Chapter 6: Part B
Basic methods and results of statistical mechanics

Zhi-Jie Tan
Wuhan University

2019 spring semester

Aim:

- derive general probability statements for a variety of situations

- describe practical methods for calculating macroscopic properties

Ensemble representative of situations of physical interests

- **microcanonical ensemble**
  Isolated system

- **canonical ensemble**
  system in contact with a heat reservoir

- **grand canonical ensemble**
  system in contact with a reservoir exchanging E and N

Ensemble representative of situations of physical interests

6.1 Isolated system

An isolated system with V, N, and the energy is in [E, E+δE]

Fundamental statistical postulate for isolated..

Probability for finding in r state:

$$P_r = \begin{cases} C & \text{if } E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

$$\Sigma P_r = 1$$

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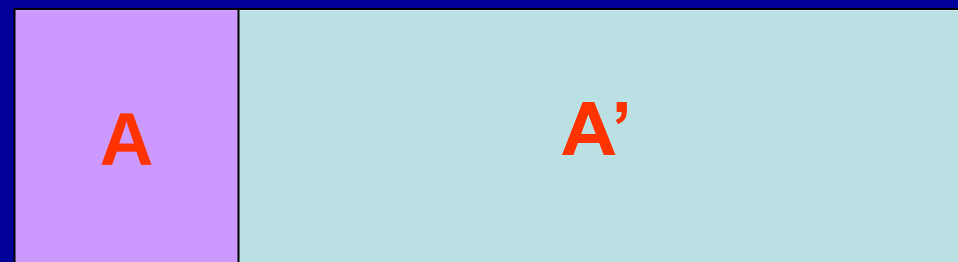
6.2 system in contact with a heat reservoir

A<<A'

In equilibrium,



What is the probability for finding in state r of energy E_r ?

$$A^{(0)} = A + A'$$

between $E^{(0)}$ and $E^{(0)} + \delta E$.

$$\boxed{E_r + E' = E^{(0)}}$$

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6.2 system in contact with a heat reservoir

$$E' = E^{(0)} - E_r.$$

If A is in state r, the accessible number for A'

$$\boxed{\Omega'(E^{(0)} - E_r)}$$

Probability to find A in state r is

$$\boxed{P_r = C'\Omega'(E^{(0)} - E_r)}$$

$$\sum_r P_r = 1$$

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6.2 system in contact with a heat reservoir

A<<A’ $\Longrightarrow$ $E_r \ll E^{(0)}$

Instead of expanding Ω(E’) at $E'=E_0$

$$\ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 E_r \cdots$$

$E_r \lll E^{(0)}$ **Neglect terms of higher order**

$$\left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 \equiv \beta$$

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6.2 system in contact with a heat reservoir

A' is so large that its T is unaffected

$$\ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \beta E_r$$

$$\Omega'(E^{(0)} - E_r) = \Omega'(E^{(0)})\, e^{-\beta E_r}$$

$\Omega'(E^{(0)})$ is just a constant independent of r,

$$P_r = C\, e^{-\beta E_r}$$

Normalization

$$C^{-1} = \sum_r e^{-\beta E_r}$$

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6.2 system in contact with a heat reservoir

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

Discussion on

$$P_r = C'\Omega'(E^{(0)} - E_r)$$

$$P_r = C\, e^{-\beta E_r}$$

$$E_r \uparrow ==> \Omega(E_0 - E_r) \downarrow$$

The situation is less

Ensemble representative of situations of physical interests

6.2 system in contact with a heat reservoir

Discussion on

$$P_r = C\, e^{-\beta E_r}$$

1, is very general result and is of fundamental important in statistical mechanics;

2, $e^{-\beta E_r}$ is called the “Boltzmann factor”, and the probability is known as “canonical distribution”.

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6.2 system in contact with a heat reservoir

Discussion on

$$P_r = C\, e^{-\beta E_r}$$

is the probability of finding r state with E_r

Then the total probability for finding E in [E,E+dE]

$$P(E) = \sum_r P_r$$

$$\Rightarrow \quad P(E) = C\Omega(E)\, e^{-\beta E}$$

Ensemble representative of situations of physical interests

6.2 system in contact with a heat reservoir

Discussion on

$$P_r = C\, e^{-\beta E_r}$$

$$P(E) = \sum_r P_r$$

E_a	E_b	E_c	E_d
1 2 3 4	5 6 7	8 9	10

$$P(E_a) = 4 \times \exp(-\beta E_a)$$

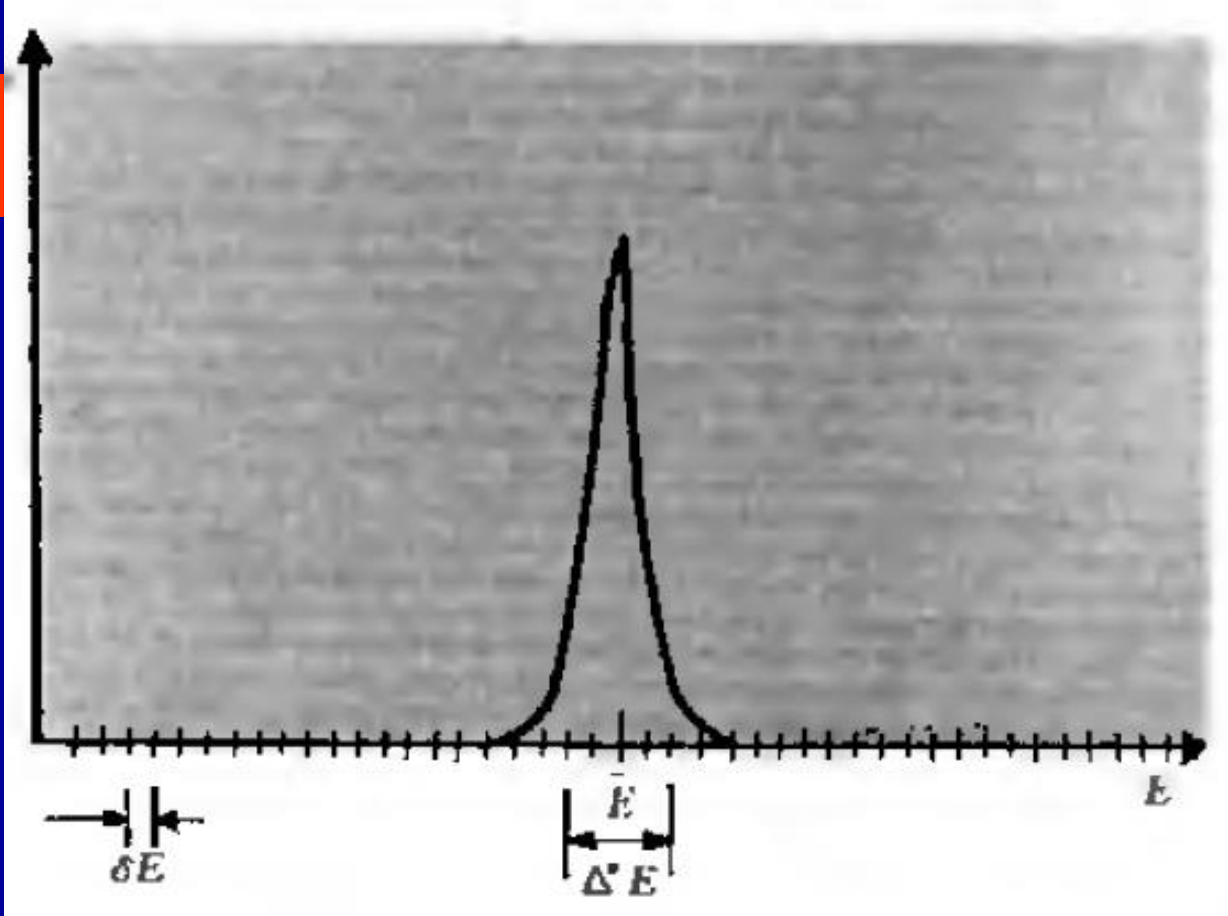
$$\Rightarrow P(E) = C\,\Omega(E)\, e^{-\beta E}$$

Ensemble representative of situations of physical interests

6.2 system in contact with a heat reservoir

Discussion on

$$\boxed{P(E) = C\Omega(E)\, e^{-\beta E}}$$



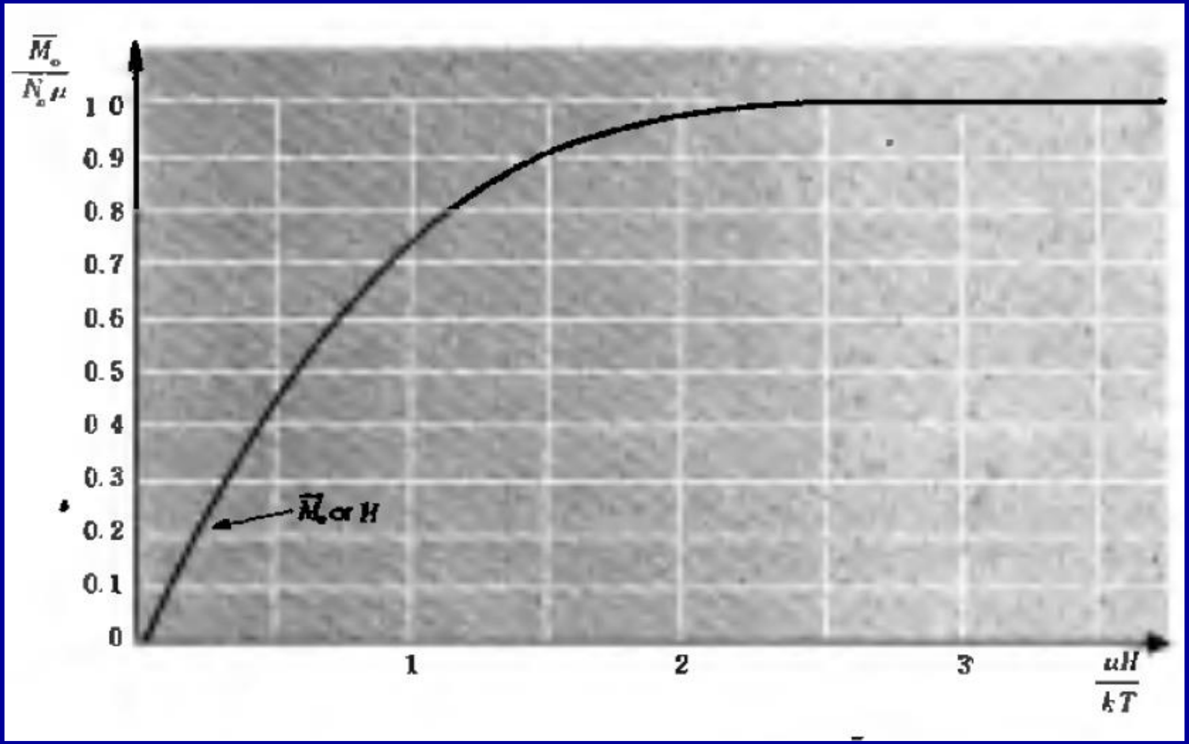
The larger A is,

The sharper is the maximum P(E)

Ensemble representative of situations of physical interests

6.3 Simple applications of canonical distribution

Paramagnetism



Ensemble representative of situations of physical interests

6.3 Simple applications of canonical distribution

Molecule in an ideal gas

$$P'(\mathbf{v})\, d^3\mathbf{v} = P(\mathbf{p})\, d^3\mathbf{p} = C\, e^{-\beta m v^2/2}\, d^3\mathbf{v}$$

Maxwell distribution for molecule velocity

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6.3 Simple applications of canonical distribution

Molecule in an ideal gas in the presence of gravity

Probability in [z, z+dz]

$$P(z)\,dz = C'\,e^{-\beta m g z}\,dz$$

Ensemble representative of situations of physical interests

6.3 Simple applications of canonical distribution

Molecule in an ideal gas in the presence of gravity

$$P(z) = P(0)\, e^{-mgz/kT}$$

Sometimes called as "law of atmosphere"

Ensemble representative of situations of physical interests

6.5 mean values in a canonical ensemble

$\boxed{\text{Mean energy}}$

Probability to find state r in canonical ensemble

$$P_r = C\, e^{-\beta E_r} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

Mean energy

$$\bar{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}}$$

$$= -\sum_r \frac{\partial}{\partial \beta}\left(e^{-\beta E_r}\right)$$

$$= -\frac{\partial}{\partial \beta} Z$$

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6.5 mean values in a canonical ensemble

Define

$$Z \equiv \sum_r e^{-\beta E_r}$$

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

Partition function

Mean energy

Energy dispersion

$$\overline{(\Delta E)^2} \equiv \overline{(E - \bar{E})^2} = \overline{E^2 - 2\bar{E}E + \bar{E}^2}$$

$$= \overline{E^2} - \bar{E}^2$$

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6.5 mean values in a canonical ensemble

1st term

$$\overline{E^2} = \frac{\sum_r e^{-\beta E_r} E_r^2}{\sum_r e^{-\beta E_r}}$$

Similarly

$$\sum_r e^{-\beta E_r} E_r^2 = -\frac{\partial}{\partial \beta}\left(\sum_r e^{-\beta E_r} E_r\right)$$

$$= \left(-\frac{\partial}{\partial \beta}\right)^2 \left(\sum_r e^{-\beta E_r}\right)$$

$$\boxed{\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}}$$

Ensemble representative of situations of physical interests

6.5 mean values in a canonical ensemble

$$\overline{E^2} = \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 = -\frac{\partial\bar{E}}{\partial\beta} + \bar{E}^2$$

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial\ln Z}{\partial\beta}$$

$$\overline{(\Delta E)^2} = -\frac{\partial\bar{E}}{\partial\beta} = \frac{\partial^2\ln Z}{\partial\beta^2}$$

> 0 means $\partial\bar{E}/\partial T \geq 0$

Ensemble representative of situations of physical interests

6.5 mean values in a canonical ensemble

$\boxed{\text{Work}}$ x **is the single external parameter**

For a quasi-static process:

$$\Delta_x E_r = \frac{\partial E_r}{\partial x} dx$$

Macroscopic work is: ***generalized force***

$$\boxed{đW = \frac{\sum_r e^{-\beta E_r}\left(-\frac{\partial E_r}{\partial x}dx\right)}{\sum_r e^{-\beta E_r}}}$$

Ensemble representative of situations of physical interests

6.5 mean values in a canonical ensemble

Work

$$\sum e^{-\beta E_r}\frac{\partial E_r}{\partial x} = -\frac{1}{\beta}\frac{\partial}{\partial x}\Big(\sum_r e^{-\beta E_r}\Big) = -\frac{1}{\beta}\frac{\partial Z}{\partial x}$$

$$đW = \frac{1}{\beta Z}\frac{\partial Z}{\partial x}dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}dx$$

Since

$$đW = \bar{X}\,dx, \qquad \bar{X} \equiv -\overline{\frac{\partial E_r}{\partial x}}$$

$$\bar{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}$$

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6.5 mean values in a canonical ensemble

Work

If x is V

$$đW = \bar{p}\, dV = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}\, dV$$

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$$

Gives the equation of state

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6.6 connection with thermodynamics

All the important quantities can be expressed completely by partition function

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$đW = \frac{1}{\beta Z}\frac{\partial Z}{\partial x}dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}dx$$

2nd law ⇒ entropy?

$$Z = Z(\beta, x)$$

$$d \ln Z = \frac{\partial \ln Z}{\partial x}dx + \frac{\partial \ln Z}{\partial \beta}d\beta$$

$$d \ln Z = \beta\, đW - \bar{E}\, d\beta$$

Ensemble representative of situations of physical interests

6.6 connection with thermodynamics

$$d \ln Z = \beta\, đW - \bar{E}\, d\beta$$

$$d \ln Z = \beta\, đW - d(\bar{E}\beta) + \beta\, d\bar{E}$$

$$\boxed{d\,(\ln Z + \beta\bar{E}) = \beta(đW + d\bar{E}) \equiv \beta\, đQ}$$

2nd law

$$dS = \frac{đQ}{T}$$

$$\boxed{S \equiv k(\ln Z + \beta\bar{E})}$$

$$S = k \ln \Omega(\bar{E})$$

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6.6 connection with thermodynamics

$$S = k(\ln Z + \beta \bar{E}) \quad \xrightarrow{???} \quad S = k \ln \Omega(\bar{E})$$

$$\sum_r \Rightarrow\Rightarrow \sum_E$$

$$\Rightarrow \quad Z = \sum_r e^{-\beta E_r} = \sum_E \Omega(E)\, e^{-\beta E}$$

Since $\Omega(E)e^{-\beta E}$ is with sharp maximum

$$\Rightarrow \quad Z = \Omega(\bar{E})\, e^{-\beta \bar{E}} \frac{\Delta^* E}{\delta E}$$

Ensemble representative of situations of physical interests

6.6 connection with thermodynamics

$$Z = \Omega(\bar{E})\, e^{-\beta \bar{E}} \frac{\Delta^* E}{\delta E}$$

$$\ln Z = \ln \Omega(\bar{E}) - \beta \bar{E} + \ln \frac{\Delta^* E}{\delta E}$$

$$\Omega \sim E^{f}; \qquad E \sim fkT; \qquad \Delta E / \delta E \sim f$$

$$\ln Z = \ln \Omega(\bar{E}) - \beta \bar{E}$$

$$S = k(\ln Z + \beta \bar{E})$$

$$S = k \ln \Omega(\bar{E})$$

OK!

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6.6 connection with thermodynamics

$$S = k(\ln Z + \beta \bar{E})$$

$$TS = kT \ln Z + \bar{E}$$

$$\boxed{F = \bar{E} - TS = -kT \ln Z}$$

<u>Macroscopic properties</u> and <u>microscopic information</u>!!!

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6.6 connection with thermodynamics

Limiting behavior:

as $T \to 0$,

$$\begin{cases} Z \to \Omega_0\, e^{-\beta E_0} \\ \bar{E} \to E_0, \end{cases}$$

$$\Rightarrow \quad S \to k[(\ln \Omega_0 - \beta E_0) + \beta E_0] = k \ln \Omega_0$$

3rd law

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6.6 connection with thermodynamics

Two sub-systems A+A'; A is at r state and A' is at s state

Total energy:

$$E_{rs}^{(0)} = E_r + E_s'$$

$$Z^{(0)} = \sum_{r,s} e^{-\beta E_{rs}^{(0)}} = \sum_{r,s} e^{-\beta(E_r + E_s')}$$

$$= \sum_{r,s} e^{-\beta E_r} e^{-\beta E_s'}$$

$$= \left(\sum_r e^{-\beta E_r}\right)\left(\sum_s e^{-\beta E_s'}\right)$$

$$Z^{(0)} = ZZ'$$

$$\ln Z^{(0)} = \ln Z + \ln Z'$$

$$\bar{E}^{(0)} = \bar{E} + \bar{E}'$$

$$S^{(0)} = S + S'$$

Ensemble representative of situations of physical interests

6.6 connection with thermodynamics

Two sub-systems A+A'; A is at r state and A' is at s state

Probability for A at r ; probability for A' at s

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad \text{and} \quad P_s = \frac{e^{-\beta' E'_s}}{\sum_s e^{-\beta' E'_s}}$$

$$P_{rs} = P_r P_s$$

$$P_{rs} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \frac{e^{-\beta' E'_s}}{\sum_s e^{-\beta' E'_s}}$$

$$\boxed{P_{rs} = \frac{e^{-\beta(E_r + E'_s)}}{\sum_r \sum_s e^{-\beta(E_r + E'_s)}}} \qquad if \quad \beta = \beta'$$

Ensemble representative of situations of physical interests

6.6 connection with thermodynamics

$$P_r = \frac{e^{-\beta E_r}}{Z}$$

$$E_r = -\frac{1}{\beta}\ln ZP_r$$

Entropy

$$S = k(\ln Z + \beta\bar{E})$$

$$\begin{aligned} S &= k\left[\ln Z + \beta\sum_r P_r E_r\right] \\ &= k\left[\ln Z - \sum_r P_r \ln (ZP_r)\right] \\ &= k\left[\ln Z - \ln Z\left(\sum_r P_r\right) - \sum_r P_r \ln P_r\right] \end{aligned}$$

$$S = -k\sum_r P_r \ln P_r$$

Ensemble representative of situations of physical interests

6.6 connection with thermodynamics

Shannon Entropy

Shannon's entropy equation:

$$H(X) = -\sum_{i=0}^{N-1} p_i \log_2 p_i$$

If we have a symbol set {A,B,C,D,E}, where the symbol occurance frequencies are:

A = 0.5 B = 0.2 C = 0.1 D = 0.1 E = 0.1

$H(X) = -[(0.5\log_2 0.5 + 0.2\log_2 0.2 + (0.1\log_2 0.1)*3)]$

$H(X) = 1.9$

Approximation methods

6.4 System with specified mean energy

The system A is denoted by its energy Er,

$$\frac{1}{a}\sum_s a_s E_s = \bar{E}$$

a: total number of microstates

a_s: .... for states with energy E_s

$$\Sigma a_s E_s = a\bar{E} = \text{constant}$$

The situation is equivalent to one where a fixed total amount of energy aE is to be distributed over all the system in the ensemble.

Approximation methods

6.4 System with specified mean energy

If a system in the ensemble is in state r with energy Er, the remaining (a-1) systems would have the total energy (aE-Er). These (a-1) systems can be distributed over very large number Φ(aE-Er).

Since aE>>Er, the same treatment like 6.3 leads to

$$\boxed{P_r \propto e^{-\beta E_r}}$$

$$\boxed{\frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = \bar{E}}$$

where $\boxed{\beta = (\partial \ln \Phi / \partial E')}$

Approximation methods

6.4 System with specified mean energy

For a system equilibrium with a heat reservoir,

$$\beta = (kT)^{-1}$$

For a system with a specified energy E,
β is determined by

$$\frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = \bar{E}$$

Approximation methods

6.7 Ensembles used as approximations

N particles in V, and energy is in [E, E+δE]

Mean value y

$$\bar{y} = \frac{\sum_r y_r}{\Omega(E)}$$

$$E < E_r < E + \delta E$$

Summation must satisfy the constraint, and may be very difficult practically !!!

The difficulty can be circumvented by

$$P(E_1) \propto \Omega(E_1)\, e^{-\beta E_1}$$

Ensuring

$$\bar{E} = given\ \ E$$

Approximation methods

6.7 Ensembles used as approximations

$$\bar{y} = \frac{\sum_r y_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} = \frac{\sum_E y_E \Omega(E) \exp(-\beta E)}{\sum_E \Omega(E) \exp(-\beta E)}$$

where $y_E = \dfrac{\sum_E y}{\Omega(E)}$

$$\frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}} = \bar{E}$$

$$\bar{y} = \frac{y_E \Omega(E) \exp(-\beta E) \times \Delta E / \delta E}{\Omega(E) \exp(-\beta E) \times \Delta E / \delta E} = y_{\bar{E}}$$

Approximation methods

6.9 Grand canonical ensembles

A can exchange with A' with *E* and *N*

Combined system A0 is isolated

$$E + E' = E^{(0)} = \text{constant}$$
$$N + N' = N^{(0)} = \text{constant}$$

Probability at r state with E_r

$$\boxed{P_r(E_r, N_r) \propto \Omega'(E^{(0)} - E_r, N^{(0)} - N_r)}$$

$$\ln \Omega'(E^{(0)} - E_r, N^{(0)} - N_r)$$
$$= \ln \Omega'(E^{(0)}, N^{(0)}) - \left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 E_r - \left[\frac{\partial \ln \Omega'}{\partial N'}\right]_0 N_r$$

Approximation methods

6.9 Grand canonical ensembles

$$\ln \Omega'(E^{(0)} - E_r, N^{(0)} - N_r)$$

$$= \ln \Omega'(E^{(0)}, N^{(0)}) - \left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 E_r - \left[\frac{\partial \ln \Omega'}{\partial N'}\right]_0 N_r$$

$$\beta \equiv \left[\frac{\partial \ln \Omega}{\partial E'}\right]_0 \quad \text{and} \quad \alpha \equiv \left[\frac{\partial \ln \Omega}{\partial N'}\right]_0$$

$$\Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \Omega'(E^{(0)}, N^{(0)})\, e^{-\beta E_r - \alpha N_r}$$

$$\boxed{P_r \propto e^{-\beta E_r - \alpha N_r}}$$

Grand canonical distribution

Approximation methods

6.9 Grand canonical ensembles

$$P_r \propto e^{-\beta E_r - \alpha N_r}$$

Grand canonical distribution

$\mu \equiv -kT\alpha$ is called the "chemical potential" of the reservoir

$$\bar{E} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} E_r}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

$$\bar{N} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} N_r}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

Work in different forms

1, Surface membrane

$$dW = \sigma dA$$

2, stretch a line

$$dW = \Gamma dL$$

3, Polarization

$$dW = \vec{\mathrm{E}} d\vec{D}$$

Work in different forms

4, magnetization

$$dW = \vec{H} d\vec{B}$$

5, P-V

$$dW = p dV$$

见：林宗涵《热力学与统计物理》北京大学出版社

Thermodynamics-integration (TI) method for calculating partition function

$$\overline{E} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$d(\ln Z_U) = \frac{dZ_U}{Z_U} = -\overline{E_U}(\beta)\,d\beta$$

$$\int_{Z_0}^{Z_\beta} d(\ln Z_U) = \int_0^{\beta_T} -\overline{E_U}(\beta)\,d\beta$$

$$\ln Z_{U_{\beta=\beta_T}} = \ln Z_{U_{\beta=0}} - \int_0^{\beta_T} \overline{E_U}(\beta)\,d\beta$$

Thermodynamics-integration method for calculating partition function

$$F_U = -k_B T \ln Z_{U_{\beta=\beta_T}} = \overline{E_U}(\beta_T) - TS$$

$$\overline{E} = -\frac{\partial \ln Z}{\partial \beta}$$

$$S = k(\ln Z + \beta \bar{E})$$

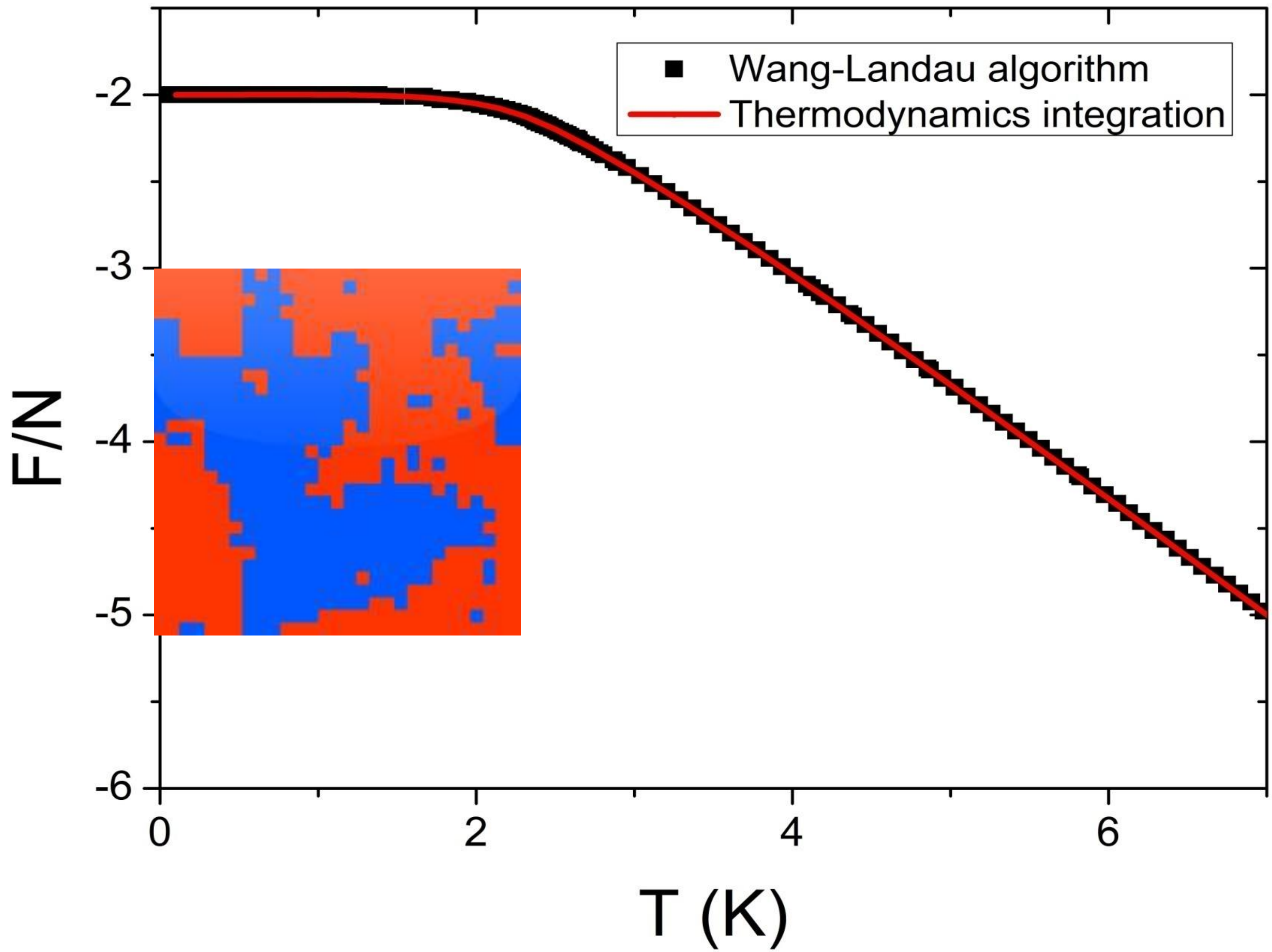
System Ⅰ： 2D Ising Model

$$E = -J \sum_{i,j} s_i s_j$$

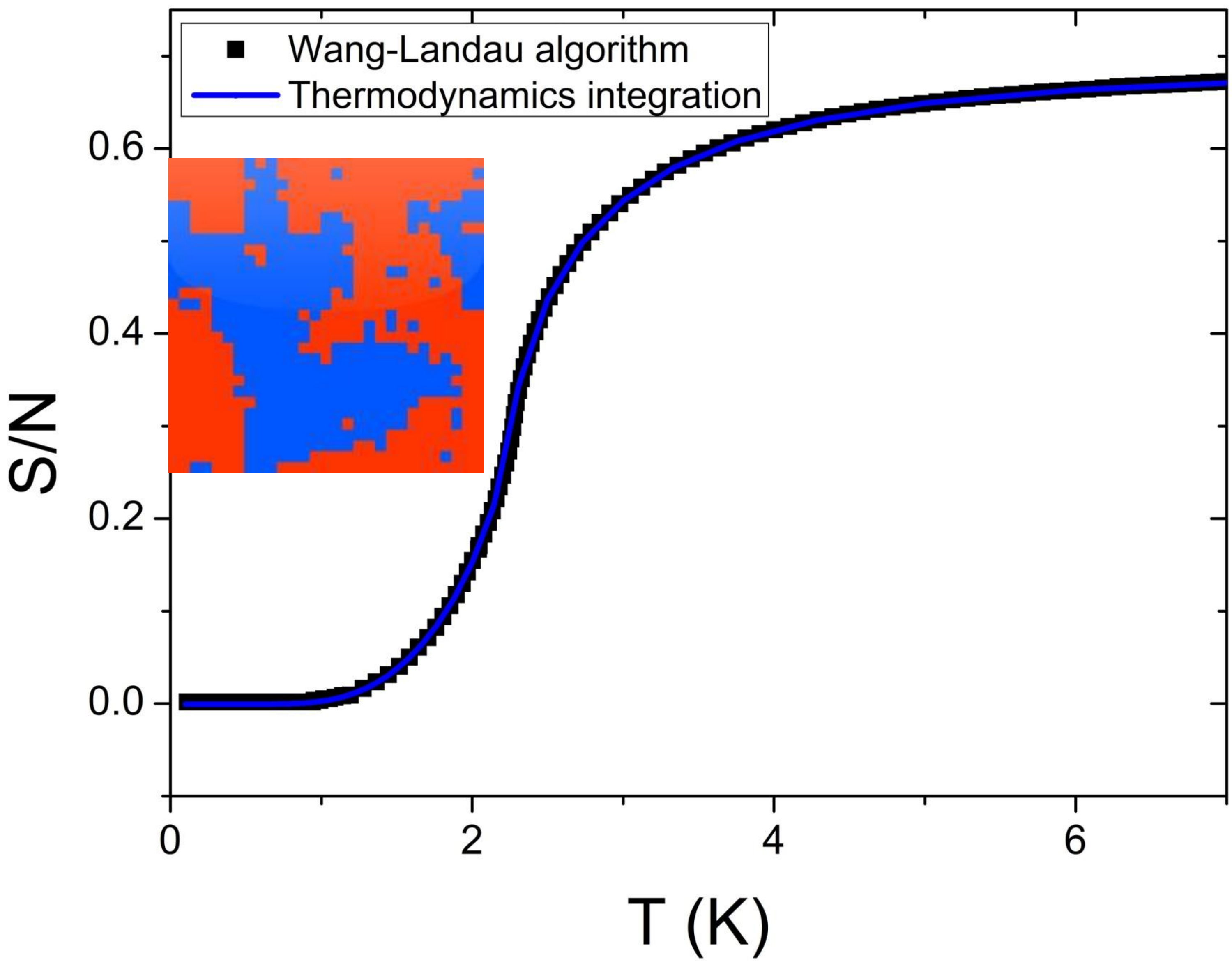
$$s_{i,j} = \pm 1$$

Where J and k_B equal to 1 in this case

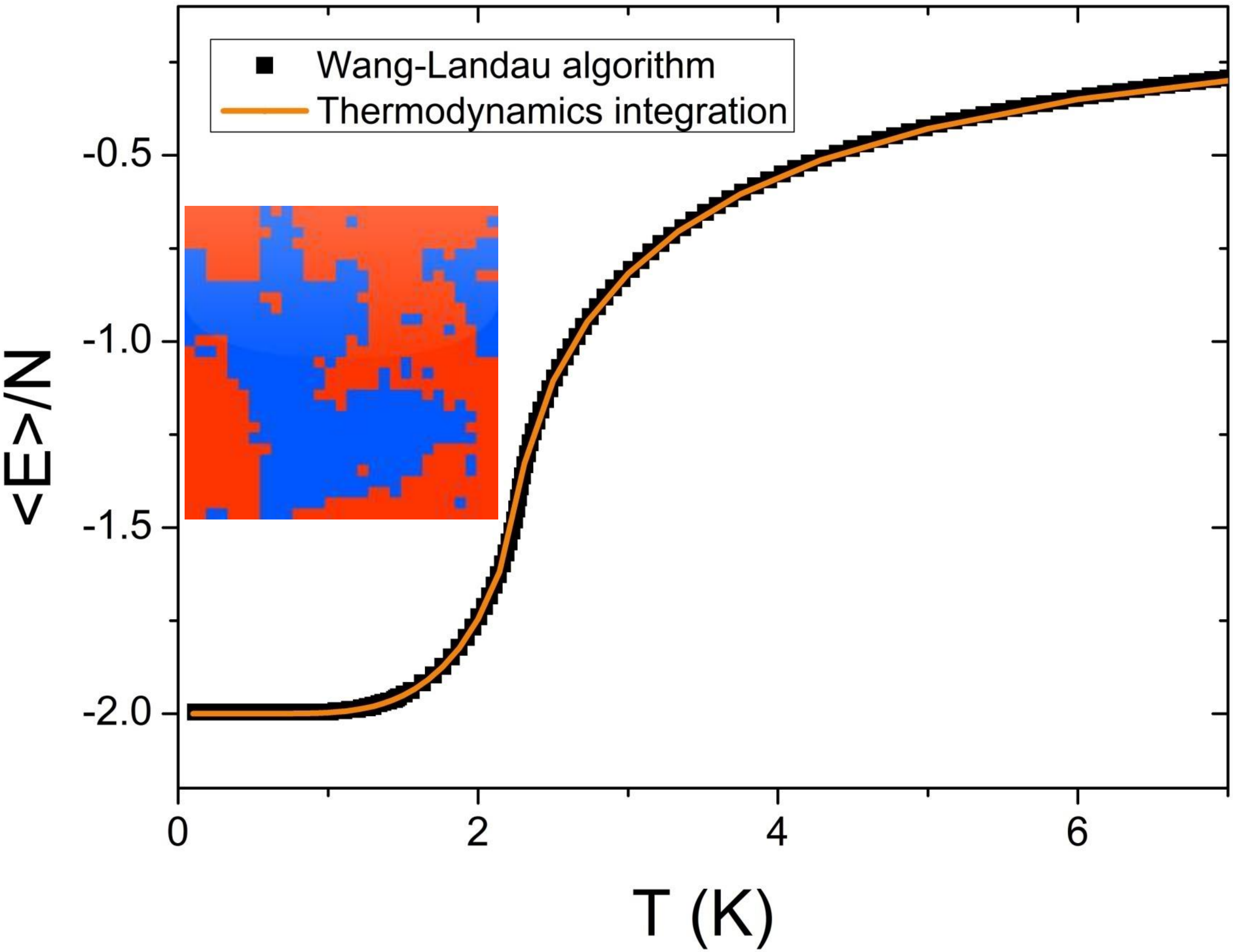
We calculated the free energy, entropy and average energy in the 256⑨256-spins system



[1] Fugao Wang & D. P. Landau, Physical Review letters, Volume 86, number 10, 2050-2053

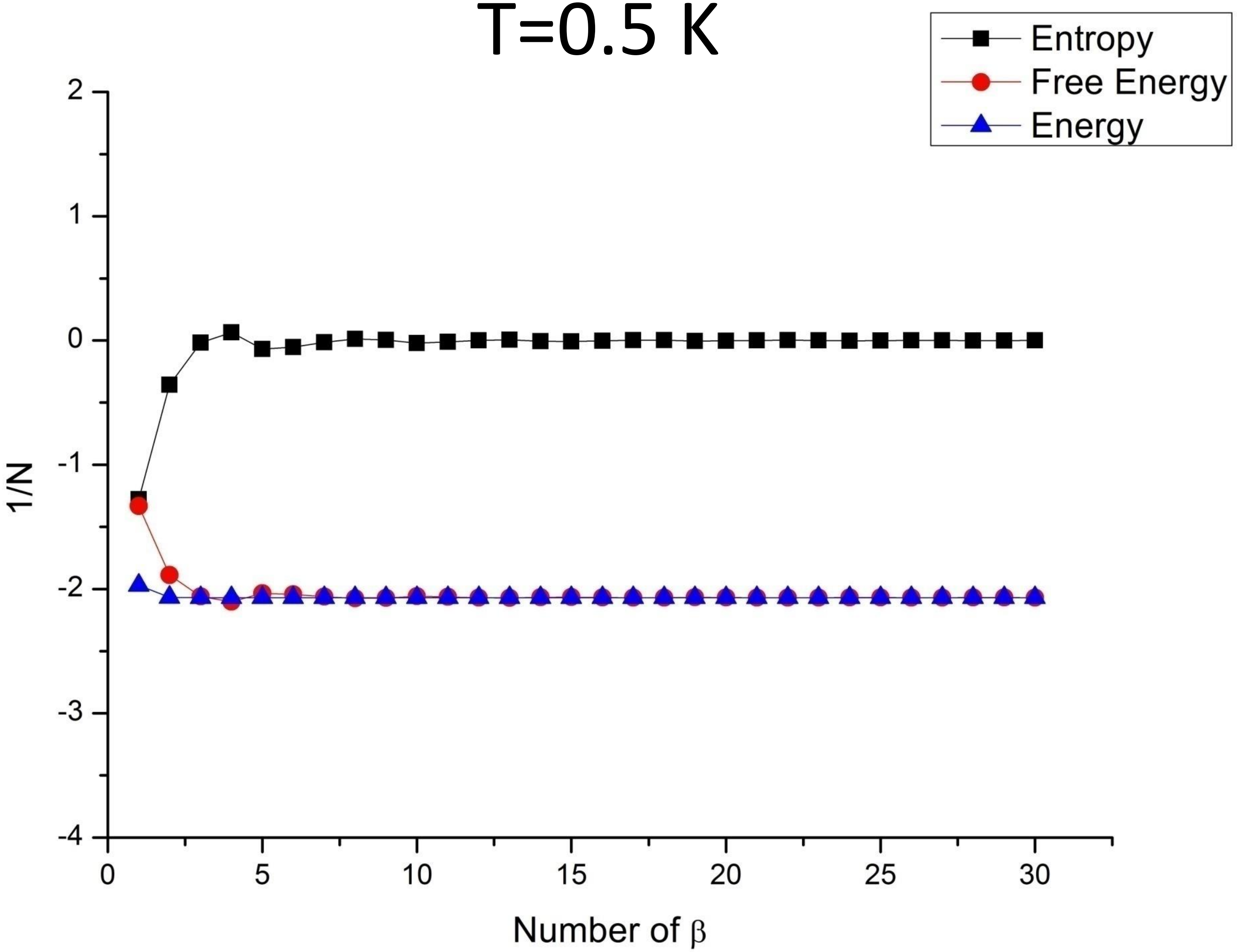


[2] Fugao Wang & D. P. Landau, Physical Review E, Volume 64, 056101



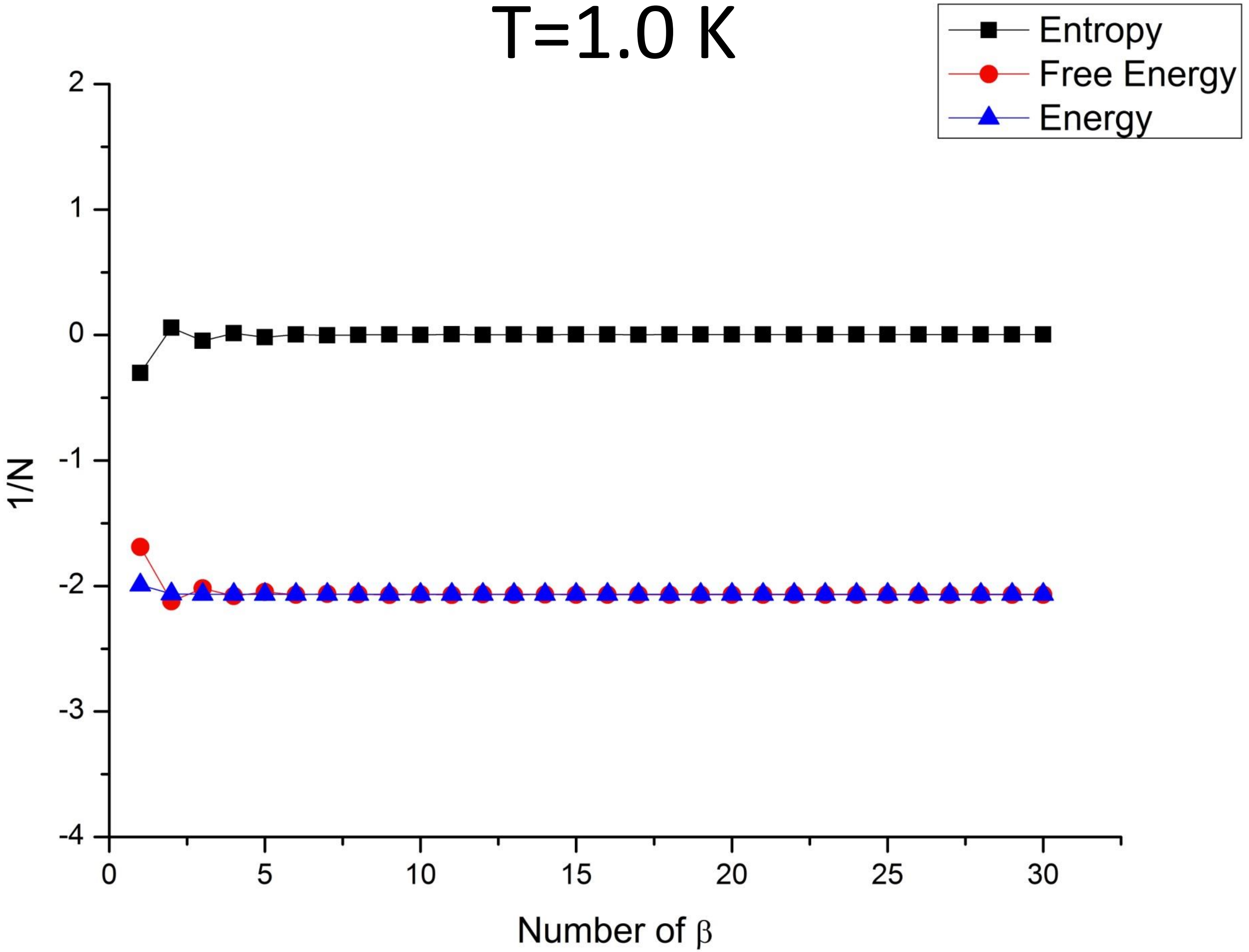
[2] Fugao Wang & D. P. Landau, Physical Review E, Volume 64, 056101

T=0.5 K



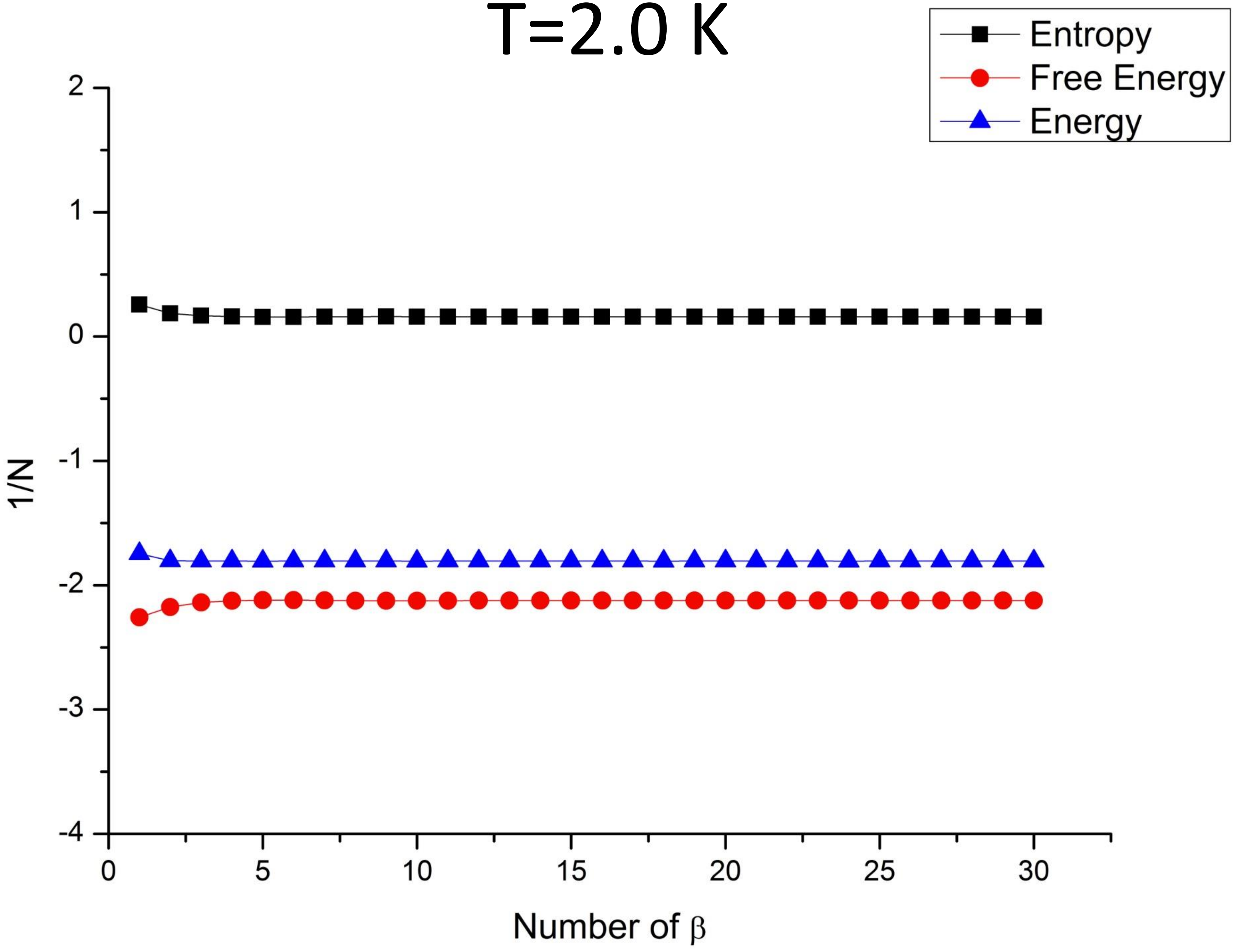
Entropy
Free Energy
Energy
2
1
0
-1
-2
-3
-4
1/N
0
5
10
15
20
25
30
Number of β

T=1.0 K

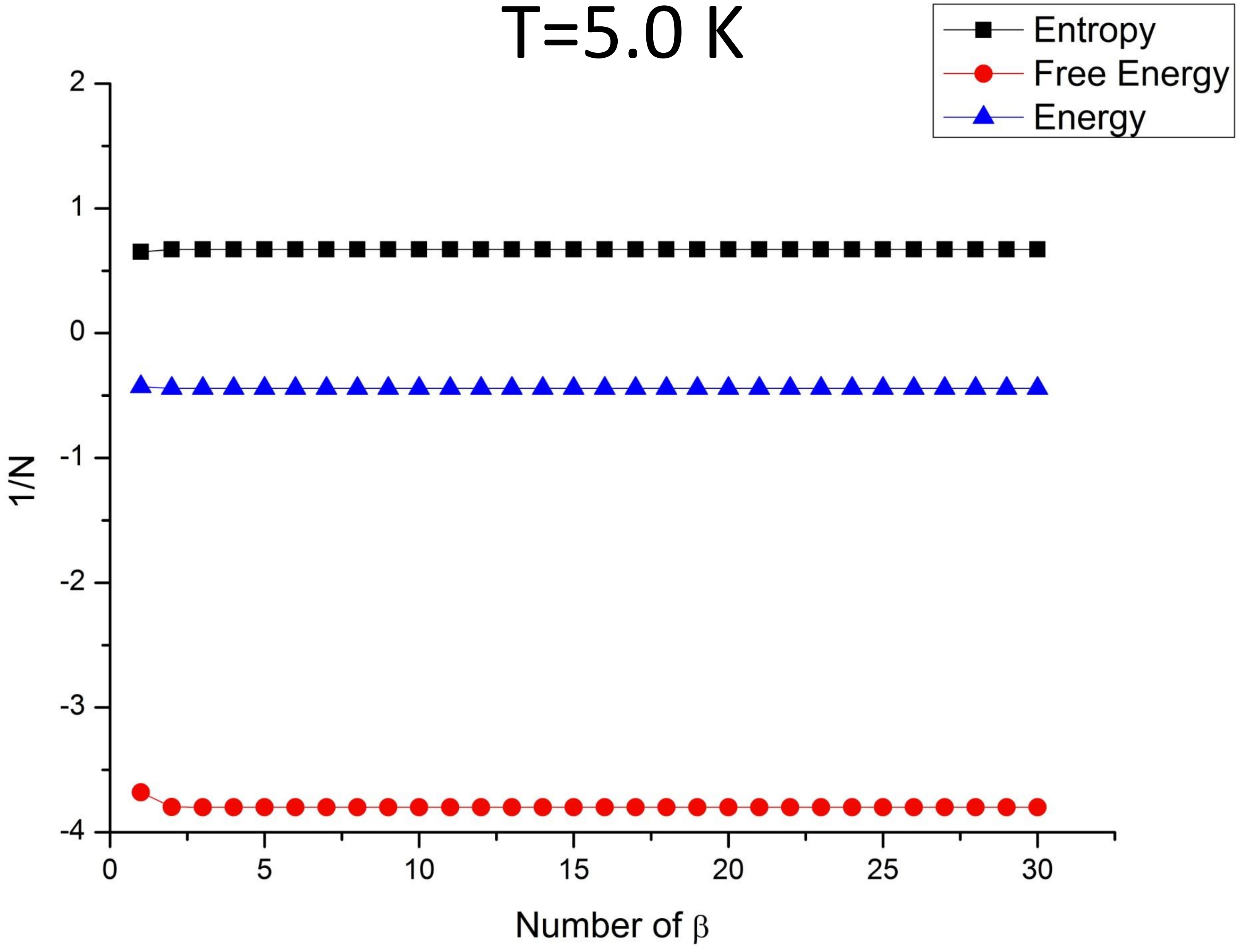


Entropy
Free Energy
Energy
2
1
0
-1
-2
-3
-4
1/N
0
5
10
15
20
25
30
Number of β

T=2.0 K


Entropy
Free Energy
Energy
2
1
0
-1
-2
-3
-4
1/N
0
5
10
15
20
25
30
Number of β

T=5.0 K


Entropy
Free Energy
Energy
2
1
0
-1
-2
-3
-4
1/N
0
5
10
15
20
25
30
Number of β

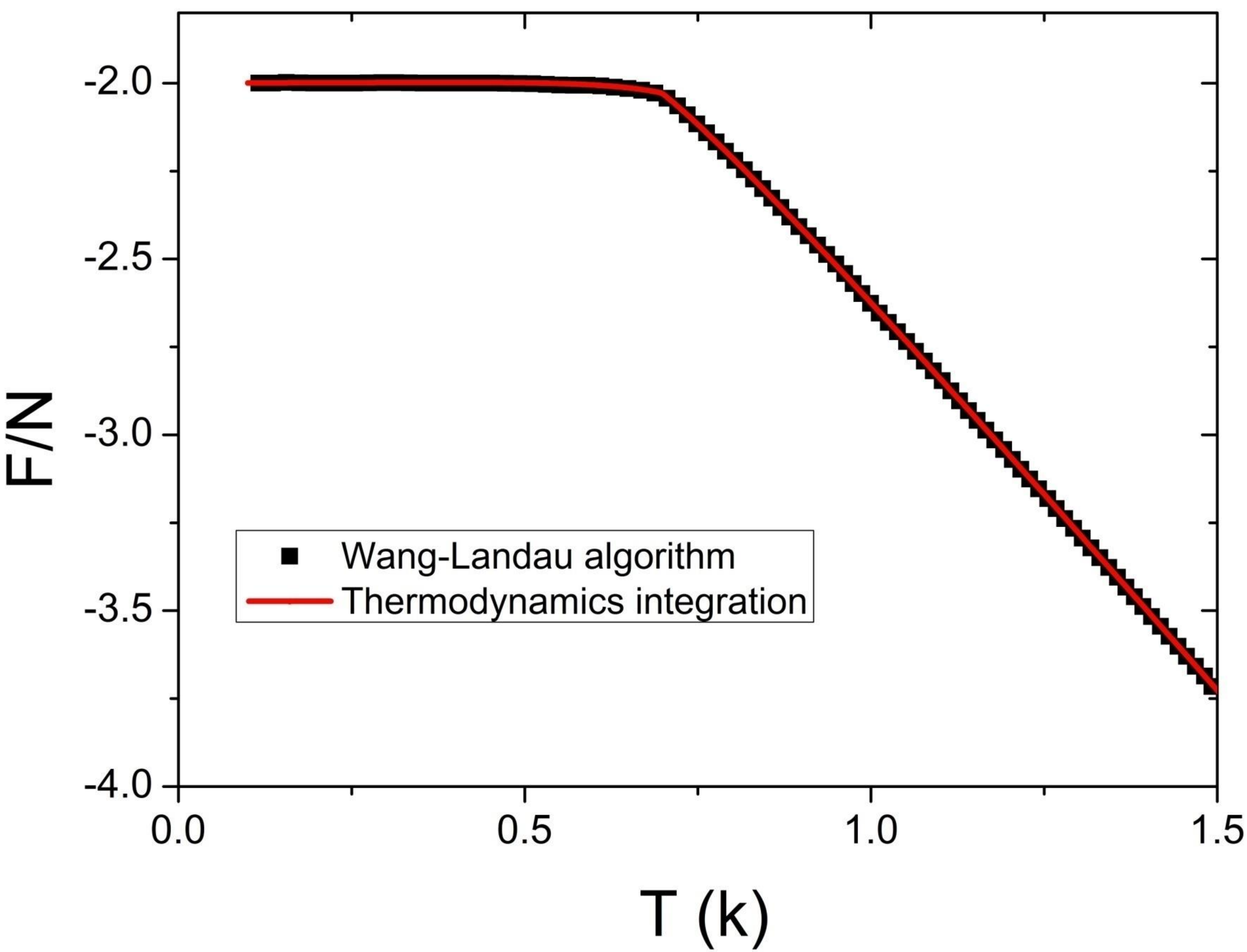
System Ⅱ： 2D Potts Model with Q=10

$$E = -J \sum_{i,j} \delta(s_i, s_j)$$

Where

$$\delta(s_i, s_j) = \begin{cases} 1 & \text{When } s_i \text{ equals to } s_j \\ 0 & \text{others} \end{cases}$$

Here J and k_B are equaling to 1



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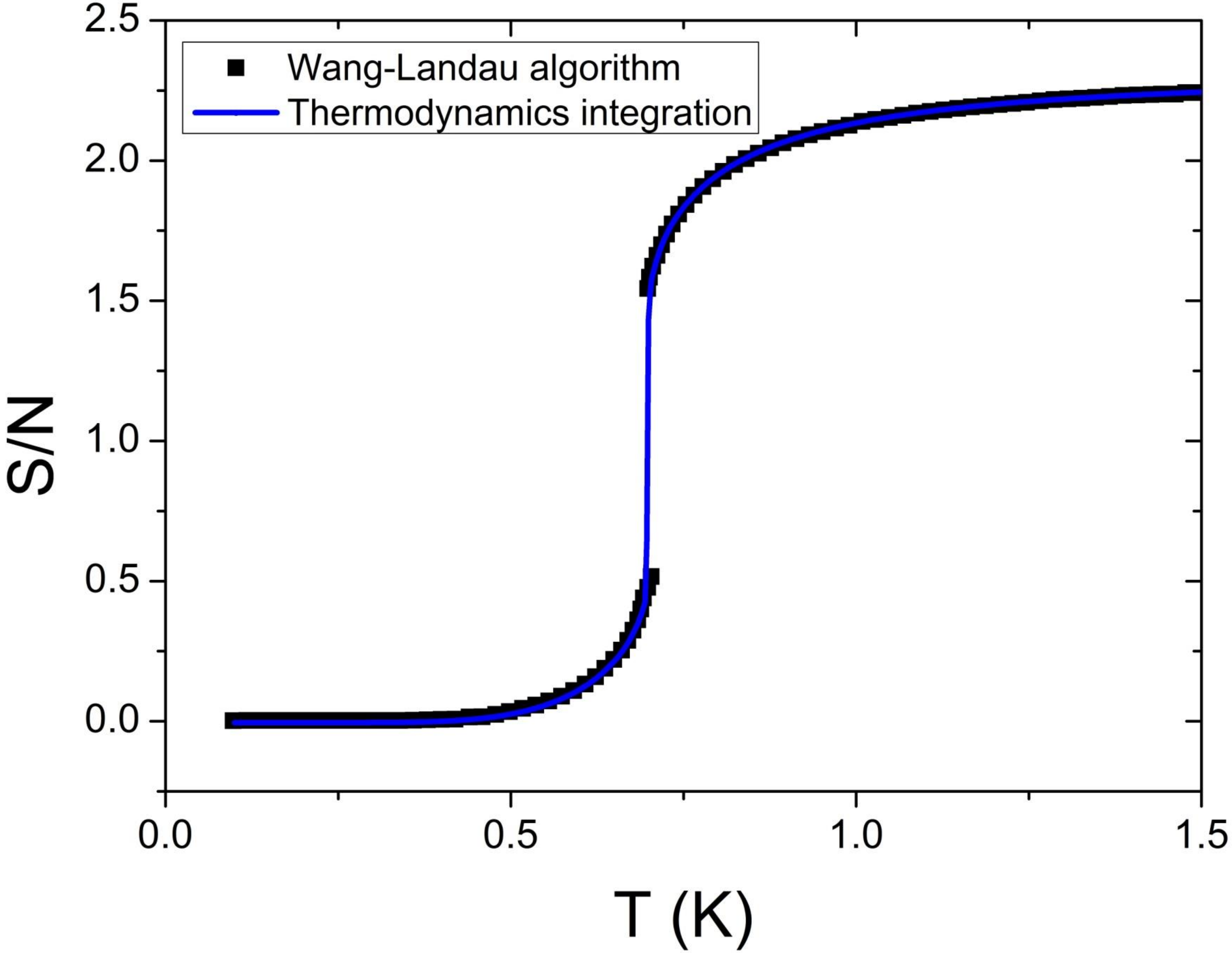
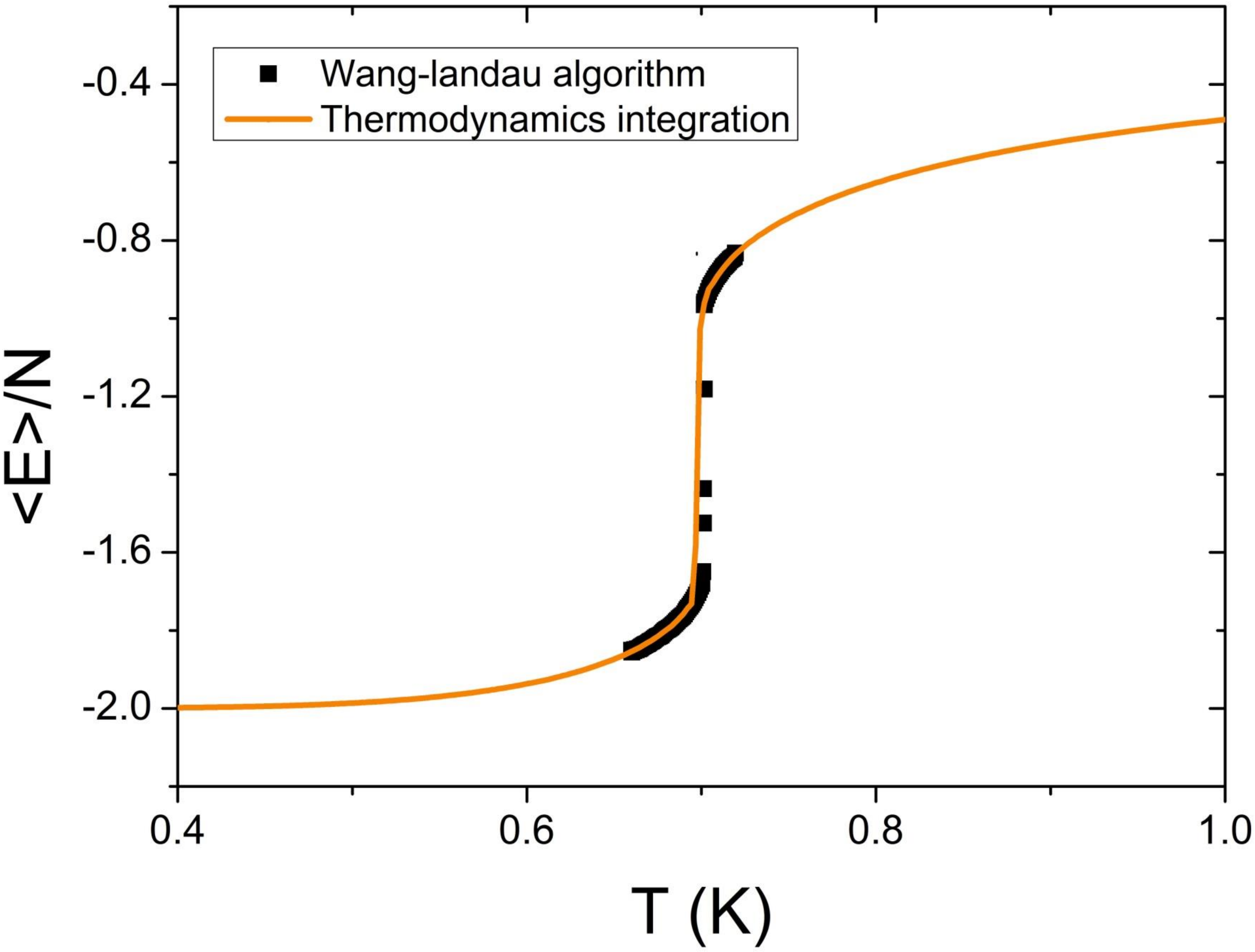


[2] Fugao Wang & D. P. Landau, Physical Review E, Volume 64, 056101



[2] Fugao Wang & D. P. Landau, Physical Review E, Volume 64, 056101

Class-work

P 233 6.11

Homework

P 233   6.1-6.5,6.6, or add 6.11