Statistical physics	Summer 2019

Entropy and thermodynamic potentials — 11.03, 2019

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1 Overview

In this lecture we continued talking about enthropy. Then we started discussing thermodynamic potentials.

2 Reminding

Let's remind us first law of thermodynamics:

$$dU = \partial Q + \partial W - \partial Q - pdV \tag{1}$$

Where for magnets we have

$$dU = \partial Q - MdH \tag{2}$$

where M - magnetisation.

We also defined Boltzmann entropy as

$$S_B = k_B ln\Omega \tag{3}$$

3 Boltzmann entropy

Let's assume we have constant temperature $T = const$. Then if we divide our volume V into small parts V_0, we have $\Omega^{(N)} = (\frac{V}{V_0})^N$ and then entropy depends on V and equals

$$S_B(V) = k_B \cdot Nln\frac{V}{V_0} \tag{4}$$

However, if we remove some volume dV from our box, we get

$$\begin{aligned} S_B(V+dV) &= k_B \cdot Nln\frac{V+dV}{V_0} \\ \partial S_B &= S_B(V+dV) - S_B(V) = k_B N\{ln\frac{V+dV}{V_0} - ln\frac{V}{V_0}\} = k_B N\, ln(\frac{V+dV}{V}) \\ \partial S_B &= k_B N\, ln(1+\frac{dV}{V}) \approx k_B N\frac{dV}{V}, \text{ since } ln(1+x) \approx x \text{ if } |x| \ll 1,\ \frac{dV}{V} \ll 1 \end{aligned} \tag{5}$$

3.1 Thermodynamic definition of change of enthropy

Let's recall

$$\begin{aligned} &pV = nRT \quad \to \quad \frac{k_B N}{V} = \frac{p}{T} \\ &\partial S_B = \frac{pdV}{T},\ T = const \ \to \ U_{\text{ideal gas}} = U(T) \text{ or } U(V) \text{ or } U(p) \ \to \ U_{\text{ideal gas}} = const \\ &dU = 0 \ \to \ 0 = \partial Q - pdV \quad \to \quad \partial S_B = \frac{(\partial Q)_{rev}}{T} \end{aligned} \tag{6}$$

So we have our definition of thermodynamic change of enthropy:

$$\partial S = \frac{(\partial Q)_{rev}}{T} \tag{7}$$

3.2 Examples

- On the graphic we can see a process with constant temperature. We have $pV = nRT = const$. Then

$$W = \int dV = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT(lnV_1 - lnV_2) = nRT\,ln\left(\frac{V_1}{V_2}\right) \tag{8}$$

  So we have

$$Q = W = nRT\,ln\left(\frac{V_1}{V_2}\right) \tag{9}$$

  And then

$$\Delta S = \int \frac{(\partial Q)_{rev}}{T} = \frac{1}{T}\int (\partial Q)_{rev} = \frac{Q}{T} \tag{10}$$

  so finally

$$\Delta S = nR\,ln\left(\frac{V_1}{V_2}\right) \tag{11}$$

  then if $V_2 > V_1 \ \to \ \Delta S > 0$.

- Another process we have shown on graphic 2. In this process $\Delta S = kR\,ln\left(\frac{V_1}{V_2}\right)$ is the same for each way, so it is not dependent on path. Then S is a function of state.
  So **S is thermodynamic potential**.

4 Thermodynamic potentials

As we already know

$$dU = TdS - p\,dV \quad \to \quad U = U(V,\, S)$$

where V, S are "neutral" various. So U is another thermodynamic potential.

Definition 1. *Free energy is defined as*

$$F = U - TS$$

Definition 2. *Gibbs free energy is defined as*

$$G = F + pV$$

All of them are functions of state, so they are thermodynamic potentials. They are "equivalent" in a way - which means that if you have one of them, you can derive others.

4.1 Example 1

$$\begin{aligned}
U &= U(v, S) \text{ - given}, \quad F = ? \\
dU &= T dS - p\, dV, \quad \text{let } V = const \;\rightarrow\; dV = 0 \\
T &= \frac{dU}{dS} = \left(\frac{dU}{dS}\right)_V, \quad V = const \\
p &= -\left(\frac{dU}{dV}\right)_S, \quad \text{so from that we have} \\
p &= p(V,\, S), \quad \text{and} \quad T = T(V,\, S). \quad \text{Then} \\
F &= U - TS = U - \left(\frac{dU}{dS}\right)_V \cdot S.
\end{aligned} \tag{12}$$

So finally we have

$$F = U - \left(\frac{dU}{dS}\right)_V \cdot S \tag{13}$$

where U is given.

4.2 Example 2

Free energy $F = F(?)$

$$\begin{aligned}
F = U - TS \quad &\rightarrow \quad dF = dU - d(TS) = T\, dS - p\, dV - (T\, dS + dT \cdot S) \\
dF = -S\, dT - p\, dV \quad &\rightarrow \quad F = F(T, V)
\end{aligned} \tag{14}$$

So finally we have

$$F = F(T, V)$$

How to find U?

$$\begin{aligned}
U &= F + TS, \quad S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad p = -\left(\frac{\partial F}{\partial V}\right)_T \\
U &= F - T \cdot \left(\frac{\partial F}{\partial T}\right)_V = -T^2 \left(\frac{\partial}{\partial T}\frac{F}{T}\right)_V
\end{aligned} \tag{15}$$