# Method of Lagrange multiplier for Fermi-Dirac and Bose Einstein Statistics Masatsugu Sei Suzuki <br> Department of Physics, SUNY at Binghamton <br> (Date: October 22, 2018) 

The distribution function for the fermion and boson systems is derived using the variational method.

## 1. Distribution function for fermions

The fermion system obeys the Pauli exclusion principle. For each state, there is no more than one particle. In order to apply the Lagrange multiplier method in the statistics in the fermion system, it is useful to introduce the concept of the density of states. We consider the particles having energy between $\varepsilon_{j}$ and $\varepsilon_{j}+\Delta \varepsilon$. The number of particles is given by

$$
N_{j}=D\left(\varepsilon_{j}\right) \Delta \varepsilon
$$

where $\Delta \varepsilon$ is constant and is chosen appropriately. Suppose that there are $M_{j}$ particles in this energy range. So the total energy is $M_{j} \varepsilon_{j}$.


For the total number $N_{j}$,

$$
\begin{aligned}
\left(1+x_{j}\right)\left(1+x_{j}\right) \ldots\left(1+x_{j}\right) \ldots & =\left(1+x_{j}\right)^{N_{j}} \\
& =\sum_{M_{j}=0}^{N_{j}} \frac{N_{j}!}{M_{j}!\left(N_{j}-M_{j}\right)!}\left(x_{j}\right)^{M_{j}}
\end{aligned}
$$

where $1+x_{j}$ means the state with the zero atom (1) and the state with the one atom $\left(x_{j}\right)$. The coefficient of $\left(x_{j}\right)^{M_{j}}$ in the expansion $\left(1+x_{j}\right)^{N_{j}}$ is given by

$$
W\left(N_{j}, M_{j}\right)=\frac{N_{j}!}{M_{j}!\left(N_{j}-M_{j}\right)!}
$$





Fig. There are $N_{j}$ atoms. Each atom is in either empty state or one-atom state with the energy between $\varepsilon_{j}$ and $\varepsilon_{j}+\Delta \varepsilon$. No other energy states are here. The occupied state with the energy between $\varepsilon_{j}$ and $\varepsilon_{j}+\Delta \varepsilon$ is denoted by red solid circles. The empty state is denoted
by blue circles. The number of atoms denoted by red solid circles is $M_{j}$. The occupation probability is $\bar{n}_{j}=\frac{M_{j}}{N_{j}}$. The number of ways in the case when $M_{\mathrm{j}}$ atoms (with the same energy $\varepsilon_{j}$ ) among $N_{\mathrm{j}}$ atoms. So the energy of this subsystem is $M_{j} \varepsilon_{j}$


Fig. $M_{j}$ particles are occupied in the energy level $\varepsilon_{j}$ (one-particle energy). The total number of states in this energy level number is $N_{j}$. The total energy is $M_{j} \varepsilon_{j}$.

There are $M_{j}$ atoms in the energy level with $M_{j} \varepsilon_{j}$. In the Fermi case there can be no more than one particle in each quantum state (Pauli exclusion principle), but the numbers $M_{j}$ are not small, and are in general of the same order of magnitude as the numbers $N_{j}$. The number of possible ways of distributing $M_{j}$ identical particles among $N_{j}$ states with not more than one particle in each is just the number of ways of selecting $M_{j}$ of the $N_{j}$ states, i.e., the number of combinations of $N_{j}$ things $M_{j}$ at a time. Thus

$$
W\left(N_{j}, M_{j}\right)=\frac{N_{j}!}{M_{j}!\left(N_{j}-M_{j}\right)!}
$$

Taking the logarithm of this expression and using the Stirling's law,

$$
\begin{aligned}
\frac{S}{k_{B}} & =\sum_{j} \ln \left[W\left(N_{j}, M_{j}\right)\right] \\
& =\sum_{j} \ln \left[\frac{N_{j}!}{M_{j}!\left(N_{j}-M_{j}\right)!}\right] \\
& =\sum_{j}\left[N_{j} \ln N_{j}-N_{j}-M_{j} \ln M_{j}+M_{j}-\left(N_{j}-M_{j}\right) \ln \left(N_{j}-M_{j}\right)+N_{j}-M_{j}\right] \\
& =\sum_{j}\left[N_{j} \ln N_{j}-M_{j} \ln M_{j}-\left(N_{j}-M_{j}\right) \ln \left(N_{j}-M_{j}\right)\right]
\end{aligned}
$$

Using the mean occupation numbers of the quantum states,

$$
\bar{n}_{j}=\frac{M_{j}}{N_{j}}
$$

the entropy $S$ can be rewritten as

$$
\frac{S}{k_{B}}=-\sum_{j} N_{j}\left[\bar{n}_{j} \ln \bar{n}_{j}+\left(1-\bar{n}_{j}\right) \ln \left(1-\bar{n}_{j}\right)\right]
$$

So we have the following expression for the entropy of a Fermi gas not in equilibrium. In thermal equilibrium, the most probable value of $\bar{n}_{j}$ is given by maximizing in $\ln W$ under the condition that $E$ and $N$ are kept constant

$$
E=\sum_{j} \varepsilon_{j} M_{j}=N \sum_{j} \varepsilon_{j} \bar{n}_{j}, \quad N=\sum_{j} M_{j}=N_{j} \sum_{j} \bar{n}_{j}
$$

Then we have

$$
\frac{\partial}{\partial \bar{n}_{j}}\left(\frac{S}{k_{B}}-\beta E-\alpha N\right)=0
$$

or

$$
\frac{\partial}{\partial \bar{n}_{j}}\left[-\bar{n}_{j} \ln \bar{n}_{j}-\left(1-\bar{n}_{j}\right) \ln \left(1-\bar{n}_{j}\right)-\beta \varepsilon_{j} \bar{n}_{j}-\alpha \bar{n}_{j}\right]=0
$$

or

$$
-\ln \bar{n}_{j}+\ln \left(1-\bar{n}_{j}\right)=\alpha+\beta \varepsilon_{j}
$$

or

$$
\frac{\bar{n}_{j}}{1-\bar{n}_{j}}=\exp \left(-\alpha-\beta \varepsilon_{j}\right)
$$

where $\alpha$ and $\beta$ are indeterminate multipliers. Then the equilibrium distribution is obtained by the formula

$$
\bar{n}_{j}=\frac{1}{e^{\alpha+\beta \varepsilon_{j}}+1},
$$

which is the Fermi-Dirac distribution function. We choose

$$
\beta=\frac{1}{k_{B} T}, \quad \alpha=-\varepsilon \mu
$$

Then we have

$$
\bar{n}_{j}=\frac{1}{e^{\beta\left(\varepsilon_{j}-\mu\right)}+1}
$$

((Determination of $\alpha$ and $\beta)$ )
We start with the expression of the entropy

$$
\frac{S}{k_{B}}=-\sum_{j} N_{j}\left[\bar{n}_{j} \ln \bar{n}_{j}+\left(1-\bar{n}_{j}\right) \ln \left(1-\bar{n}_{j}\right)\right]
$$

$$
\begin{aligned}
-\bar{n}_{j} \ln \bar{n}_{j}-\left(1-\bar{n}_{j}\right) \ln \left(1-\bar{n}_{j}\right) & =-\bar{n}_{j} \ln \bar{n}_{j}+\bar{n}_{j} \ln \left(1-\bar{n}_{j}\right)-\ln \left(1-\bar{n}_{j}\right) \\
& =-\bar{n}_{j} \ln \left(\frac{\bar{n}_{j}}{1-\bar{n}_{j}}\right)-\ln \left(1-\bar{n}_{j}\right) \\
& =\bar{n}_{j} \ln \left(\frac{1-\bar{n}_{j}}{\bar{n}_{j}}\right)+\ln \left(\frac{1}{1-\bar{n}_{j}}\right) \\
& =\frac{\alpha+\beta \varepsilon_{j}}{1+e^{\alpha+\beta \varepsilon_{j}}}+\ln \left[1+e^{-\left(\alpha+\beta \varepsilon_{j}\right)}\right]
\end{aligned}
$$

Thus we have

$$
\begin{aligned}
S & =k_{B} \sum_{j} N_{j}\left\{\frac{\alpha+\beta \varepsilon_{j}}{1+e^{\alpha+\beta \varepsilon_{j}}}+\ln \left[1+e^{-\left(\alpha+\beta \varepsilon_{j}\right)}\right]\right\} \\
& =k_{B}(\alpha N+\beta U)+k_{B} \sum_{j} N_{j} \ln \left[1+e^{-\left(\alpha+\beta \varepsilon_{j}\right)}\right]
\end{aligned}
$$

where

$$
\begin{aligned}
& N=\sum_{j} N_{j} \bar{n}_{j}=\sum_{j} \frac{N_{j}}{1+e^{\alpha+\beta \varepsilon_{j}}}, \\
& U=\sum_{j} N_{j} \varepsilon_{j} \bar{n}_{j}=\sum_{j} \frac{N_{j} \varepsilon_{j}}{1+e^{\alpha+\beta \varepsilon_{j}}}
\end{aligned}
$$

We note that

$$
\begin{aligned}
\frac{\partial S}{\partial U} & =k_{B}\left(\frac{\partial \alpha}{\partial U} N+\beta+U \frac{\partial \beta}{\partial U}\right) \\
& -k_{B} \sum_{j} N_{j} \frac{e^{-\left(\alpha+\beta \varepsilon_{j}\right)}}{1+e^{-\left(\alpha+\beta \varepsilon_{j}\right)}}\left[\frac{\partial \alpha}{\partial U}+\frac{\partial \beta}{\partial U} \varepsilon_{j}\right] \\
& =k_{B}\left(\frac{\partial \alpha}{\partial U} N+\beta+U \frac{\partial \beta}{\partial U}\right) \\
& -k_{B} \sum_{j} N_{j} \bar{n}_{j}\left[\frac{\partial \alpha}{\partial U}+\frac{\partial \beta}{\partial U} \varepsilon_{j}\right] \\
& =k_{B}\left(\frac{\partial \alpha}{\partial U} N+\beta+U \frac{\partial \beta}{\partial U}\right)-k_{B}\left(N \frac{\partial \alpha}{\partial U}+\frac{\partial \beta}{\partial U} U\right) \\
& =k_{B} \beta
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial S}{\partial N} & =k_{B}\left(\alpha+N \frac{\partial \alpha}{\partial N}+U \frac{\partial \beta}{\partial N}\right) \\
& -k_{B} \sum_{j} N_{j} \frac{e^{-\left(\alpha+\beta \varepsilon_{j}\right)}}{1+e^{-\left(\alpha+\beta \varepsilon_{j}\right)}}\left[\frac{\partial \alpha}{\partial N}+\frac{\partial \beta}{\partial N} \varepsilon_{j}\right] \\
& =k_{B}\left(\alpha+N \frac{\partial \alpha}{\partial N}+U \frac{\partial \beta}{\partial U}\right) \\
& -k_{B} \sum_{j} N_{j} \bar{n}_{j}\left(\frac{\partial \alpha}{\partial N}+\frac{\partial \beta}{\partial N} \varepsilon_{j}\right) \\
& =k_{B}\left(\alpha+N \frac{\partial \alpha}{\partial N}+U \frac{\partial \beta}{\partial U}\right)-k_{B}\left(N \frac{\partial \alpha}{\partial N}+U \frac{\partial \beta}{\partial N}\right) \\
& =k_{B} \alpha
\end{aligned}
$$

Using the thermodynamic relation,

$$
d S=\frac{1}{T} d U+\frac{P}{T} d V-\frac{\mu}{T} d N
$$

we have

$$
\begin{aligned}
& \left(\frac{\partial S}{\partial U}\right)=k_{B} \beta=\frac{1}{T} \\
& \left(\frac{\partial S}{\partial N}\right)=k_{B} \alpha=-\frac{\mu}{T}
\end{aligned}
$$

leading to

$$
\beta=\frac{1}{k_{B} T}, \quad \alpha=-\frac{\mu}{k_{B} T}=-\beta \mu
$$

((Note))
I learned this method in the class of Semiconductor Physics, when I was a sophomore student. In the first day, my teacher (Prof. Umejiro Yoshida) explained the Schrödinger equation for free electrons and electron states in the quantum box. In the second day of the class, he explained the Fermi-Dirac distribution function using above method. I did not understand the significant point of this method since I was not familiar with the Pauli exclusion principle, the difference between boson and fermion, the grand canonical ensemble, and so on. After 40 years, I realize that this
method is one of the best ways to teach the physics of semiconductor for beginners who are not familiar with the principle of statistical thermodynamics.

## 2. Distribution function for bosons

For bosons, there is no limitation on the number of atoms occupied on each state. We consider a state with energy $\varepsilon_{j}$. In this state, there are more than one particles denoted by $s(s=1,2,3, \ldots$, $\left.N_{j}\right)$. The $s$-th particle is in the $\left|m_{s}\right\rangle$ state with the energy $m_{s} \varepsilon_{j}$. The total energy is

$$
M_{j} \varepsilon_{j}=\left(m_{1}+m_{2}+\ldots\right) \varepsilon_{j}
$$

For the total number $N_{j}$,

$$
\begin{aligned}
\left(1+x_{j}+x_{j}^{2}+\ldots\right)^{N_{j}} & =\left(1-x_{j}\right)^{-N_{j}} \\
& =\sum_{M_{j}=0}^{N_{j}} \frac{\left(N_{j}-1+M_{j}\right)!}{M_{j}!\left(N_{j}-1\right)!}\left(x_{j}\right)^{M_{j}}
\end{aligned}
$$

In the expansion $\left(1+x_{j}+x_{j}^{2}+\ldots.\right)=\left(1-x_{j}\right)^{-1},\left(x_{j}\right)^{n}$ is the state with $n$ atoms, where $n$ is an integer between 0 and infinity. The coefficient of $\left(x_{j}\right)^{M_{j}}$ in the expansion is

$$
W\left(N_{j}, M_{j}\right)=\frac{\left(N_{j}-1+M_{j}\right)!}{M_{j}!\left(N_{j}-1\right)!}
$$

We take the logarithm of this expression and neglecting unity in comparison with the very large numbers $N_{j}+M_{j}$ and $M_{j}$. Using the Stirling's approximation, we have

$$
\begin{aligned}
\frac{S}{k_{B}} & =\sum_{j} \ln \left[W\left(N_{j}, M_{j}\right)\right] \\
& =\sum_{j} \ln \left[\frac{\left(N_{j}-1+M_{j}\right)!}{M_{j}!\left(N_{j}-1\right)!}\right] \\
& \approx \sum_{j} \ln \left[\frac{\left(N_{j}+M_{j}\right)!}{M_{j}!N_{j}!}\right] \\
& =\sum_{j}\left[\left(N_{j}+M_{j}\right) \ln \left(N_{j}+M_{j}\right)-\left(N_{j}+M_{j}\right)-M_{j} \ln M_{j}+M_{j}-N_{j} \ln N_{j}+N_{j}\right] \\
& =\sum_{j}\left[\left(N_{j}+M_{j}\right) \ln \left(N_{j}+M_{j}\right)-M_{j} \ln M_{j}-N_{j} \ln N_{j}\right]
\end{aligned}
$$

Using the mean occupation numbers of the quantum states,

$$
\bar{n}_{j}=\frac{M_{j}}{N_{j}}
$$

the entropy $S$ can be rewritten as

$$
\frac{S}{k_{B}}=\sum_{j} N_{j}\left[\left(\bar{n}_{j}+1\right) \ln \left(\bar{n}_{j}+1\right)-\bar{n}_{j} \ln \bar{n}_{j}\right]
$$

So we have the following expression for the entropy of a Bose gas not in equilibrium. In thermal equilibrium, the most probable value of $\bar{n}_{j}$ is given by maximizing in $\ln W$ under the condition that $E$ and $N$ are kept constant

$$
\begin{aligned}
& E=\sum_{j} \varepsilon_{j} M_{j}=N_{j} \sum_{j} \varepsilon_{j} \bar{n}_{j}, \\
& N=\sum_{j} M_{j}=N_{j} \sum_{j} \bar{n}_{j}
\end{aligned}
$$

Note that $M_{\mathrm{j}}$ is the number of bosons with the energy $\varepsilon_{j}$.
((Note)) Derivation of the formula: $\quad W\left(N_{j}, M_{j}\right)=\frac{\left(N_{j}-1+M_{j}\right)!}{M_{j}!\left(N_{j}-1\right)!}$
We consider an example. Suppose that that $|2\rangle$ with energy $2 \varepsilon_{j}=2 \hbar \omega_{j},|5\rangle$ with energy $5 \varepsilon_{j}=5 \hbar \omega_{j},|0\rangle$ with energy $0 \varepsilon_{j}=0 \hbar \omega_{j},|3\rangle$ with energy $3 \varepsilon_{j}=3 \hbar \omega_{j}$, and $|1\rangle$ with energy $1 \varepsilon_{j}=1 \hbar \omega_{j}$

which is equivalent to

where the barrier is denoted by black mark (4). It follows that there are $2+5+0+3+1=11$ bosons (red mark) with the energy $\varepsilon_{j}=\hbar \omega_{j} ; \frac{(11+4-1)!}{11!(5-1)!}=\frac{14!}{11!4!}=91$

Then we have

$$
\frac{\partial}{\partial \bar{n}_{j}}\left(\frac{S}{k_{B}}-\beta E-\alpha N\right)=0,
$$

or

$$
\frac{\partial}{\partial \bar{n}_{j}}\left[\left(\bar{n}_{j}+1\right) \ln \left(\bar{n}_{j}+1\right)-\bar{n}_{j} \ln \bar{n}_{j}-\beta \varepsilon_{j} \bar{n}_{j}-\alpha \bar{n}_{j}\right]=0
$$

or

$$
\ln \left(\bar{n}_{j}+1\right)-\ln \bar{n}_{j}=\alpha+\beta \varepsilon_{j}
$$

or

$$
\frac{1+\bar{n}_{j}}{\bar{n}_{j}}=\exp \left(\alpha+\beta \varepsilon_{j}\right)
$$

where $\alpha$ and $\beta$ are indeterminate multipliers. Thus the equilibrium distribution is given by the formula

$$
\bar{n}_{j}=\frac{1}{e^{\alpha+\beta \varepsilon_{j}}-1}
$$

which is the Bose-Einstein distribution function, where

$$
\beta=\frac{1}{k_{B} T}, \quad \alpha=-\beta \mu
$$

((Determination of $\alpha$ and $\beta)$ )
Entropy

$$
\begin{aligned}
S & =k_{B} \sum_{j} N_{j}\left[\left(\bar{n}_{j}+1\right) \ln \left(\bar{n}_{j}+1\right)-\bar{n}_{j} \ln \bar{n}_{j}\right] \\
& =k_{B} \sum_{j} N_{j}\left[\bar{n}_{j} \ln \left(\frac{\bar{n}_{j}+1}{\bar{n}_{j}}\right)+\ln \left(\bar{n}_{j}+1\right)\right]
\end{aligned}
$$

Thus we have

$$
\begin{aligned}
S & =k_{B} \sum_{j} N_{j}\left\{\frac{\alpha+\beta \varepsilon_{j}}{e^{\alpha+\beta \varepsilon_{j}}-1}-\ln \left[1-e^{-\left(\alpha+\beta \varepsilon_{j}\right)}\right]\right\} \\
& =k_{B}(\alpha N+\beta U)-k_{B} \sum_{j} N_{j} \ln \left[1-e^{-\left(\alpha+\beta \varepsilon_{j}\right)}\right]
\end{aligned}
$$

where

$$
\begin{aligned}
& N=\sum_{j} N_{j} \bar{n}_{j}=\sum_{j} \frac{N_{j}}{e^{\alpha+\beta \varepsilon_{j}}-1}, \\
& U=\sum_{j} N_{j} \varepsilon_{j} \bar{n}_{j}=\sum_{j} \frac{N_{j} \varepsilon_{j}}{e^{\alpha+\beta \varepsilon_{j}}-1}
\end{aligned}
$$

We note that

$$
\begin{aligned}
\frac{\partial S}{\partial U} & =k_{B}\left(\frac{\partial \alpha}{\partial U} N+\beta+U \frac{\partial \beta}{\partial U}\right) \\
& -k_{B} \sum_{j} N_{j} \frac{e^{-\left(\alpha+\beta \varepsilon_{j}\right)}}{1-e^{-\left(\alpha+\beta \varepsilon_{j}\right)}}\left[\frac{\partial \alpha}{\partial U}+\frac{\partial \beta}{\partial U} \varepsilon_{j}\right] \\
& =k_{B}\left(\frac{\partial \alpha}{\partial U} N+\beta+U \frac{\partial \beta}{\partial U}\right) \\
& -k_{B} \sum_{j} N_{j} \bar{n}_{j}\left[\frac{\partial \alpha}{\partial U}+\frac{\partial \beta}{\partial U} \varepsilon_{j}\right] \\
& =k_{B}\left(\frac{\partial \alpha}{\partial U} N+\beta+U \frac{\partial \beta}{\partial U}\right)-k_{B}\left(N \frac{\partial \alpha}{\partial U}+\frac{\partial \beta}{\partial U} U\right) \\
& =k_{B} \beta
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial S}{\partial N} & =k_{B}\left(\alpha+N \frac{\partial \alpha}{\partial N}+U \frac{\partial \beta}{\partial N}\right) \\
& -k_{B} \sum_{j} N_{j} \frac{e^{-\left(\alpha+\beta \varepsilon_{j}\right)}}{1-e^{-\left(\alpha+\beta \varepsilon_{j}\right)}}\left[\frac{\partial \alpha}{\partial N}+\frac{\partial \beta}{\partial N} \varepsilon_{j}\right] \\
& =k_{B}\left(\alpha+N \frac{\partial \alpha}{\partial N}+U \frac{\partial \beta}{\partial U}\right) \\
& -k_{B} \sum_{j} N_{j} \bar{n}_{j}\left[\frac{\partial \alpha}{\partial N}+\frac{\partial \beta}{\partial N} \varepsilon_{j}\right] \\
& =k_{B}\left(\alpha+N \frac{\partial \alpha}{\partial N}+U \frac{\partial \beta}{\partial U}\right)-k_{B}\left(N \frac{\partial \alpha}{\partial N}+U \frac{\partial \beta}{\partial N}\right) \\
& =k_{B} \alpha
\end{aligned}
$$

Using the thermodynamic relation,

$$
d S=\frac{1}{T} d U+\frac{P}{T} d V-\frac{\mu}{T} d N
$$

we have

$$
\begin{aligned}
& \left(\frac{\partial S}{\partial U}\right)=k_{B} \beta=\frac{1}{T} \\
& \left(\frac{\partial S}{\partial N}\right)=k_{B} \alpha=-\frac{\mu}{T}
\end{aligned}
$$

leading to

$$
\beta=\frac{1}{k_{B} T}, \quad \alpha=-\frac{\mu}{k_{B} T}
$$

## 3. Grand canonical system (Robertson)

In the grand canonical formalism, the entropy is given as usual as

$$
S=-k_{B} \sum_{i} p_{i} \ln p_{i}
$$

and maximized subject to the conditions,

$$
\begin{aligned}
& U=\sum_{i} p_{i} E_{i} \\
& 1=\sum_{i} p_{i} \\
& N=\sum_{i} p_{i} N_{i}
\end{aligned}
$$

the final condition corresponding to an indeterminacy in the number of particles, and generalizable to more than one species of particle. $N_{i}$ represents the number of particles in the system when its state is designated by the subscript i . When S is maximized, the $p_{i}{ }^{\prime} s$ are found to be

$$
p_{i}(N)=\frac{1}{Z_{G}} \exp \left(\beta \mu N-\beta E_{i}\right)=\frac{1}{Z_{G}} z^{N} \exp \left[-\beta E_{i}(N)\right]
$$

where $Z_{G}$ is the partition function of the grand canonical ensemble. The entropy S is obtained as

$$
\begin{aligned}
S & =-k_{B} \sum_{N} \sum_{i} p_{i}(N) \ln p_{i}(N) \\
& =-k_{B} \sum_{N} \sum_{i} p_{i}(N)\left[N \ln z-\ln Z_{G}-\beta E_{i}(N)\right]+ \\
& =-k_{B} \beta \mu\langle N\rangle_{G}+k_{B} \ln Z_{G}+k_{B} \beta U \\
& =\frac{U-\mu\langle N\rangle_{G}}{T}+k_{B} \ln Z_{G}
\end{aligned}
$$

or

$$
S T=U-\mu\langle N\rangle_{G}+k_{B} T \ln Z_{G}
$$

or

$$
U-S T-\mu\langle N\rangle_{G}=-k_{B} T \ln Z_{G}
$$

or

$$
F-G=-k_{B} T \ln Z_{G}=-P V
$$

or

$$
P V=k_{B} T \ln Z_{G}=-\Phi_{G}
$$

## REFERENCES

M. Toda, R. Kubo and N. Saito, Statistical Physics I; Equilibrium Statistical Mechanics Springer, 1983).
L.D. Landau and E.M. Lifshitz, Statistical Physics (Pergamon Press, 1980).
D. ter Haar, Elements of statistical mechanics, third edition (Butterworth Heinemann, 1995).
H.S. Robertson, Statistical Thermodynamics (PRP Prentice Hall, 1993).

