PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 21:

Introduction to statistical mechanics – Microcanonical vs canonical ensembles

Reading: Chapter 6.1 and 6.5

1. **Microcanonical ensemble and multiplicity factor**
2. **Boltzmann's entropy in the context of a heat bath**
3. **Canonical ensemble**

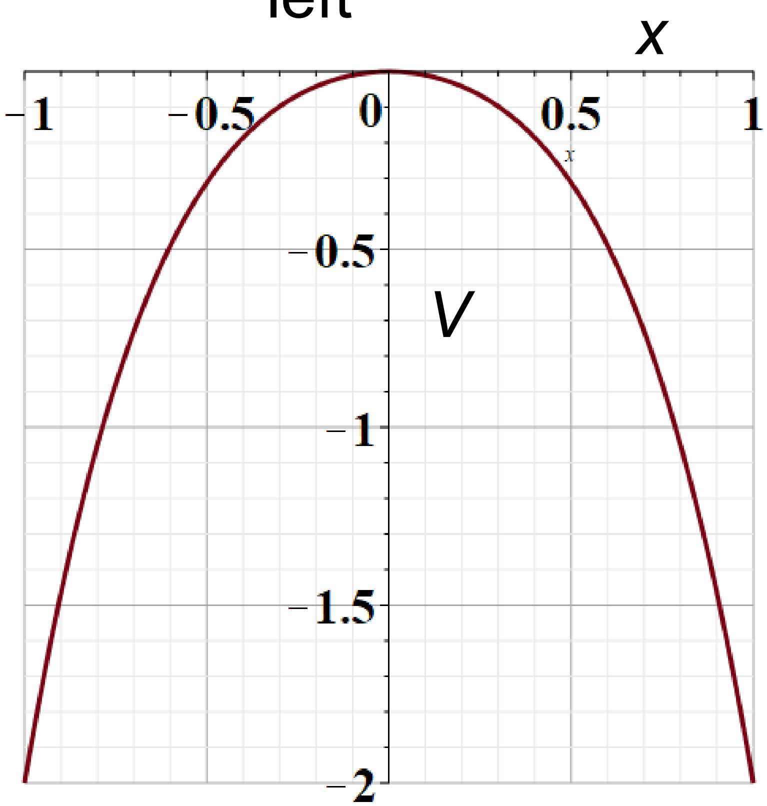
18	Mon: 03/08/2021	5.5	Dilute solutions	#16	03/10/2021
19	Wed: 03/10/2021	5.6	Chemical equilibria	#17	03/12/2021
20	Fri: 03/12/2021	Chap. 1-5	Review		
	Mon: 03/15/2021	No class	*APS March Meeting*	Take Home Exam	
	Wed: 03/17/2021	No class	*APS March Meeting*	Take Home Exam	
	Fri: 03/19/2021	No class	*APS March Meeting*	Take Home Exam	
21	Mon: 03/22/2021	Chap. 6.1 & 6.5	Microcanonical and canonical ensembles		

Comment on last question on mid term –

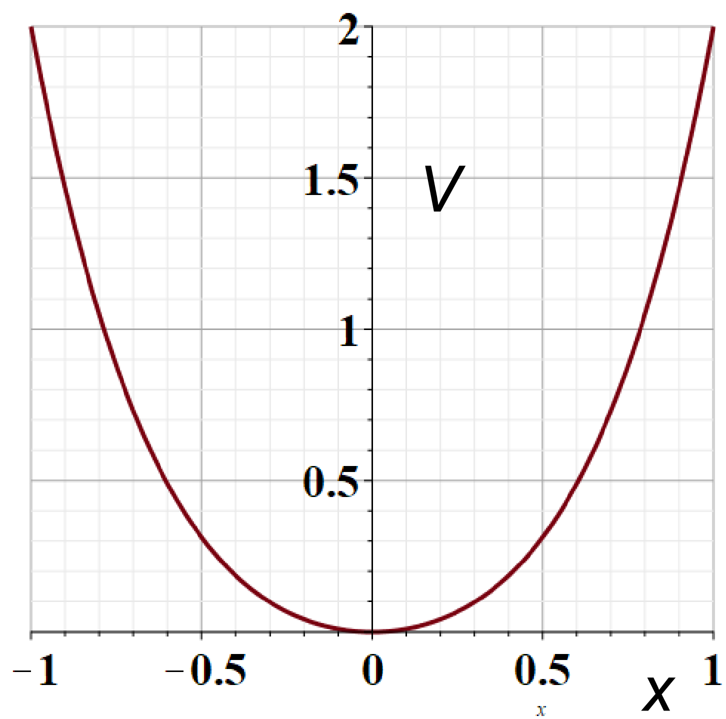
The curves below represent a potential function V(x)

Which of them have a stable equilibrium point?

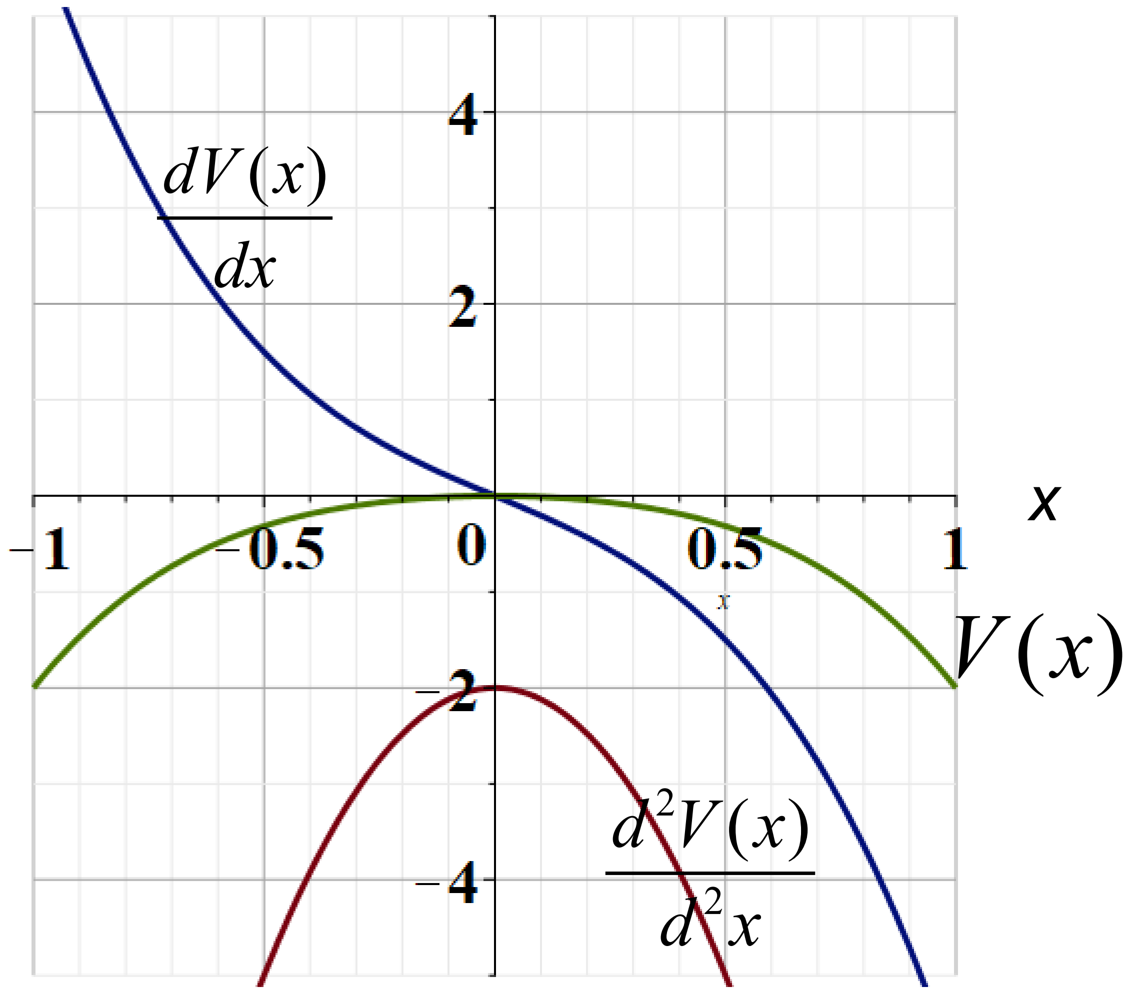
left



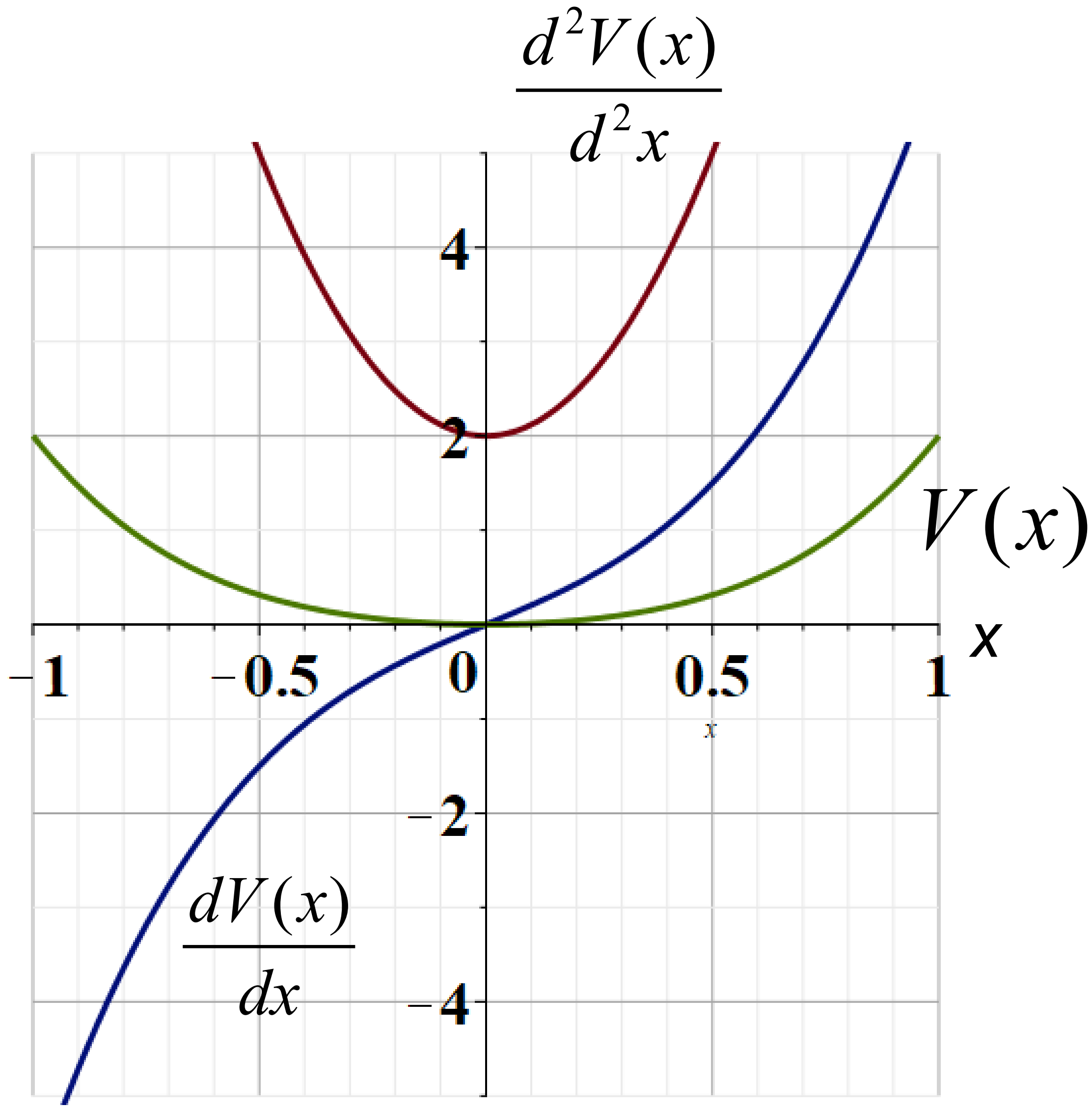
right



Left curve



Right curve



Introduction to statistical mechanics –

Up to now our discussion of statistical mechanics has been focused on the analysis of the multiplicity function Ω which, for an isolated system, describes the number of "micro" states which have the same values of the microstate variables such as N,V, U for a free electron gas. The literature refers to this as a "micro canonical ensemble".

For this micro canonical ensemble, Boltzmann used the multiplicity function to calculate the entropy --

$$S = k_B \ln(\Omega(N,V,U))$$

For a mono atomic ideal gas having N particles in a volume V at an energy U --

$$\Omega(N,V,U) \approx \frac{V^N}{h^{3N}N!}\frac{\pi^{3N/2}}{(3N/2)!}\left(\sqrt{2MU}\right)^{3N}$$

$$\approx \left(\frac{V}{N}\left(\frac{4\pi MU}{3Nh^2}\right)^{3/2} e^{5/2}\right)^N$$

$$S(N,V,U) \approx Nk_B\left(\ln\left(\frac{V}{N}\left(\frac{4\pi MU}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right)$$

Sackur-Tetrode expression for the entropy

Now consider the notion of the micro canonical system in terms of probabilities. The tacit assumption is that each micro state of our system is equally likely.

Consider a given ensemble -- with multiplicity function $\Omega = \Omega(U, V, N)$

We will label a given micro state by i and its probability is

$$p_i = \frac{1}{\Omega} \quad \text{with} \quad \sum_{i=1}^{\Omega} p_i = 1$$

Boltzmann's entropy function $S = k \ln \Omega$

can be expressed in terms of the probabilities as

$$S = -k \sum_{i=1}^{\Omega} (p_i \ln p_i) = -k \sum_{i=1}^{\Omega} \left(\frac{1}{\Omega} \ln \frac{1}{\Omega} \right) = k \ln \Omega$$

We will then introduce a "canonical ensemble"

Important equation for micro canonical ensemble:

$$S = k \ln \Omega$$

where Ω is the multiplicity function.

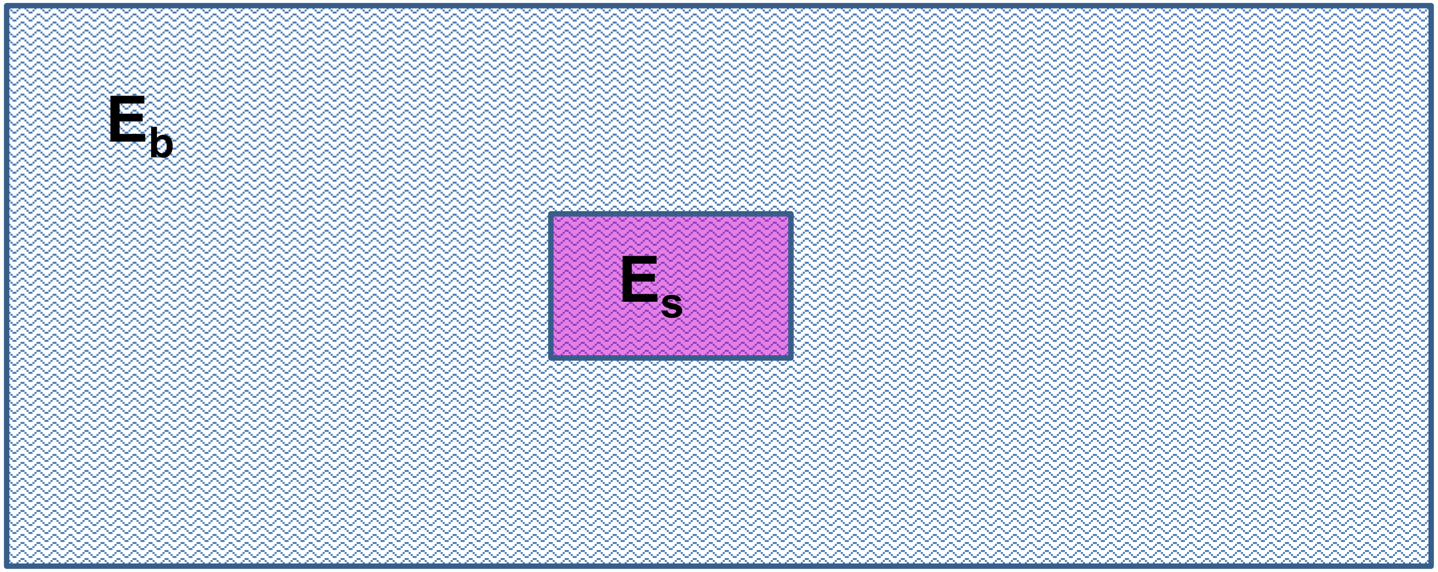
Important equation for canonical ensemble:

$$F = -kT \ln Z$$

where Z is called the partition function

Now, we would like to extend the analysis of an isolated system to that of a system within a heat bath. The system within the heat bath will be analyzed in terms of a "canonical ensemble" --

Canonical ensemble:



Canonical ensemble in terms of the internal energies of the bath (b), system (s), and total

$$U_{tot} = U_s + U_b \qquad\qquad U_s << U_b$$

Probability that system is energy U_s :

$$\mathcal{P}_s = \frac{\Omega_s(U_s)\Omega_b\left(U_{tot} - U_s\right)}{\sum_{s'}\Omega_s(U_{s'})\Omega_b\left(U_{tot} - U_{s'}\right)} \approx \frac{\Omega_b\left(U_{tot} - U_s\right)}{\sum_{s'}\Omega_b\left(U_{tot} - U_{s'}\right)}$$

$$\ln \mathcal{P}_s = C + \ln \Omega_b\left(U_{tot} - U_s\right)$$

$$\approx C + \ln \Omega_b\left(U_{tot}\right) - U_s\left(\frac{\partial \ln \Omega_b\left(U\right)}{\partial U}\right)_{U_{tot}} + \cdots$$

Canonical ensemble (continued)

$$\ln \mathcal{P}_s = C + \ln \Omega_b\left(U_{tot} - U_s\right)$$

$$\approx C + \ln \Omega_b\left(U_{tot}\right) - U_s \left(\frac{\partial \ln \Omega_b\left(U\right)}{\partial U}\right)_{U_{tot}} + \cdots$$

Note that: $\left(\frac{\partial k_B \ln \Omega_b\left(U\right)}{\partial U}\right)_{U_{tot}} \approx \left(\frac{\partial S_b(U)}{\partial U}\right)_{V,N} = \frac{1}{T_b}$

$$\ln \mathcal{P}_s \approx C + \ln \Omega_b\left(U_{tot}\right) - U_s \left(\frac{1}{k_B T_b}\right) + \cdots$$

$$\Rightarrow \mathcal{P}_s = C' e^{-U_s/k_B T_b}$$

Canonical ensemble:

$$\mathcal{P}_s = C' e^{-U_s/k_B T_b}$$

$$= \frac{1}{Z} e^{-U_s/k_B T_b}$$

where: $Z \equiv \sum_{s'} e^{-U_{s'}/k_B T_b}$ "partition function"

Calculations using the partition function:

$$Z(T) \equiv \sum_{s'} e^{-U_{s'}/k_B T} = \sum_{s'} e^{-\beta U_{s'}} \quad \text{where } \beta = \tfrac{1}{k_B T}$$

Canonical ensemble continued – average energy of system:

$$\langle U_s \rangle = \frac{1}{Z}\sum_{s'} U_{s'} e^{-U_{s'}/k_B T} = \frac{1}{Z}\sum_{s'} U_{s'} e^{-\beta U_{s'}}$$

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

$$\beta \equiv \frac{1}{kT}$$

Heat capacity for canonical ensemble:

$$C_V = \frac{\partial \langle U_s \rangle}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial \langle U_s \rangle}{\partial \beta}$$

$$= \frac{1}{k_B T^2}\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{1}{k_B T^2}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2\right)$$

$$= \frac{1}{kT^2}\left(\langle U_s{}^2 \rangle - \langle U_s \rangle^2\right)$$

Comment – Note that in this formulation we are accessing the system energies U_s while typically we only know the individual particle energies.   For real evaluations, additional considerations will be needed.

Analyzing the relationship of the partition function with the notion of entropy

According to our previous statements, let us suppose that

$$S = -k\sum_s \mathcal{P}_s \ln \mathcal{P}_s \quad \text{for} \quad \mathcal{P}_s = \frac{e^{-\beta U_s}}{Z}$$

$$S = -k\sum_s \frac{e^{-\beta U_s}}{Z} \ln\left(\frac{e^{-\beta U_s}}{Z}\right) = -k\sum_s \frac{e^{-\beta U_s}}{Z}\left(-\beta U_s - \ln Z\right)$$

$$\Rightarrow S = k\beta\langle U\rangle + k\ln Z = \frac{1}{T}\langle U\rangle + k\ln Z$$

$$\Rightarrow ST - \langle U\rangle = kT\ln Z$$

$$F = -kT\ln Z$$

- Helmholtz free energy

Note that the Helmholtz free energy is given by

$$F = U - TS$$

Recap:

Microcanonical ensemble: Internal energy U

$$S(U,V,N) = k_B \ln\left(\Omega(U,V,N)\right)$$

$$U(S,V,N) \quad \Rightarrow dU = TdS - PdV + \mu dN$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{k_B}{\Omega}\left(\frac{\partial \Omega}{\partial U}\right)_{V,N}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{k_B}{\Omega}\left(\frac{\partial \Omega}{\partial V}\right)_{U,N}$$

$$\mu = \left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{k_B}{\Omega}\left(\frac{\partial \Omega}{\partial N}\right)_{U,V}$$

Canonical ensemble

Partition function; keep N constant

$$Z \equiv \sum_{s'} e^{-U_{s'}/k_B T} \equiv \sum_{s'} e^{-\beta U_{s'}} = Z(T,V) \equiv Z(\beta,V)$$

$$F(T,V) = U - TS = -k \ln Z(T,V)$$

Generalization --

$$F(T,V,N) = -kT \ln Z(T,V,N)$$

$$dF = -SdT - PdV + \mu dN$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S = \left(\frac{-\partial(kT \ln Z)}{\partial T}\right)_{V,N} = -k \ln Z - kT\left(\frac{\partial(\ln Z)}{\partial T}\right)_{V,N}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P = -kT\left(\frac{\partial(\ln Z)}{\partial V}\right)_{T,N}$$

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu = -kT\left(\frac{\partial(\ln Z)}{\partial N}\right)_{T,V}$$

Example: Canonical distribution for free particles

Classical canonical distribution for N free particles of mass m moving in d dimensions in box of length L

$$Z(T,V,N)=\frac{1}{N!h^{dN}}\int_{0\leq r_i\leq L} d^{dN}r\int d^{dN}p\; e^{-\frac{\beta}{2m}\left(\sum_i p_i^2\right)}$$

$$=\frac{L^{dN}}{N!h^{dN}}\left(2\pi mkT\right)^{dN/2}$$

$$=\frac{1}{N!}\left(L\right)^{dN}\left(\frac{2\pi mkT}{h^2}\right)^{dN/2}$$

For $d=3$, $L^3\equiv V$

$$Z(T,V,N)=\frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

Compare with microcanonical ensemble:

$$\Omega(U,V,N)=\frac{V^N}{N!\Gamma\left(\frac{3N}{2}+1\right)}\left(\frac{2\pi mU}{h^2}\right)^{3N/2}$$

Example of a canonical ensemble consisting of 2 particles

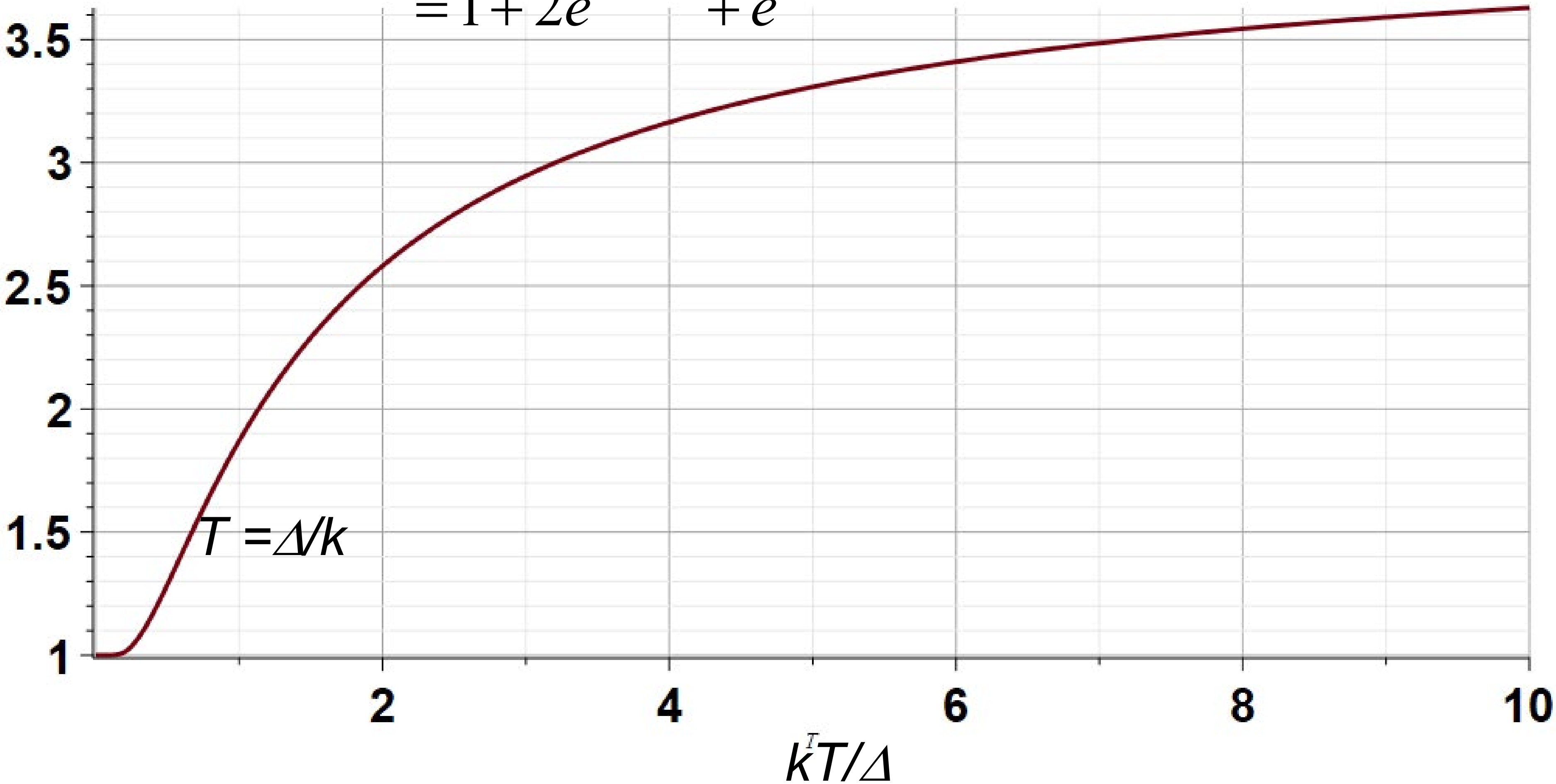
Consider a system consisting of 2 distinguishable particles. Each particle can be in one of two microstates with single-particle energies 0 and Δ. The system is in equilibrium with a heat bath at temperature T.

s	ε_1	ε_2	U_s
1	0	0	0
2	0	Δ	Δ
3	Δ	0	Δ
4	Δ	Δ	2Δ

$$Z = \sum_s e^{-U_s/kT} = 1 + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-2\Delta/kT} = 1 + 2e^{-\Delta/kT} + e^{-2\Delta/kT}$$

$$Z = \sum_s e^{-U_s/kT} = 1 + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-2\Delta/kT}$$

$$= 1 + 2e^{-\Delta/kT} + e^{-2\Delta/kT}$$



Model results for Helmholtz free energy and internal energy