Van der Waals Fluid – Deriving the Fundamental Relation

$$ds = \frac{1}{T}du + \frac{P}{T}dv$$

$$\Downarrow$$

$$ds = \frac{cR}{u + a/v}du + \left(\frac{R}{v-b} - \frac{a}{v^2}\frac{cR}{u + a/v}\right)dv$$

$$\Downarrow$$

$$\boxed{s = R\ln(v-b) + cR\ln(u + a/v) + const}$$

How do we integrate the differential above to get the fundamental relation?

Pitfalls of Integration of Functions of Multiple Variables

$$ds = \frac{cR}{u + a/v}du + \left(\frac{R}{v-b} - \frac{a}{v^2}\frac{cR}{u + a/v}\right)dv \quad \Longleftrightarrow \quad ds = \frac{\partial s}{\partial u}du + \frac{\partial s}{\partial v}dv$$

Naïve approach: term-by-term “integration”:

$$ds = cRd\left(\ln(u + a/v)\right) + Rd\left(\ln(v-b)\right) + \frac{cR}{u + a/v}d\left(a/v\right) =$$

$$= cRd\left(\ln(u + a/v)\right) + Rd\left(\ln(v-b)\right) + cRd\left(\ln(u + a/v)\right)$$

After integration:

$$s = 2cR\ln(u + a/v) + R\ln(v-b) + const$$

- Wrong answer! This is because we treated variables as constants

Pitfalls of Integration of Functions of Multiple Variables

The correct way of integrating ds (note that although it works for the particular example of Van der Waals fluid, it is not generally applicable):

$$ds = \frac{cR}{u + a/v} du + \left(\frac{R}{v-b} - \frac{a}{v^2} \frac{cR}{u + a/v} \right) dv$$

$$ds = \frac{cR}{u + a/v} du + \frac{R}{v-b} dv + \frac{cR}{u + a/v} d(a/v)$$

$$ds = \frac{cR}{u + a/v} d(u + a/v) + \frac{R}{v-b} dv$$

Now we have functions of the same arguments as differentials. Now integration is legitimate:

$$s = R \ln(v - b) + cR \ln(u + a/v) + const$$

General Method of Integration

Problem: We have a differential form:

$$ds = M(u,v)du + N(u,v)dv$$

We also know that this form is an exact differential of a function $s(u,v)$:

$$ds = \frac{\partial s(u,v)}{\partial u}du + \frac{\partial s(u,v)}{\partial v}dv \quad \text{where} \quad \frac{\partial s(u,v)}{\partial u} = M(u,v) \quad \frac{\partial s(u,v)}{\partial v} = N(u,v)$$

We can do “partial” integration of a differential equation above (assuming v is constant):

$$\frac{\partial s(u,v)}{\partial u} = M(u,v) \quad \Longrightarrow \quad s(u,v) = \int M(u,v)du + C(v)$$

Note that the “constant” of integration must depend on v for the above procedure to be correct

General Method of Integration

1. "Partial" integration in u

$$s(u,v)=\int M(u,v)du+C(v)$$

2. Partial derivative in v

$$\frac{\partial s(u,v)}{\partial v}=\int\frac{\partial M(u,v)}{\partial v}du+\frac{dC(v)}{dv}$$

3. Substitution of $N(u,v)$ for $\frac{\partial s(u,v)}{\partial v}$

$$\frac{dC(v)}{dv}=N(u,v)-\int\frac{\partial M(u,v)}{\partial v}du$$

4. Integrating both sides with respect to v, we obtain $C(v)$

Step 5 Substitute $C(v)$

The procedure above looks like a case of circular logic, but it always works

General Method of Integration Applied to VdW Fluid

Let us apply the 5-step algorithm described above to the case of VdW fluid

$$ds = \frac{cR}{u+a/v}du + \left(\frac{R}{v-b} - \frac{a}{v^2}\frac{cR}{u+a/v}\right)dv$$

$$M(u,v) = \frac{cR}{u+a/v} \qquad N(u,v) = \left(\frac{R}{v-b} - \frac{a}{v^2}\frac{cR}{u+a/v}\right)$$

1. “Partial” integration in u ($s(u,v) = \int M(u,v)du + C(v)$)

$$s(u,v) = \int \frac{cR}{u+a/v}du + C(v) = cR\ln(u+a/v) + C(v)$$

General Method of Integration Applied to VdW Fluid

2. Partial derivative in v

$$s(u,v)=cR\ln\left(u+a/v\right)+C(v) \quad \Rightarrow \quad \frac{\partial s(u,v)}{\partial v}=-\frac{a}{v^2}\frac{cR}{u+a/v}+\frac{dC(v)}{dv}$$

3. Substitution of $N(u,v)$ for $\dfrac{\partial s(u,v)}{\partial v}$

$$\frac{dC(v)}{dv}=N(v,y)+\frac{a}{v^2}\frac{cR}{u+a/v}=\left(\frac{R}{v-b}-\frac{a}{v^2}\frac{cR}{u+a/v}\right)+\frac{a}{v^2}\frac{cR}{u+a/v}=\frac{R}{v-b}$$

General Method of Integration Applied to VdW Fluid

4. Integration of both sides with respect to v, we obtain $C(v)$

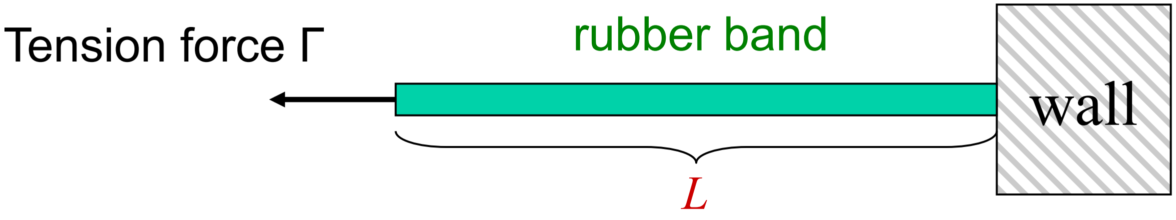
$$C(v) = \int \frac{dC(v)}{dv} dv = \int \frac{R}{v-b} dv = R\ln\left(v-b\right) + const$$

5. Substitution of $C(v)$ back into the expression for $s(u,v)$

$$s(u,v) = cR\ln\left(u + a/v\right) + R\ln\left(v-b\right) + const$$

Rubber Band or Polymer

This example will show spectacular macroscopic manifestations of entropy – *elasticity of an ideal rubber band is not due to "elastic energy" but is due to entropy!*



Let us chose the extensive coordinates of the system:

- Internal energy U, is always a coordinate
- Length of the rubber band L

The fundamental relation will have a form: $S(U,L)$

If we are not going to bend or twist the rubber band, we have enough coordinates to find the equilibrium state of the rubber band.

Rubber band or Polymer

Experimental observations:

1. Energy of the rubber band *in equilibrium with the environment* is *independent of the length of the rubber band* and is proportional to temperature:

$$U = cL_0T$$

- first experimental "equation of state"

where L_0 is the equilibrium length (constant)

2. Tension Γ is proportional to change in length:

$$\Gamma = f(T)\frac{(L - L_0)}{L_0}$$

- second experimental "equation of state"

Hooke's law

3. Tension increases with increasing T for fixed length L.

Rubber band or Polymer

The differential form of the fundamental relation is:

$$ds = \frac{1}{T}du - \frac{\Gamma}{T}dl \qquad \Rightarrow \qquad dS = \frac{1}{T}dU - \frac{\Gamma}{T}dL$$

Since mixed second partial derivatives of S must be equal:

$$\frac{\partial}{\partial L}\left(\frac{1}{T}\right)_U = \frac{\partial}{\partial U}\left(-\frac{\Gamma}{T}\right)_L$$

Rubber band or Polymer

Differentiability condition:

$$\boxed{\frac{\partial}{\partial L}\left(\frac{1}{T}\right)_U = \frac{\partial}{\partial U}\left(-\frac{\Gamma}{T}\right)_L}$$

Equations of state:

$$\boxed{\frac{1}{T} = \frac{cL_0}{U} \qquad -\frac{\Gamma}{T} = -\frac{cf(T)}{U}(L - L_0)}$$

$$\frac{\partial}{\partial L}\left(\frac{1}{T}\right)_U = \frac{\partial}{\partial L}\left(\frac{cL_0}{U}\right)_U = 0 \;\Rightarrow\; \frac{\partial}{\partial U}\left(-\frac{\Gamma}{T}\right)_L = \frac{\partial}{\partial U}\left(-\frac{cf(T)}{U}(L - L_0)\right)_L = 0$$

$$\Rightarrow\; \frac{\partial}{\partial U}\left(\frac{f(T)}{U}\right) = 0 \;\Rightarrow\; f(T) = \frac{B}{L_0}U$$

where B is a constant

Rubber band or Polymer

Now we can substitute the equations of state into the differential for dS:

$$dS = \frac{1}{T}dU - \frac{\Gamma}{T}dL \quad \Rightarrow \quad dS = \frac{cL_0}{U}dU - cB\frac{(L-L_0)}{L_0}dL$$

Integrating, we obtain:

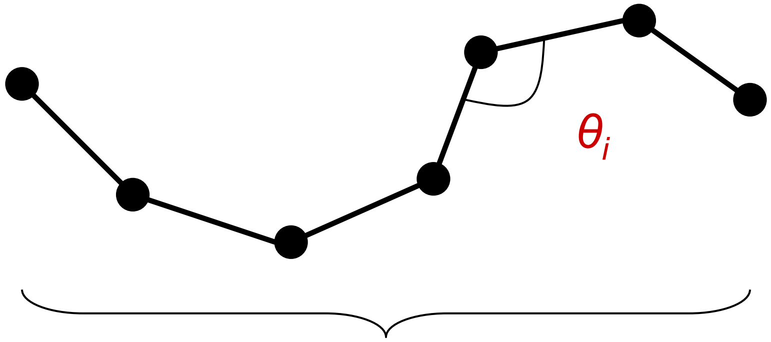
$$\boxed{S = cL_0\ln(U) - \frac{cB}{2}\frac{(L-L_0)^2}{L_0} + const}$$

We see that entropy decreases with increasing length of the rubber band (polymer chain). Therefore, the tendency of the rubber band to shrink is driven not by minimizing elastic energy (in our model there is no elastic energy) but by maximizing entropy

Polymer : microscopic model

A model polymer consists of monomers that are connected by rigid rods. The monomers are can rotate with respect to each other at zero energy cost. This is why the energy does not depend on the macroscopic length of the polymer.

$N = 7$ monomers



U does not depend on θ_i

L – macroscopic length of a polymer chain

Polymer : microscopic model

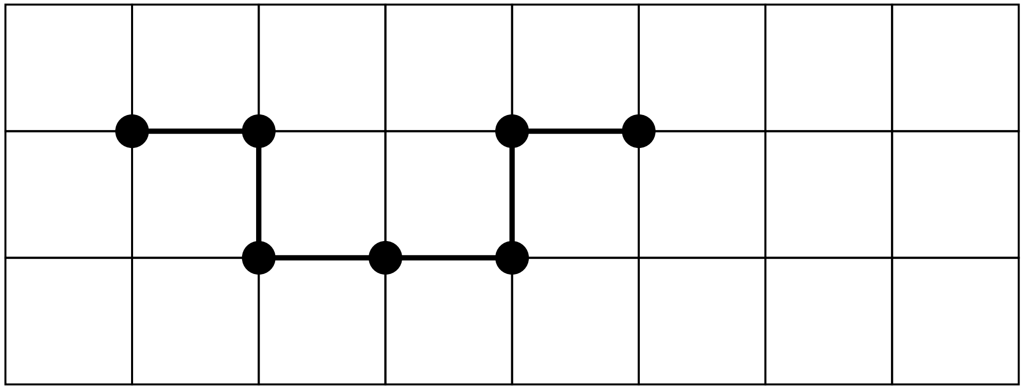
We will examine a toy model of 2D polymer where monomers sit on a square lattice

Number of monomers, N, is fixed

N = 7

Polymer length, L,
is not constrained

L = 4

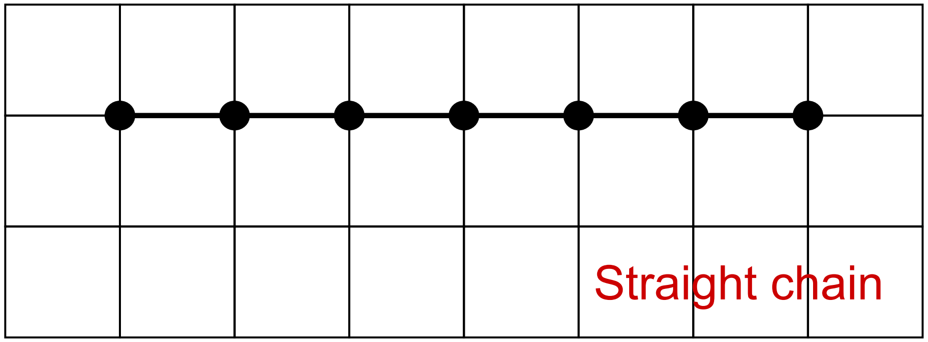


Polymer: microscopic model

L = 6

Single microstate Ω = 1

S ~ ln(Ω)=0

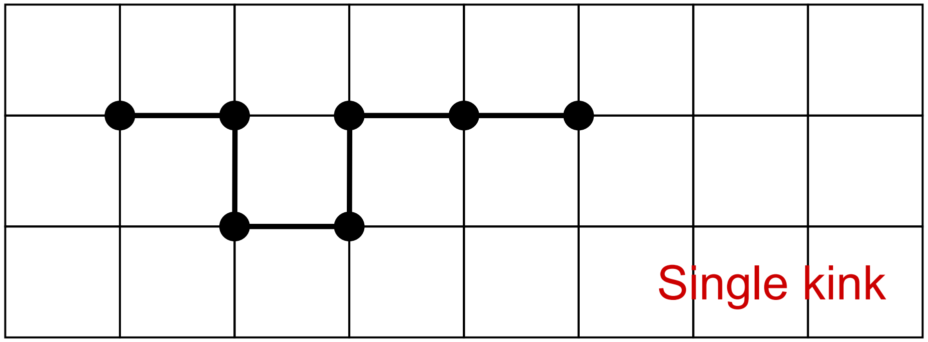


L = 4

Number of microstates (assuming monomers cannot occupy the same volume):

Ω = 8+6+4+2 ?

S ~ ln(Ω) > 0



These states have the same energy

The number of microstates rises dramatically with decreasing length, so the entropy increases with decreasing length. State with L = 0 has the highest entropy.