. In second quantization the partition function of the free system is then given by

$$\begin{aligned} Z_0(T,\mu,V) &= \sum_m \langle m| e^{-\beta \sum_k (\varepsilon_k - \mu)\, \underset{\sim}{a}_k^\dagger\, \underset{\sim}{a}_k} |m\rangle \\ &= \sum_m e^{-\beta \sum_k (\varepsilon_k - \mu) \hat{n}_k^{(m)}}\,, \end{aligned} \tag{23}$$

where the second line is obtained by using the fact that $|m\rangle$ is an eigenstate of $\underset{\sim}{n}_k$. Using the fact that $\hat{n}_k^{(m)} = \{0,1\}$ for fermions and $\hat{n}_k^{(m)} = \{0,1,2,3,\ldots\}$ for bosons, we recover the partion functions for the free Bose-Einstein and Fermi-Dirac gases (9) and (10).

3 Including interactions

In this section we discuss how one can include the effect of interactions in the partition sum in the so called mean-field approximation. We consider a uniform system of interacting fermions. As a single particle basis it is convenient to use eigenstates of the momentum operator, i.e., plane waves. For a system of volume V, these are

$$\frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}\,. \tag{24}$$

At the end of the calculation one can take the limit $V \to \infty$. Thus, the single particle states are labeled by the momentum $\vec{k}$. In order not to overload the equations, we will in general suppress the arrow on the momentum. Since it usually should be clear what is meant, we hope that this will not lead to confusion.

We start by considering a system consisting of non-relativistic particles. To be concrete, we consider a system of fermions, described by the Hamiltonian

$$\underset{\sim}{H} = \sum_k \varepsilon_k \underset{\sim}{a}_k^\dagger\, \underset{\sim}{a}_k + \frac{1}{2} \sum_{k,k',q} V(q)\, \underset{\sim}{a}_{k+q}^\dagger\, \underset{\sim}{a}_{k'-q}^\dagger\, \underset{\sim}{a}_{k'}\, \underset{\sim}{a}_k\,, \tag{25}$$

where the sum over k includes possible sums over internal degrees of freedom like spin and isospin. The partition sum, which is given by

$$Z(T,\mu,V) = \sum_m \langle m| e^{-\beta(\underset{\sim}{H} - \mu\, \underset{\sim}{N})} |m\rangle \tag{26}$$

is formally expanded

$$Z(T,\mu,V) = \sum_m \langle m|[1-\beta(\underset{\sim}{H}-\mu\,\underset{\sim}{N}) + \frac{1}{2}\beta(\underset{\sim}{H}-\mu\,\underset{\sim}{N})\sum_n |n\rangle\langle n|\beta(\underset{\sim}{H}-\mu\,\underset{\sim}{N}) + \ldots]|m\rangle\,, \tag{27}$$

where we have introduced a complete set of states in the second-order term. We restrict the sum over n to the term with $n=m$. This is the first step in obtaining a mean-field approximation. Then one can resum the exponential

$$Z(T,\mu,V) \simeq \sum_m e^{-\beta\langle m|\underset{\sim}{H}-\mu\underset{\sim}{N}|m\rangle}\,. \tag{28}$$

We now have to compute expectation values of the Hamiltonian. It is easily seen that only matrix elements involving $\hat{n}_k^{(m)} = \langle m|\underset{\sim}{n}_k|m\rangle$ are non-zero. One finds

$$\langle m|\underset{\sim}{H}|m\rangle = \sum_k \varepsilon_k^0 \hat{n}_k^{(m)} + \frac{1}{2}\sum_{kk'}\left[V(0)-\frac{1}{\nu}V(k-k')\right]\hat{n}_k^{(m)}\hat{n}_{k'}^{(m)}\,, \tag{29}$$

where ν is the spin and isospin degeneracy. In symmetric nuclear matter $\nu=4$, while in neutron matter $\nu=2$. In order to simplify things, we introduce the notation $U(k-k') = V(0) - \frac{1}{\nu}V(k-k')$.

The partition sum, as it stands, cannot be performed analytically. Thus, in order to perform the partition sum, we linearize in the difference between the occupation number and its average, $\delta_k^{(m)} = \hat{n}_k^{(m)} - \bar{n}_k$. Only the interaction term, which is quadratic in $\hat{n}_k^{(m)}$ needs to be linearized. Thus, we write

$$\begin{aligned}\hat{n}_k^{(m)}\hat{n}_{k'}^{(m)} &= \bar{n}_k\bar{n}_{k'} + \bar{n}_k\delta_{k'}^{(m)} + \bar{n}_{k'}\delta_k^{(m)} + \delta_k^{(m)}\delta_{k'}^{(m)} \\ &\simeq \bar{n}_k\hat{n}_{k'}^{(m)} + \bar{n}_{k'}\hat{n}_k^{(m)} - \bar{n}_k\bar{n}_{k'}\,,\end{aligned} \tag{30}$$

where we have dropped terms of second order in $\delta_k^{(m)}$ in the second line. Using the fact that $U(k,k') = U(k',k)$, one then finds

$$\begin{aligned}\langle m|\underset{\sim}{H}|m\rangle &= \sum_k\left[\varepsilon_k^0 + \sum_k U(k,k')\bar{n}_{k'}\right]\hat{n}_k^{(m)} \\ &- \frac{1}{2}\sum_{kk'}U(k,k')\bar{n}_k\bar{n}_{k'}\,.\end{aligned} \tag{31}$$

which we determine below. The term in square brackets we identify with the in-medium single particle energy

$$\varepsilon_k = \varepsilon_k^0 + \sum_{k'}U(k,k')\bar{n}_{k'}\,. \tag{32}$$

Now, the partition function in the mean-field approximation is given by

$$Z_{mf}(T,\mu,V;\{\bar{n}_k\}) = e^{\frac{\beta}{2}\sum_{kk'} U(k,k')\bar{n}_k\bar{n}_{k'}} \sum_m e^{-\beta\sum_k(\varepsilon_k-\mu)\hat{n}_k^{(m)}}\,, \tag{33}$$

where we have indicated that the partition function depends on the mean occupation numbers $\{\bar{n}_k\}$. The partition sum can now be performed, just like in the free case

$$Z_{mf}(T,\mu,V;\{\bar{n}_k\}) = e^{\frac{\beta}{2}\sum_{kk'} U(k,k')\bar{n}_k\bar{n}_{k'}} \prod_k (1+e^{-\beta(\varepsilon_k-\mu)})\,, \tag{34}$$

and one finds the thermodynamic potential in the mean-field approximation

$$\begin{aligned}\bar{\Omega}_{mf}(T,\mu,V;\{\bar{n}_k\}) &= -k_B T \ln Z_{mf}(T,\mu,V;\{\bar{n}_k\}) \\ &= -\frac{1}{2}\sum_{kk'} U(k,k')\bar{n}_k\bar{n}_{k'} - k_B T\sum_k \ln(1+e^{-\beta(\varepsilon_k-\mu)})\end{aligned} \tag{35}$$

Here, the average occupation numbers $\{\bar{n}_k\}$ are a set of parameters, that should be determined by minimizing the thermodynamic potential. Remembering that the in-medium single-particle energy ε_k depends on $\bar{n}_k$, we find

$$\frac{\delta\bar{\Omega}}{\delta\bar{n}_k} = -\sum_{k'} U(k,k')\left[\bar{n}_{k'} - \frac{1}{e^{\beta(\varepsilon_{k'}-\mu)}+1}\right] = 0\,. \tag{36}$$

We note that the last equality holds for any potential $U(k,k')$ if the term in square brackets vanishes. Thus, we finally arrive at the Fermi-Dirac distribution with an in-medium single-particle energy

$$n_k = \frac{1}{e^{\beta(\varepsilon_k-\mu)}+1}\,. \tag{37}$$

The mean-field thermodynamic potential is then given by $\bar{\Omega}$, evaluated at the stationary point, where (37) is satisfied

$$\Omega_{mf}(T,\mu,V) = -\frac{1}{2}\sum_{kk'} U(k,k')n_k n_{k'} - k_B T\sum_k \ln(1+e^{-\beta(\varepsilon_k-\mu)})\,. \tag{38}$$

Note that eq. (37) is an implicit equation for the distribution function, since the single particle energy depends on n_k. This reflects the fact that the mean-field approximation is a self consistent approximation. We will return to this point later, when we discuss the diagrammatic interpretation of the mean-field approximation.

As a consequence of the stationarity (36), Ω_{mf} has some nice properties. For instance, the average particle number is given by

$$N = -\frac{\partial \Omega}{\partial \mu} = \sum_k \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1} = \sum_k n_k \, . \tag{39}$$

Here, the implicit dependence on μ through the Fermi-Dirac distribution does not contribute. This is because it gives rise to terms of the form

$$\sum_k \frac{\delta \Omega}{\delta n_k} \frac{\partial n_k}{\partial \mu} \, , \tag{40}$$

which vanish because of (36). Similarly, one finds for the entropy

$$\begin{aligned} S &= -\frac{\partial \Omega}{\partial T} = k_B \sum_k \left[\ln(1 + e^{-\beta(\varepsilon_k - \mu)}) + \beta(\varepsilon_k - \mu) n_k \right] \\ &= -k_B \sum_k \left[n_k \ln n_k + (1 - n_k) \ln(1 - n_k) \right] \, , \end{aligned} \tag{41}$$

which is the expression for the entropy of a non-interacting Fermi gas, except that the occupation numbers n_k depend on the in-medium single-particle energies ε_k. This form of the entropy is characteristic for a mean-field approximation, since the particle move as independent particles in a static field. Corrections to this general form of the entropy appear when correlations are taken into account.