Problem 3.3-1. Fundamental relation from the equations of state

Equations of state: $T = \frac{3As^2}{v}$ $P = \frac{As^3}{v^2}$

a) To find the chemical potential, let us use the Gibbs-Duhem relation. Since the independent variables are s and v, it is convenient to use the Gibbs-Duhem relation in the energy representation:

$$d\mu = -s dT + v dP \quad \Rightarrow \quad d\mu = -sd\left(\frac{3As^2}{v}\right) + vd\left(\frac{As^3}{v^2}\right)$$

$$\Rightarrow \quad d\mu = \frac{3As^3}{v^2}dv - \frac{6As^2}{v}ds - \frac{2As^3}{v^2}dv + \frac{3As^2}{v}ds \quad \Rightarrow$$

$$d\mu = \frac{As^3}{v^2}dv - \frac{3As^2}{v}ds \quad \Rightarrow \quad d\mu = -d\left(\frac{As^3}{v}\right) \quad \Rightarrow \quad \mu = -\frac{As^3}{v} + const$$

Problem 3.3-1. Fundamental relation from the equations of state

Molar form of the Euler equation of state in the energy representation is:

$$u = Ts - Pv + \mu$$

Substituting the equations of state into this equation:

$$u = \frac{3As^2}{v}s - \frac{As^3}{v^2}v - \frac{As^3}{v} + const = \frac{As^3}{v} + const$$

$$\boxed{u = \frac{As^3}{v} + const}$$

Problem 3.3-1. Fundamental relation from the equations of state

Now let us directly integrate the molar form of the equations of state:

$$du = Tds - Pdv$$ ⇨ $$du = \frac{3As^2}{v}ds - \frac{As^3}{v^2}dv$$ ⇨

$$du = \frac{3As^2}{v}ds - \frac{As^3}{v^2}dv = d\left(\frac{As^3}{v}\right)$$ ⇨ $$u = \frac{As^3}{v} + const$$

Problem 3.5-1. Fundamental relation from the equations of state

c) Equations of state: $P = \frac{u}{v}\frac{c+buv}{a+buv}$ $\qquad T = \frac{u}{a+buv}$

Equations of state are functions of u and v, so convenient to work in the entropy representation in molar form:

$$ds = \left(\frac{\partial s}{\partial u}\right)_v du + \left(\frac{\partial s}{\partial v}\right)_u dv = \frac{1}{T}du + \frac{P}{T}dv$$

where $\frac{1}{T} = \frac{a}{u} + bv$ $\qquad \frac{P}{T} = \frac{c}{v} + bu$

Are these equations of state compatible?

$$\left(\frac{\partial^2 s}{\partial u \partial v}\right) = \left(\frac{\partial^2 s}{\partial v \partial u}\right) \quad \Rightarrow \quad \frac{\partial\left(\frac{P}{T}\right)}{\partial u} = \frac{\partial\left(\frac{1}{T}\right)}{\partial v} \quad \Rightarrow \quad b = b$$

Yes

Problem 3.5-1. Fundamental relation from the equations of state

$$ds = \frac{1}{T}du + \frac{P}{T}dv \quad \Rightarrow \quad ds = \left(\frac{a}{u} + bv\right)du + \left(\frac{c}{v} + bu\right)dv$$

$$ds = \frac{a}{u}du + bv(du) + \frac{c}{v}dv + bu(dv) = ad\ln(u) + bv(du) + cd\ln(v) + bu(dv)$$

$vdu = d(uv)$ - This is wrong because v is a variable, not a constant

(same problem in 3.3-1)

$$\begin{aligned} ds &= ad\ln(u) + bv(du) + cd\ln(v) + bu(dv) = ad\ln(u) + cd\ln(v) + b(u(dv) + v(du)) \\ &= ad\ln(u) + cd\ln(v) + bd(uv) \end{aligned}$$

$$\boxed{s = a\ln(u) + c\ln(v) + buv + const}$$

Problem 3.5-6. VdW and ideal gas in equilibrium

In this problem, temperature, pressure and molar volumes of the van der Waals fluid and the ideal gas are the same in equilibrium

VdW: $$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Ideal: $$P = \frac{RT}{v} \Rightarrow v = \frac{RT}{P}$$

Substituting this molar volume into the equation of state for VdW:

$$P = \frac{RT}{\frac{RT}{P} - b} - \frac{aP^2}{(RT)^2}$$

Here P is the only unknown, so need to solve for P

After simple algebra: $$P = RT\left(\frac{1}{b} - \frac{RT}{a}\right) = 3.5 \cdot 10^7 [Pa]$$

Problem 3.6-1. Microwave Background Radiation

Fundamental relation $S = \frac{4}{3} b^{1/4} U^{3/4} V^{1/4}$

Equation of state $U = bVT^4$

Substituting U into expression for S: $S = \frac{4}{3} bVT^3$

Isentropic process: $S_{\text{initial}} = S_{\text{final}} = S$ $2V_i = V_f$

$$\frac{4}{3} bV_i T_i^3 = \frac{4}{3} bV_f T_f^3 = 2\frac{4}{3} bV_i T_f^3 \Rightarrow T_i^3 = 2T_f^3 \Rightarrow T_f = \frac{1}{\sqrt[3]{2}} T_i$$

Note that energy of the background radiation is not conserved, it constantly decreases! Where does it go?

Problem 3.7-2. Rubber Band

Equation of state of the rubber band is: $U = cL_0T$

Since T is constant, U is also constant: $dT = 0 \qquad dU = 0$

From the conservation of energy: $dU = \delta W + \delta Q = 0$

$$\delta Q = -\delta W$$

Calculating work from the second equation of state: $\Gamma = bT\dfrac{L - L_0}{L_1 - L_0}$

$$\delta W = bT\frac{L - L_0}{L_1 - L_0}dL$$

We obtain:

$$\delta Q = -bT\frac{L - L_0}{L_1 - L_0}dL$$

Problem 3.8-1. Paramagnet

The fundamental relation of a simple paramagnetic system is:

$$U = NRT_0 \exp\left(\frac{S}{NR} + \frac{I^2}{N^2 I_0^2}\right)$$

Equations of state:

$$T = \left(\frac{\partial U}{\partial S}\right)_{I,N} = T_0 \exp\left(\frac{S}{NR} + \frac{I^2}{N^2 I_0^2}\right)$$

$$B_e = \left(\frac{\partial U}{\partial I}\right)_{S,N} = \frac{2IRT_0}{NI_0^2} \exp\left(\frac{S}{NR} + \frac{I^2}{N^2 I_0^2}\right)$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,I} = RT_0\left(1 - \frac{S}{NR} - \frac{2I^2}{N^2 I_0^2}\right) \exp\left(\frac{S}{NR} + \frac{I^2}{N^2 I_0^2}\right)$$

Problem 3.8-1. Paramagnet

The Euler equation: $U = TS + B_e V + \mu N$

Substituting the equations of state into the Euler equation:

$$U = RT_0 \exp\left(\frac{S}{NR} + \frac{I^2}{N^2 I_0^2}\right)\left(\frac{S}{R} + \frac{2I^2}{NI_0^2} + 1 - \frac{S}{R} - \frac{2I^2}{NI_0^2}\right)$$

$$\Downarrow$$

$$U = RT_0 \exp\left(\frac{S}{NR} + \frac{I^2}{N^2 I_0^2}\right)$$

This coincides with the postulated fundamental relation

Problem 3.9-6. Model of a solid insulator

Fundamental relation:

$$u = As^{4/3}\exp\left(b(v - v_0)^2 + \frac{s}{3R}\right)$$

a) Show that at s→0, T→0

$$T = \frac{\partial u}{\partial s} = A\exp\left(b(v - v_0)^2 + \frac{s}{3R}\right)\left(\frac{4}{3}s^{1/3} + \frac{s^{4/3}}{3R}\right)$$

Clearly T→0 as s→0 independent on the value of v

Problem 3.9-6. Model of a solid insulator

b) Show that $c_v \sim T^3$ at $T \to 0$

$$u = As^{4/3}\exp\left(b(v-v_0)^2 + \frac{s}{3R}\right)$$

Let us calculate T/u:

$$T = A\exp\left(b(v-v_0)^2 + \frac{s}{3R}\right)\left(\frac{4}{3}s^{1/3} + \frac{s^{4/3}}{3R}\right)$$

$$\frac{T}{u} = \left(\frac{4}{3s} + \frac{1}{3R}\right) \Longrightarrow T = u\left(\frac{4}{3s} + \frac{1}{3R}\right)$$

Since s→0 at T→0, we can simplify the expression for T at low temperature: $T \sim \frac{u}{s}$

On the other hand, from the fundamental relation at low T, we obtain: $u \sim s^{4/3}$

Substituting into the expression for T: $T \sim s^{1/3} \Longrightarrow s \sim T^3$

Since $T \sim \frac{u}{s} \Longrightarrow u \sim Ts \sim T^4$

$$\boxed{c_v = \left(\frac{\partial u}{\partial T}\right)_v \sim \frac{\partial T^4}{\partial T} \sim T^3}$$

This is valid for real insulators – heat capacity vanishes as T^3 at low temperatures

Problem 3.9-6. Model of a solid insulator

c) Show that $c_v \sim R$ at T→∞

s is a monotonically increasing function of u and T so $s\to\infty$, $T\to\infty$ (this is not trivial, related to the fact that second derivative of u with respect to s is positive)

$$T = u\left(\frac{4}{3s} + \frac{1}{3R}\right) \approx \frac{u}{3R} \quad \Rightarrow \quad u \approx 3RT$$

$$\boxed{c_v = \left(\frac{\partial u}{\partial T}\right)_v \approx \frac{\partial(3RT)}{\partial T} \approx 3R}$$

d) Show that $\alpha \to 0$ as $P\to 0$

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \qquad P = -\left(\frac{\partial u}{\partial v}\right)_S \qquad u = As^{4/3}\exp\left(b(v-v_0)^2 + \frac{s}{3R}\right)$$

$$P = -2Ab(v-v_0)As^{4/3}\exp\left(b(v-v_0)^2 + \frac{s}{3R}\right) = -2b(v-v_0)u \quad \Rightarrow \quad v = v_0 - \frac{P}{2bu}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{P}{2bu^2}\left(\frac{\partial u}{\partial T}\right)_p \to 0 \quad \text{when} \quad P \to 0$$

Numerical Problem – Helium and Water

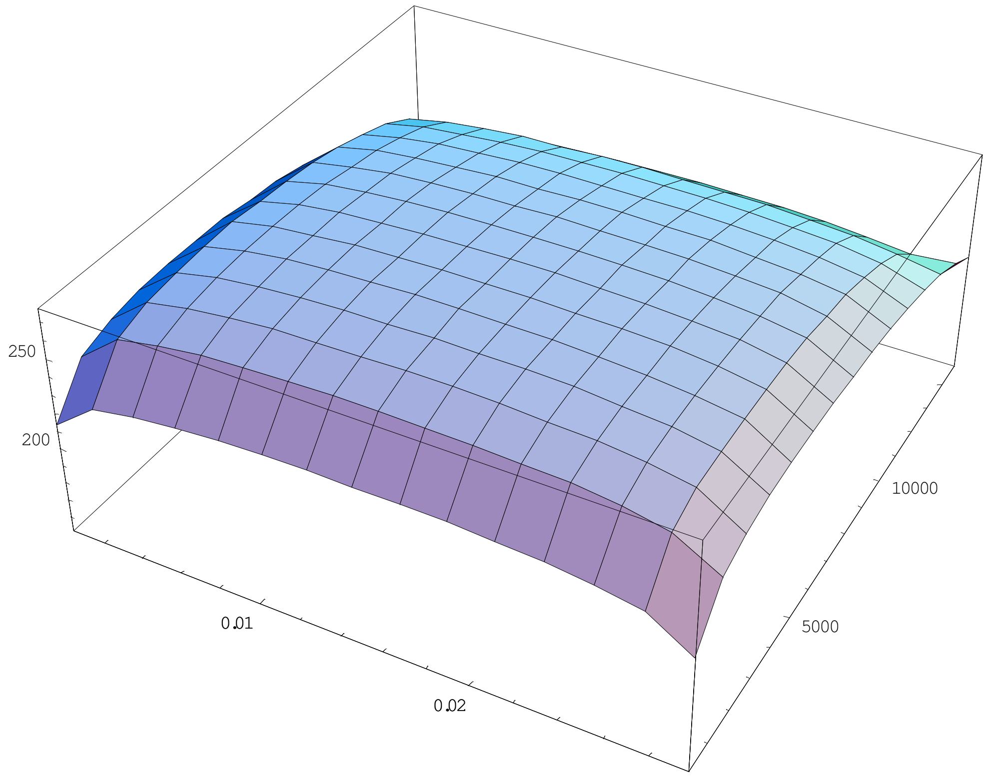
Using the known form of the fundamental relation for the VdW fluid, we can plot entropy of the composite system as:

```
R = 8.3144;V0 = 0.03;U0 = 15000;

ah = 0.00346;bh = 23.7 10^-6;ch = 1.5;(* helium *)

aw = 0.544;bw = 30.5 10^-6;cw = 3.1;(* water*)

Plot3D[R Log[(Vh - bh) (Uh + ah/Vh)^ch] + R Log[(V0 - Vh - bw) (U0 - Uh + aw/(V0 - Vh))^cw], {Vh, 0.01 V0, 0.99 V0}, {Uh, 0.01 U0, 0.99 U0}, PlotRange -> All]
```

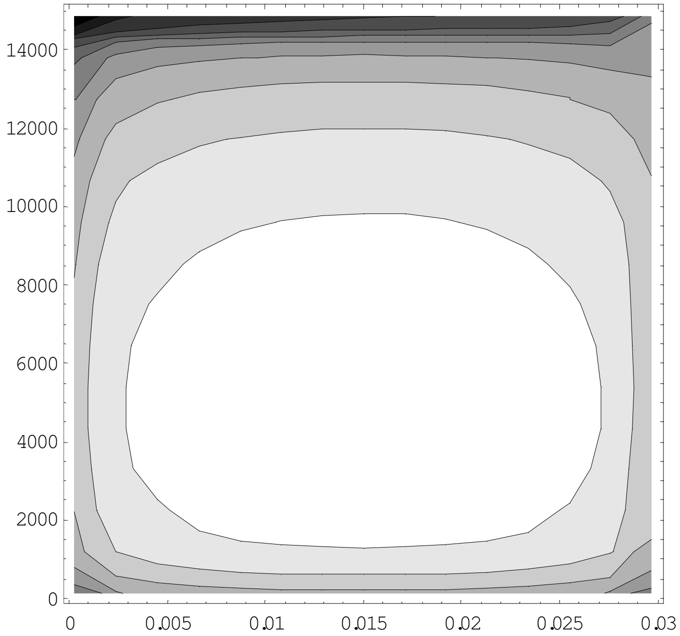


```
-SurfaceGraphics-
```

Numerical Problem – Helium and Water

Same plot in the contour format:

```
ContourPlot[R Log[(Vh - bh) (Uh + ah / Vh)^ch] + R Log[(V0 - Vh - bw) (U0 - Uh + aw / (V0 - Vh))^cw], {Vh, 0.01 V0, 0.99 V0}, {Uh, 0.01 U0, 0.99 U0}, PlotRange -> All]
```



```
-ContourGraphics-
```

Numerical Problem – Helium and Water

Now we can numerically solve for the volume and energy of helium that maximize the entropy of the composite (water + helium) system

$$\mathbf{mve = FindMinimum\left[-R\,Log\left[(Vh - bh)(Uh + ah/Vh)^{ch}\right] - R\,Log[(V0 - Vh - bw)(U0 - Uh + aw/(V0 - Vh))^{cw}], \{Vh, 0.01\,V0, 0.99\,V0\}, \{Uh, 0.001\,U0, 0.999\,U0\}\right]}$$

```
{-273.848,{Vh → 0.0150799,Uh → 4903.03}}
```

$$\mathbf{Vh1 = Vh\,/.\,mve[[2,1]]}$$

```
0.0150799
```

$$\mathbf{Uh1 = Uh\,/.\,mve[[2,2]]}$$

```
4903.03
```

Substituting thus obtained values of the volume and energy into the VdW equations of state, we find the values of temperature and pressure of helium in equilibrium

$$\mathbf{T = \frac{Uh1 + ah/Vh1}{ch\,R}}$$

```
393.154
```

$$\mathbf{P = T\frac{R}{Vh1 - bh} - \frac{ah\,ch\,R}{Uh1\,Vh1\,Vh1 + ah\,Vh1}}$$

```
217109.
```

Numerical Problem – Helium and Water

Now, to find the equilibrium state of the system we use two temperature equations of state and the pressure equation of state for the two VdW fluids:

$$\mathbf{T0 = 300}$$

$$300$$

$$\mathbf{eq1 = Uh + ah/Vh == ch\,R\,T0}$$

$$\mathrm{Uh} + \frac{0.00346}{\mathrm{Vh}} == 3741.48$$

$$\mathbf{eq2 = Uw + aw/(V0 - Vh) == cw\,R\,T0}$$

$$\mathrm{Uw} + \frac{0.544}{0.03 - \mathrm{Vh}} == 7732.39$$

$$\mathbf{eq3} = \frac{\mathbf{R}}{\mathbf{Vh - bh}} - \frac{\mathbf{ah\,ch\,R}}{\mathbf{Uh\,Vh^2 + ah\,Vh}} == \frac{\mathbf{R}}{\mathbf{V0 - Vh - bw}} - \frac{\mathbf{aw\,cw\,R}}{\mathbf{Uw\,(V0 - Vh)^2 + aw\,(V0 - Vh)}}$$

$$\frac{8.3144}{-0.0000237 + \mathrm{Vh}} - \frac{0.0431517}{0.00346\,\mathrm{Vh} + \mathrm{Uh}\,\mathrm{Vh}^2} == -\frac{14.0214}{0.544(0.03 - \mathrm{Vh}) + \mathrm{Uw}\,(0.03 - \mathrm{Vh})^2} + \frac{8.3144}{0.0299695 - \mathrm{Vh}}$$

$$\mathbf{NSolve[\{eq1, eq2, eq3\}, \{Vh, Uh, Uw\}]}$$

$$\{\{\mathrm{Uh} \to 3668.54 - 599.249\,I, \mathrm{Uw} \to 7714.26 + 0.00343921\,I, \mathrm{Vh} \to 6.9252\times 10^{-7} - 5.68961\times 10^{-6}\,I\},$$
$$\{\mathrm{Uh} \to 3668.54 + 599.249\,I, \mathrm{Uw} \to 7714.26 - 0.00343921\,I, \mathrm{Vh} \to 6.9252\times 10^{-7} + 5.68961\times 10^{-6}\,I\}, \{\mathrm{Uh} \to 3741.25, \mathrm{Uw} \to 7695.87, \mathrm{Vh} \to 0.0151061\},$$
$$\{\mathrm{Uh} \to 3741.36, \mathrm{Uw} \to 4753.18, \mathrm{Vh} \to 0.0298174\}, \{\mathrm{Uh} \to 3741.36, \mathrm{Uw} \to -7106.08, \mathrm{Vh} \to 0.0299633\}\}$$

Physically meaningful solutions have real-valued volumes and energies. There are three such solutions.

Numerical Problem – Helium and Water

Three physically meaningful solutions:

```
1   {Uh → 3741.25095377012062`,Uw → 7695.86692894271351`, Vh → 0.0151061206931622615`},
2   {Uh → 3741.36396037953744`,Uw → 4753.17737520313787`, Vh → 0.0298174015408398 14`},
3   {Uh → 3741.36452555181753`,Uw → –7106.08071201483948`, Vh → 0.0299633385449733715`}
```

They correspond to three volume ratios of helium to water:

1.01425   163.295   817.298

Some of you have stated that the first solution (Vh/Vw = 1.01425) is the one that should be experimentally observed as it maximizes the total entropy of helium plus water. This is incorrect since the system is not adiabatically isolated from the environment in part (b) of this problem. Therefore, the total entropy of helium, water AND the environment must be maximized by the correct solution. At this point, you do not have enough information to decide which of the three solutions is correct – we will learn this later in the course. It will turn out that the right solution is Vh/Vw =817.298. This solution minimizes energy of the system. This solution is consistent with our intuition that water vapor should condense into liquid at room temperature and pressure close to atmospheric, and thus occupy small volume. Note that the internal energy of water for solution #3 is negative, which means that the absolute value of the (negative) potential energy exceeds the kinetic energy and thus the system is bound (remember mechanics and astronomy), or “condensed” in the language of thermodynamics.