Formulars in Statistical Physics[*]

A.I.B[1,2]

[1]College of Life Science, ZheJiang University
[2]Insititude of Quantitative Biology, ZheJiang University

January 1, 2024

1 Maxwell-Bolztmann Distribution

1.1 Maximum likelihood distribution

$$E = \sum_{i=1}^{M} \varepsilon_i$$
$$N = \sum_{\lambda} a_\lambda \tag{1.1}$$
$$E = \sum_{\lambda} \varepsilon_\lambda a_\lambda$$

Suppose the probability is proportional to the number of microstates,use a_λ to represent the distribution of particles according to energy levels and g_λ to represent the degeneracy:

$$P(\{a_\lambda\}) \propto W(\{a_\lambda\}) \tag{1.2}$$

To maxmize the W, there should be:

$$\delta ln W(a_\lambda) = 0 \tag{1.3}$$

And without Pauli exclusion principle, we can write:

$$W(\{a_\lambda\}) = \frac{N!}{\prod_\lambda a_\lambda} \prod_\lambda g_\lambda^{a_\lambda} \tag{1.4}$$

The first term indicates two particals can swap between energy levels, and the second term indicates the swap within the energy levels.

Stirling's Formula

$$ln N! = N(ln N - 1) \ (N \to \infty) \tag{1.5}$$

Use Stirling's Formula, we can deduce from (1.4)and(1.3):

$$-\sum_\lambda ln(\frac{a_\lambda}{g_\lambda})\delta a_\lambda = 0$$
$$\widetilde{a_\lambda} = g_\lambda e^{-\alpha - \beta\varepsilon_\lambda} \tag{1.6}$$

---

[*]This note is Based on LinZongHan *Thermodynamics and Statistical Physics and Pathria*

1.2 Macroscopic thermodynamic quantities

Define subsystem partition function Z as:

$$Z = \sum_{\lambda} g_{\lambda} e^{-\beta \varepsilon_{\lambda}} \tag{1.7}$$

We can obtain thermodynamic quantities from the partition function($\beta = \frac{1}{kT}$):

$$E = -N\frac{\partial}{\partial \beta} lnZ$$
$$\overline{Y_l} = -\frac{N}{\beta}\frac{\partial}{\partial y_l} lnZ \tag{1.8}$$
$$S = Nk(lnZ - \beta\frac{\partial}{\partial \beta} lnZ)$$

And specifically, let $y_l = V$:

$$p = -\frac{N}{\beta}\frac{\partial}{\partial V} lnZ \tag{1.9}$$

Also, we can dudece from the fundamental equation of thermodynamics:

$$dQ = d\overline{E} - \sum_{l} \overline{Y_l} dy_l$$
$$= \sum_{\lambda} \varepsilon_{\lambda} d\overline{a_{\lambda}} + \sum_{\lambda} a_{\lambda} d\varepsilon_{\lambda} - \sum_{l} \overline{Y_l} dy_l \tag{1.10}$$

$$\sum_{\lambda} a_{\lambda} d\varepsilon_{\lambda} = d(\sum_{\lambda} \varepsilon_{\lambda} a_{\lambda}) - \sum_{l} \overline{Y_l} dy_l$$
$$= \sum_{\lambda}(\sum_{l} \frac{\partial \varepsilon_{\lambda}}{\partial y_l} dy_l)\overline{a_{\lambda}}$$
$$= \sum_{l}(\sum_{\lambda} \frac{\partial \varepsilon_{\lambda}}{\partial y_l} da_{\lambda})\overline{a_{\lambda}} \tag{1.11}$$
$$= \sum_{l} \overline{Y_l} dy_l$$

Thus:

$$dQ = \sum_{\lambda} \varepsilon_{\lambda} d\overline{a_{\lambda}} \tag{1.12}$$

In above we use the relationship:

$$\overline{Y_l} = \frac{\partial E}{\partial y_l} = \sum_{\lambda} \frac{\partial \varepsilon_{\lambda}}{\partial y_l}\overline{a_{\lambda}} \tag{1.13}$$

Which indicates, in an adiabatic process, the energy levels change, but the distribution does not.

1.3 Classical limit in thermodynamics

The subsystem partition function can be write as the formate of integration:

$$Z = \sum_{n=0}^{\infty} e^{-\beta \varepsilon_n} \xrightarrow{\frac{\Delta \varepsilon_n}{kT} \ll 1} Z = \int \cdots \int \frac{dq_1 \cdots dq_r dp_1 \cdots dp_r}{h^r} e^{-\beta \varepsilon} \tag{1.14}$$

e.g.1 : Monatomic ideal gas subsystem partition function

$$Z = \frac{1}{h^3} \int_{-\infty}^{+\infty} e^{-\beta \frac{p^2}{2m}} \, d\Omega$$

$$d\Omega = dp_1 dp_2 dp_3 dq_1 dq_2 dq_3$$

(1.15)

And the result is:

$$Z = \frac{V}{h^3} (2\pi mkT)^{3/2}$$

(1.16)

2 Ensemble Theory

2.1 Microcanonical Ensemble

N-dimensional sphere volume: The N-dimensional sphere volume should have the formate like $V_n = C_n R^n$, and $S_n = \frac{dV_n}{dR} = nC_n R^{n-1}$

Gauss integration:

$$\int_{-\infty}^{+\infty} e^{-x^2} \, dx = \sqrt{\pi}$$

(2.1)

With Gauss integration, we can constract:

$$(\pi)^{N/2} = \int \cdots \int e^{-(x_1^2 + \cdots + x_N^2)} dx_1 \ldots dx_N$$

(2.2)

We can obtain from $S_n = \frac{dV_n}{dR} = nC_n R^{n-1}$:

$$\prod_{i=1} Ndx_i = NC_N R^{N-1} dR$$

(2.3)

Thus:

$$\begin{aligned}
(\pi)^{N/2} &= \int \cdots \int e^{-(x_1^2 + \cdots + x_N^2)} dx_1 \ldots dx_N \\
&= \int_{-\infty}^{+\infty} e^{-R^2} NC_N R^{N-1} dR \\
&= \frac{1}{2} NC_N \int_{-\infty}^{+\infty} e^{-R^2} (R^2)^{N/2-1} dR^2 \\
&= \frac{1}{2} N\Gamma(\frac{N}{2}) C_N
\end{aligned}$$

(2.4)

And obtain the N-dimensional sphere volume from above:

$$V_N = C_N R^N = \frac{2R^N \pi^{N/2}}{N\Gamma(\frac{N}{2})} = \frac{R^N \pi^{N/2}}{\Gamma(\frac{N}{2} + 1)}$$

(2.5)

2.2 Entropy of Microcanonical Ensemble

Microcanonical ensemble has fixed parameters (N, V, E), and the energy E can have a small dviation:

$$E < H(q, p) < E + \Delta E$$

(2.6)

Define entropy of microcanonical ensemble as:

$$S(N, V, E) = kln\Gamma(E)$$
$$S(N, V, E) = kln\Sigma(E) \tag{2.7}$$
$$S(N, V, E) = kln\omega(E)$$

$\Sigma(E)$ is the volume in phase space:

$$\Sigma(E) = \int_{H(q,p) \leq E} d\Omega \ (d\Omega = dq_1 \ldots dq_r dp_1 \ldots dp_r) \tag{2.8}$$

Suppose the Hamiltonian has the formation:

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \tag{2.9}$$

From the formula of N-dimensional sphere's volume, we can obtain the formation of entropy:

$$\begin{aligned}
S(N, V, E) &= \int dq_1 \ldots dq_{3N} \int_{\sum_{i=1}^{3N} \frac{p_i^2}{2m}} dp_1 \ldots dp_{3N} \\
&= V^N \int_{\sum_{i=1}^{3N} \frac{p_i^2}{2m}} dp_1 \ldots dp_{3N} \\
&\xrightarrow{x_i = \frac{p_i}{\sqrt{2mE}}} V^N (2mE)^{3N/2} \int_{\sum_{i=1}^{3N}} dx_1 \ldots dx_{3N} \\
&= V^N (2mE)^{3N/2} \frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2} + 1)}
\end{aligned} \tag{2.10}$$

And S has the formation:$\Sigma(E) \propto E^{N/2}$ or write as $\Sigma(M) \propto E^M$ where $M \to \infty$
To proof three formations of entropy indeed equal to each other when $n \to \infty$:

$$\omega(E) = \frac{\partial \Sigma(E)}{\partial E} \qquad \Gamma(E) = \omega(E) \cdot \Delta \tag{2.11}$$

$$\begin{aligned}
ln\Sigma(E) &\propto MlnE \\
ln\omega(E) &\propto (M-1)lnME = MlnE + O(lnM)
\end{aligned} \tag{2.12}$$

Thus, when $M \to \infty$, $ln\Sigma(E) = ln\omega(E)$. Also:

$$\begin{aligned}
ln\Gamma(E) &= ln(\Sigma(E + \Delta) - \Sigma(E)) \\
&= ln(\Sigma(E)) + ln(\frac{\Sigma(E + \Delta)}{\Sigma(E)} - 1) \\
&= ln(\Sigma(E)) - ln((1 + \frac{\Delta}{E})^M - 1) \\
&= ln(\Sigma(E)) - ln(\frac{M\Delta}{E}) \\
&= ln(\Sigma(E)) - O(lnM)
\end{aligned} \tag{2.13}$$

As discribed above, we can proof when $M \to \infty$, $ln(\Sigma(E)) = ln(\omega(E)) = ln(\Gamma(E))$. And from the result of (2.10), we can deduce the entropy of monatomic ideal gas:

$$\begin{aligned}
S(N, V, E) &= kln(\Sigma(E)) \\
&= k[NlnV + \frac{3N}{2}ln(2mE) + \frac{3N}{2}ln\pi - \frac{3N}{2}(ln(\frac{3N}{2}) - 1)] \\
&= NKln(\frac{4\pi mE}{3N})^{\frac{3N}{2}} + \frac{3}{2}Nk
\end{aligned} \tag{2.14}$$

The last step uses Stirling's formula.

From the fundamental equation of thermodynamics:

$$dU = TdS - pdV \tag{2.15}$$

We can obtain:

$$\frac{1}{T} = \frac{\partial U}{\partial S} = \frac{\partial E}{\partial S} = \frac{3Nk}{2U} \tag{2.16}$$

$$p = -(\frac{\partial U}{\partial V})_S = \frac{NkT}{V} \tag{2.17}$$

2.3   Theorem of Equipartition of Energy

First we take the ensemble average of $< x_i \frac{\partial H}{\partial x_j} >$ into consideration:

$$
\begin{aligned}
< x_i \frac{\partial H}{\partial x_j} > &= \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega^r}{\int e^{-\beta H} d\omega^r} \\
&= \frac{-\frac{1}{\beta} \int x_i \frac{\partial}{\partial x_j} e^{-\beta H} dx_j \frac{d\omega^r}{dx_j}}{\int e^{-\beta H} d\omega^r}
\end{aligned}
\tag{2.18}
$$

Integral by parts:

$$
\begin{aligned}
-\frac{1}{\beta} \int x_i \frac{\partial}{\partial x_j} e^{-\beta H} dx_j \frac{d\omega^r}{dx_j} &= -\frac{1}{\beta} e^{-\beta H} x_i |_{x_j^{sub}}^{x_j^{upper}} + \frac{1}{\beta} \int (\frac{\partial x_i}{\partial x_j}) e^{-\beta H} dx_j \\
&= \frac{1}{\beta} \int \delta_{ij} e^{-\beta H} dx_j
\end{aligned}
\tag{2.19}
$$

The last step uses the edge condition, thus:

$$< x_i \frac{\partial H}{\partial x_j} > = \frac{\frac{1}{\beta} \int \delta_{ij} e^{-\beta H} dw^r}{\int e^{-\beta H} d\omega^r} = \delta_{ij} kT \tag{2.20}$$

Specifically:

$$
\begin{aligned}
< p_i \frac{\partial H}{\partial p_i} > &= - < p_i \dot{q}_i >= kT \\
< q_i \frac{\partial H}{\partial q_i} > &= < q_i \dot{p}_i >= kT
\end{aligned}
\tag{2.21}
$$

Then, we take the hamiltonian into consideration:

$$H = \sum_{i=1}^{3N} A_i P_i^2 + B_i Q_i^2 \tag{2.22}$$

This is the formation after canonical transformation. And we can obtain from (2.22):

$$\sum_{i=1}^{3N} < P_i \frac{\partial H}{\partial P_i} + Q_i \frac{\partial H}{\partial Q_i} >= 2H \tag{2.23}$$

Use (2.21), we can obtain:

$$< H >= \frac{3N}{2} kT \tag{2.24}$$

And (2.21) also indicates the contribution of each free degree to internal energy is $\frac{1}{2} kT$

3 Fundamental Laws of Thermodynamics

4 Maxwell Relationship

4.1 Basic Relationship of Partial Differential

$$(\frac{\partial f}{\partial g})_h(\frac{\partial g}{\partial f})_h = 1$$
$$(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x(\frac{\partial z}{\partial x})_y = -1 \tag{4.1}$$

$$\frac{\partial(f,g)}{\partial(x,y)} = 1/\frac{\partial(x,y)}{\partial(f,g)}$$
$$\frac{\partial(f,g)}{\partial(x,y)} = \frac{\partial(f,g)}{\partial(h,\omega)}\frac{\partial(h,\omega)}{\partial(x,y)} \tag{4.2}$$
$$\frac{\partial(f,g)}{\partial(x,g)} = (\frac{\partial f}{\partial x})_g$$

4.2 Basic Maxwell Relationship

The thermodynamic function U, H, F, G is state function, us G as example:

$$G \equiv U + PV - TS \tag{4.3}$$

$$dG = -SdT + Vdp \tag{4.4}$$

The state function should fulfill the relationship:

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T} \tag{4.5}$$

Thus the Maxwell Relationship related to Gibbs function G is:

$$-(\frac{\partial S}{\partial P})_T = (\frac{\partial V}{\partial T})_P \tag{4.6}$$

And use the Jacobian to discribe Maxwell Relationship generally:

$$\frac{\partial(S,T)}{\partial(x,y)} = \frac{\partial(V,p)}{\partial(x,y)} \tag{4.7}$$

Which uses the the third equation in (4.2)
And all state function can have its Maxwell Relationship:
e.g. Maxwell Relationship related to entropy S

$$S = \frac{1}{T}dU + \frac{p}{T}dV \tag{4.8}$$

$$(\frac{\partial(\frac{p}{T})}{\partial U})_V = (\frac{\partial(\frac{1}{T})}{\partial V})_U \tag{4.9}$$

4.3 Heat Capacity and Thermodynamical Functions

Define C_y as:

$$C_y = \frac{dQ_y}{dT} = (\frac{\partial Q}{\partial T})_y \qquad (4.10)$$

Use $dQ = TdS$:

$$C_V = (\frac{\partial U}{\partial T})_V = T(\frac{\partial S}{\partial T})_V$$
$$C_P = (\frac{\partial H}{\partial T})_p = t(\frac{\partial S}{\partial T})_p \qquad (4.11)$$

Use measurable quantity to discribe the relationship between C_v and C_p:

$$C_p - C_v = T[(\frac{\partial S}{\partial T})_p - (\frac{\partial S}{\partial T})_V] \qquad (S = S(T, V(T, p)))$$
$$= T[(\frac{\partial S}{\partial T})_V + (\frac{\partial S}{\partial V})_T(\frac{\partial V}{\partial T})_p - (\frac{\partial S}{\partial T})_V] \qquad (4.12)$$
$$= T(\frac{\partial p}{\partial T})_V(\frac{\partial V}{\partial T})_p$$

The last step used Maxwell Relationship. And we can deduce some partial differential relationship of the heat capacity:

$$dU = (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV$$
$$= C_V dT + [T(\frac{\partial p}{\partial T})_V - p]dV \qquad (4.13)$$

As U is a state function, we can otain:

$$\frac{\partial C_V}{\partial V} = \frac{\partial[T(\frac{\partial p}{\partial T})_V - p]}{\partial T} \qquad (4.14)$$

Obtained after simplification:

$$(\frac{\partial C_V}{\partial V})_T = T(\frac{\partial^2 p}{\partial T^2})_V \qquad (4.15)$$

Similarly:

$$(\frac{\partial C_p}{\partial p})_T = -T(\frac{\partial^2 V}{\partial T^2})_p \qquad (4.16)$$

From (4.13) and $dS = \frac{1}{T}dU + \frac{p}{T}dV$, we obtain a new relationship discribed by measurable quantities:

$$dS = \frac{C_V}{T}dT + (\frac{\partial p}{\partial T})_V dT \qquad (4.17)$$

Use(4.13) and (4.15), integrate with any path (*always uses* $(T_0, V_0) \to (T, V_0) \to (T, V)$), we can obtain state function U and S.