

Exercises for a course at the
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Non-Equilibrium Thermodynamics of Heterogeneous Systems:
The Square Gradient Model

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1st Lecture

1.1. When the temperature is below the critical temperature, there are according to the figure two stable molar volumes for any pressure. The smaller one represents the liquid molar volume and the higher one, the vapor molar volume. Use Gibbs-Duhem's equation

$$\int_{p^l}^{p^g} V_W dp = 0$$

where V_W is the volume calculated from the van der Waals equation of state, to derive the constant pressure-line that has equal areas with the curve under and above the line. Derive expressions for the pressure, p_{EA} , and the coexisting densities of liquid and vapor as a function of temperature (Maxwell's equal area rule).

1.2. The equilibrium concentration profile is such that

$$F = \int c(x)F(x)dx$$

has a minimum for a given total number of moles

$$N = \int c(x)dx$$

Use the Euler-Lagrange method to show that the Lagrange multiplier μ is given for the equilibrium temperature T by:

$$\mu \equiv \mu_W(c(x), T) - m \frac{d^2 c(x)}{dx^2}$$

1.3. Show that it follows from the constant nature of μ that

$$p_{\perp}(x) = p_W(c(x), T) + \frac{m}{2} \left(\frac{dc(x)}{dx} \right)^2 - mc(x) \frac{d^2 c(x)}{dx^2}$$

is also constant.

1.4. The value of m for water is about 3×10^{-20} J/mol². Give an estimate of the surface tension, using a surface thickness of 1 nm and known densities of water liquid and water vapor to estimate the derivative.

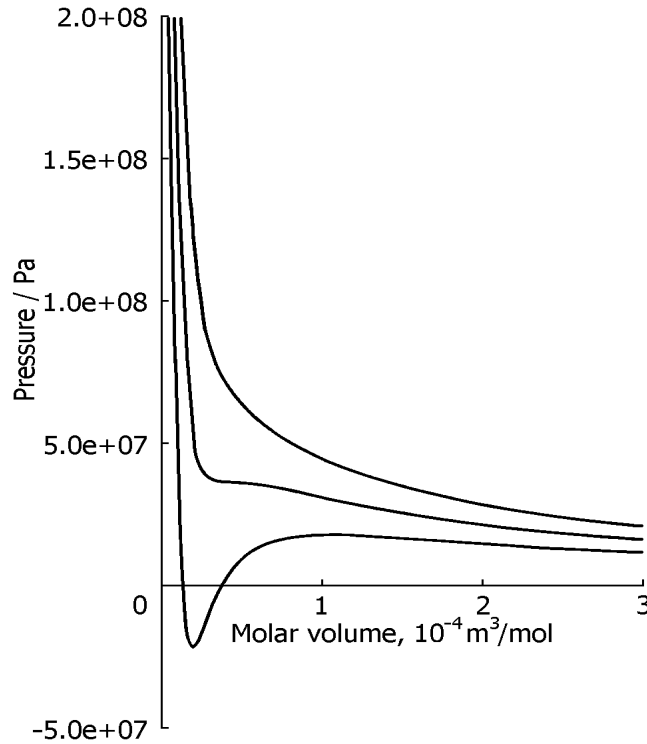


Figure 1: The pressure of water in Pascal according to the van der Waals equation. Three isotherms are given, for $T < T_c$, $T = T_c$ and $T > T_c$.

1.5. Show the following identity for local property $a(x, t)$:

$$\begin{aligned} c(x, t) \frac{da(x, t)}{dt} &= \frac{\partial c(x, t) a(x, t)}{\partial t} + \frac{\partial c(x, t) v(x, t) a(x, t)}{\partial x} \\ &= \frac{\partial c(x, t) a(x, t)}{\partial t} + \frac{\partial J(x, t) a(x, t)}{\partial x} \end{aligned}$$

Use this identity to show that:

$$c(x, t) \frac{dV(x, t)}{dt} = \frac{\partial v(x, t)}{\partial x}$$

2nd Lecture

2.1. The variation in density of A across a vapor-liquid interface between $a = 0$ and $b = 5$ nm is given by $c_A(x) = Cx^3 + 50$ mol/m³. The vapor density is $c_A^g = 50$ mol/m³ and the liquid density is $c_A^l = 50000$ mol/m³. Determine the value of C and the position of the equimolar surface.

2.2. Explain why there is no term proportional to dp in the Gibbs equation for the densities per unit of volume $du = Tds + \sum_{j=1}^n \mu_j dn_j$.

4th Lecture

4.1. The equation of motion is

$$Mc(x, t) \frac{dv(x, t)}{dt} = M \left[\frac{\partial J(x, t)}{\partial t} + \frac{\partial J(x, t) v(x, t)}{\partial x} \right] = - \frac{\partial p_{\perp}(x, t)}{\partial x}$$

The total energy per mole is the sum of the internal energy and the kinetic energy and is given by

$$E(x, t) = U(x, t) + \frac{1}{2}Mv^2(x, t)$$

As the total energy is conserved it satisfies

$$\frac{\partial c(x, t) E(x, t)}{\partial t} = -\frac{\partial J_e(x, t)}{\partial x}$$

where the total energy flux is given by

$$J_e(x, t) \equiv J(x, t) E(x, t) + p_{\parallel}(x, t) v(x, t) + J'_q(x, t)$$

$J'_q(x, t)$ is the measurable heat flux. Show that the internal energy density satisfies

$$\begin{aligned} \frac{\partial c(x, t) U(x, t)}{\partial t} + \frac{\partial}{\partial x} [J(x, t) H(x, t) - p_{\perp}(x, t) v(x, t)] \\ = -\frac{\partial J'_q(x, t)}{\partial x} - p_{\perp}(x, t) \frac{\partial v(x, t)}{\partial x} \end{aligned}$$

4.2. Use the balance equations for the one-component case to show that J , $p_{\perp} + MJv$ and $J_q + \frac{1}{2}MJv^2$ are independent of x .

5th Lecture

5.1. Show that substitution of the definitions

$$\begin{aligned} T^s &\equiv \frac{h^{\text{exc}} - \mu_{eq}(T^s)c^{\text{exc}}}{s^{\text{exc}}} = \frac{(Ts)^{\text{exc}} + g^{\text{exc}} - \mu_{eq}(T^s)c^{\text{exc}}}{s^{\text{exc}}} \\ \mu^s &\equiv \mu_{eq}(T^s) \end{aligned}$$

and

$$\begin{aligned} \gamma^s &\equiv \gamma^{\text{exc}} \quad , \quad c^s \equiv c^{\text{exc}} \quad , \quad u^s \equiv u^{\text{exc}} \quad , \quad h^s \equiv h^{\text{exc}} \\ s^s &\equiv s^{\text{exc}} \quad , \quad g^s \equiv \mu_{eq}(T^s)c^{\text{exc}} \quad , \quad f^s \equiv f^{\text{exc}} - g^{\text{exc}} + \mu_{eq}(T^s)c^{\text{exc}} \end{aligned}$$

into

$$\begin{aligned} \gamma^{\text{exc}} &= f^{\text{exc}} - g^{\text{exc}} \\ u^{\text{exc}} &= f^{\text{exc}} + (Ts)^{\text{exc}} = (Ts)^{\text{exc}} + \gamma^{\text{exc}} + g^{\text{exc}} \\ h^{\text{exc}} &= u^{\text{exc}} - \gamma^{\text{exc}} = (Ts)^{\text{exc}} + g^{\text{exc}} \\ g^{\text{exc}} &= h^{\text{exc}} - (Ts)^{\text{exc}} \end{aligned}$$

gives

$$\begin{aligned} \gamma^s &= f^s - \mu_{eq}(T^s)c^s = f^s - \mu^s c^s \\ u^s &= f^s + T^s s^s = T^s s^s + \gamma^s + \mu_{eq}(T^s)c^s = T^s s^s + \gamma^s + \mu^s c^s \\ h^s &= u^s - \gamma^s = T^s s^s + \mu_{eq}(T^s)c^s = T^s s^s + \mu^s c^s \\ g^s &= h^s - T^s s^s = \mu_{eq}(T^s)c^s = \mu^s c^s \end{aligned}$$

5.2. Give the excess molar density for an arbitrary dividing surface in terms of the distance to the equimolar surface and the densities in the homogeneous phase.

6th Lecture

6.1. Show that the entropy production is equal to

$$\sigma^s = J_q^l(x^s) \left[\frac{1}{T^l(x^s)} - \frac{1}{T^g(x^s)} \right] - J \left[\frac{\mu^l(T^g(x^s)) - \mu^g(T^g(x^s))}{T^g(x^s)} \right]$$

if one uses the measurable heat flux on the liquid side.

6.2. The continuous resistivity profile and the enthalpy profile both have a plateau in the vapor and in the liquid phase. In the most simple model the change over from one plateau to the other is sharp at positions x_r and x_h . Show, using that the resistivity in the vapor is much larger than in the liquid and that the enthalpy in the vapor is large and positive while it is large and negative in the liquid, that the value of the cross coefficient depends very much on the relative location of the cross over positions.

7th Lecture

Show that the Gibbs relation for the mixture

$$T\rho \frac{ds}{dt} = \rho \frac{du}{dt} - \sum_{i=1}^{n-1} \rho \psi_i \frac{d\xi_i}{dt} + p\rho \frac{dv}{dt} - v_\beta \frac{\partial \gamma_{\alpha\beta}}{\partial x_\alpha}$$

gives the Gibbs relation for the one-component system with fluxes and gradients in the x direction alone.

7.2. Substitute the balance laws in the Gibbs relation and verify that the expressions for the entropy flux and production are correct.

8th Lecture

8.2. Verify that in a stationary binary mixture with only fluxes and gradients in the x -direction, and neglecting viscous and gravitational forces,

$$\rho v, J_1 - \rho \xi_1 v, p_\perp + \rho v^2 \text{ and } J_e \equiv J_q + \rho e v + p v$$

are independent of x , where $e \equiv u + \frac{1}{2}v^2$.