

Solutions 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. It is convenient to change variables in the expression above and integrate over the volume, because v_W is a multiple valued function. The equal area pressure p_{EA} must obey:

$$\int_{v^l}^{v^g} d(Vp) - \int_{v^l}^{v^g} p_W dV = p_{EA}(V^g - V^l) + RT \ln \left(\frac{V^l - B}{V^g - B} \right) + A \left(\frac{1}{V^l} - \frac{1}{V^g} \right) = 0$$

The points connected by this pressure have $\mu^g - \mu^l = 0$. The pressure in the liquid and the vapor are also the same

$$p_{EA} = \frac{RT}{V^l - B} - \frac{A}{(V^l)^2} = \frac{RT}{V^g - B} - \frac{A}{(V^g)^2}$$

Given the temperature, these are two equations for the unknown molar volumes. The solution gives these molar volumes and shows that they are a function of the temperature alone. Further substitution into van der Waals equation of state, gives the pressure as a function of the temperature.

1.2. According the Euler-Lagrange this constraint minimum is give by the minimum of

$$F - \mu N = \int c(x) [F(x) - \mu] dx$$

The Euler-Lagrange equation is

$$\frac{\partial c(x) [F(x) - \mu]}{\partial c(x)} - \frac{d}{dx} \frac{\partial c(x) [F(x) - \mu]}{\partial [dc(x)/dx]} = 0$$

Using

$$F(x) = F_W(c(x), T) + \frac{m}{2c(x)} \left(\frac{dc(x)}{dx} \right)^2$$

this gives

$$\mu_W(c(x), T) - \mu - m \frac{d^2 c(x)}{dx^2} = 0$$

The resulting expression for the chemical potential is

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

1.3. In order to prove this we multiply the expression for μ found in problem 1.2. with $dc(x)/dx$. This gives

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

This can be rewritten as

$$\begin{aligned} \frac{dc(x) [\mu - \mu_W(c(x), T)]}{dx} &= -c(x) \frac{d\mu_W(c(x), T)}{dx} - \frac{m}{2} \frac{d}{dx} \left(\frac{dc(x)}{dx} \right)^2 \\ &= -m \frac{d}{dx} \left[c(x) \frac{d^2c(x)}{dx^2} \right] \end{aligned}$$

The second equality followed using the expression for μ found in problem 1.2. Using Gibbs-Duhem for the van der Waals contribution, Eq.(23.8), this gives

$$-m \frac{d}{dx} \left[c(x) \frac{d^2c(x)}{dx^2} \right] = -\frac{dp_W(c(x), T)}{dx} - \frac{m}{2} \frac{d}{dx} \left(\frac{dc(x)}{dx} \right)^2$$

It follows that

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

is constant

1.4. The density of water is about 5×10^4 mol/m³. The density of the vapor is on a comparative scale negligible. This gives as an estimate of the density gradient 5×10^{13} mol/m⁴. We apply Eq.(23.16) and find $\gamma = 75 \times 10^{-3}$ N/m for the water-vapor interface. The result is close to what is found experimentally (72×10^{-3} J/m²). From the gradient in the molar density profile at room temperature we obtain for comparison, $\gamma = 61 \times 10^{-3}$ N/m for the water-vapor interface.

1.5. Straightforward differentiation and the use of Eq.(23.18) gives the first identity. Substituting $a(x, t) = V(x, t)$ gives the second.

2nd Lecture

2.1. The density function at b gives

$$C(5 \times 10^{-9})^3 + 50 = 5 \times 10^4 \Rightarrow C = 4 \times 10^{29} \text{ mol/m}^6$$

For the equimolar surface, we have:

$$\int_0^d Cx^3 dx = - \int_d^b (Cx^3 - 49950) dx \Rightarrow \frac{1}{4} C d^4 = -\frac{1}{4} C (b^4 - d^4) + 49950(b - d)$$

This results in the position $d = 3.75$ nm. The equimolar surface is close to the liquid side.

2.2. The Gibbs equation for the total internal energy is

$$dU = TdS - pdV + \sum_{j=1}^n \mu_j dN_j$$

Substituting $U = uV$, $S = sV$ and $N_j = n_jV$, we find

$$V du + u dV = VT ds + ST dV - p dV + V \sum_{j=1}^n \mu_j dn_j + \sum_{j=1}^n \mu_j n_j dV$$

Bringing all the terms with dV to the right and the others to the left gives

$$V \left(du - T ds - \sum_{j=1}^n \mu_j dn_j \right) = \left(-u + ST - p + \sum_{j=1}^n \mu_j n_j \right) dV = 0$$

It follows that

$$du = Tds + \sum_{j=1}^n \mu_j dn_j$$

This shows that there is no term proportional to dp in the Gibbs equation for the densities per unit of volume.

In the same way one may show that there is no term proportional to $d\gamma$ in the Gibbs equation for the densities per unit of surface area.

4th Lecture

4.1. Substituting the expression for the energy flux into the conservation of energy equation one obtains

$$c(x, t) \frac{dE(x, t)}{dt} = -\frac{\partial}{\partial x} [p_{\parallel}(x, t)v(x, t) + J'_q(x, t)]$$

For the kinetic energy one finds

$$c(x, t) \frac{d}{dt} \left(\frac{1}{2} M v^2(x, t) \right) = -v(x, t) \frac{\partial}{\partial x} p_{\perp}(x, t)$$

Subtracting this equation from the one for the energy balance gives

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

Using $U(x, t) = H(x, t) - p_{\parallel}(x, t)V(x, t)$ this can be written as

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

This is equivalent to

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

which is what we set out to prove.

4.2. In a stationary state the balance equation for the molar density becomes

$$\frac{dc(x)v(x)}{dx} \equiv \frac{dJ(x)}{dx} = 0$$

It follows that J is independent of x . Note that the reference frame is such that the velocity of the surface is zero. It follows from the equation of motion that

$$\frac{dp_{\perp}(x)}{dx} = -M \frac{dJ(x)v(x)}{dx} = -\frac{dMJv(x)}{dx}$$

From this equation it follows that $p_{\perp} + MJv$ is independent of x . From the balance of internal energy one has

$$\frac{dJ_q(x)}{dx} = v(x) \frac{dp_{\perp}(x)}{dx}$$

where the total heat flux is as usual related to the measurable heat flux by $J_q(x) \equiv J'_q(x) + Jh(x)$. Using the equation obtained from the equation of motion it follows that

$$\frac{dJ_q(x)}{dx} = -v(x) \frac{dMJv(x)}{dx} = -\frac{1}{2} \frac{dMJv^2(x)}{dx}$$

As a consequence $J_q(x) + \frac{1}{2}MJv^2(x)$ is also position independent.

5th Lecture

5.1. The algebra is straightforward.

5.2. The excess molar density for an arbitrary dividing surface is given by

$$\begin{aligned} c^s &= \int [c(x) - c^g(x)\theta(x^s - x) - c^l(x)\theta(x - x^s)] dx \\ &= \int [c(x) - c^g(x)\theta(x^{es} - x) - c^l(x)\theta(x - x^{es})] dx \\ &\quad + \int_{x^{es}}^{x^s} [c^l(x) - c^g(x)] dx \\ &= \int_{x^{es}}^{x^s} [c^l(x) - c^g(x)] dx \end{aligned}$$

To linear order in the distance this gives

$$c^s = \delta^s [c^l(x^{es}) - c^g(x^{es})]$$

6th Lecture

6.1. The entropy production in terms of the total heat flux is given by

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

We substitute

$$J_q(x^s) = J_q^l(x^s) + H^1(x^s) J$$

This gives

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

Using

$$H^1 = \frac{d(\mu^l/T)}{d(1/T)}$$

this gives

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

if one uses the measurable heat flux on the liquid side. Note that now one takes the chemical potential difference at the temperature of the vapor.

6.2. In the simple model the continuous resistivity and enthalpy profile are given by

$$\begin{aligned} r_{qq}(x) &= r_{qq}^g \theta(x^r - x) + r_{qq}^l \theta(x - x^r) \\ h(x) &= h^g \theta(x^h - x) + h^l \theta(x - x^h) \end{aligned}$$

The integral relation for the cross coefficient is

$$r_{\mu q}^s = r_{\mu q}^s = \int_{x^{s,g}}^{x^{s,l}} r_{qq}(x) [h(x^{s,g}) - h(x)] dx$$

Using that $x^{s,g} < x^r, x^h < x^{s,l}$ it follows that

$$\begin{aligned}
r_{q\mu}^s &= r_{\mu q}^s = \int_{x^{s,g}}^{x^{s,l}} [r_{qq}^g \theta(x^r - x) + r_{qq}^l \theta(x - x^r)] [h^g - h^g \theta(x^h - x) + h^l \theta(x - x^h)] dx \\
&= \int_{x^{s,g}}^{x^{s,l}} [r_{qq}^g \theta(x^r - x) + r_{qq}^l \theta(x - x^r)] (h^g + h^l) \theta(x - x^h) dx \\
&= (h^g + h^l) \int_{x^h}^{x^{s,l}} [r_{qq}^g \theta(x^r - x) + r_{qq}^l \theta(x - x^r)] dx
\end{aligned}$$

The result is

$$r_{q\mu}^s = r_{\mu q}^s = \begin{cases} (h^g + h^l) r_{qq}^g (x^r - x^h) & \text{for } x^h < x^r \\ (h^g + h^l) r_{qq}^l (x^{s,l} - x^h) & \text{for } x^h > x^r \end{cases}$$

In view of the fact that $r_{qq}^g \gg r_{qq}^l$ the resulting value depends very much on the relative location of x^h and x^r .

7th Lecture

Using that there is only one components and that the velocity and the gradients are all only in the x-direction the Gibbs equation for the mixture reduces to

$$\begin{aligned}
T\rho \frac{ds}{dt} &= \rho \frac{du}{dt} + p_{\parallel} \rho \frac{dv}{dt} - v_x \frac{\partial \gamma_{xx}}{\partial x} \\
&= \frac{\partial \rho u}{\partial t} + \frac{\partial \rho v_x u}{\partial x} + p_{\parallel} \frac{\partial v_x}{\partial x} - v_x \frac{\partial (p_{\perp} - p_{\parallel})}{\partial x} \\
&= \frac{\partial \rho u}{\partial t} + \frac{\partial (\rho v_x u + p_{\parallel} v_x)}{\partial x} - v_x \frac{\partial p_{\perp}}{\partial x} \\
&= \frac{\partial \rho u}{\partial t} + \frac{\partial [v_x (\rho h - p_{\perp})]}{\partial x} + p_{\perp} \frac{\partial v_x}{\partial x} \\
&= \frac{\partial \rho u}{\partial t} + \frac{\partial [v_x (\rho h - p_{\perp})]}{\partial x} + p_{\perp} \rho \frac{dv}{dt}
\end{aligned}$$

Multiplying the last equation with v gives

$$T \frac{ds}{dt} = v \left\{ \frac{\partial \rho u}{\partial t} + \frac{\partial [v_x (\rho h - p_{\perp})]}{\partial x} \right\} + p_{\perp} \frac{dv}{dt}$$

This is the equation used for the one-component system. The densities are now per kg while they were per mole. This can easily be corrected by multiplying the equation with the molar mass.

7.2. The balance laws are

$$\begin{aligned}
\frac{d\rho}{dt} &= -\rho \nabla \cdot \mathbf{v} \Leftrightarrow \rho \frac{dv}{dt} = \nabla \cdot \mathbf{v} \\
\rho \frac{d\xi_k}{dt} &= -\nabla \cdot \mathbf{J}_k \\
\rho \frac{du}{dt} &= -\nabla \cdot \mathbf{J}_q - \pi_{\alpha\beta} v_{\beta\alpha} - p \nabla \cdot \mathbf{v} + v_{\beta} \frac{\partial \gamma_{\alpha\beta}}{\partial x_{\alpha}}
\end{aligned}$$

When we substitute these balance laws into the Gibbs relation

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

we obtain

$$\begin{aligned}
T\rho \frac{ds}{dt} &= -\nabla \cdot \mathbf{J}_q - \pi_{\alpha\beta} v_{\beta\alpha} - p \nabla \cdot \mathbf{v} + v_{\beta} \frac{\partial \gamma_{\alpha\beta}}{\partial x_{\alpha}} + \sum_{i=1}^{n-1} \psi_i \nabla \cdot \mathbf{J}_k + p \nabla \cdot \mathbf{v} - v_{\beta} \frac{\partial \gamma_{\alpha\beta}}{\partial x_{\alpha}} \\
&= -\nabla \cdot \mathbf{J}_q - \pi_{\alpha\beta} v_{\beta\alpha} + \sum_{i=1}^{n-1} \psi_i \nabla \cdot \mathbf{J}_k
\end{aligned}$$

Dividing by the temperature one gets

$$\begin{aligned}\rho \frac{ds}{dt} &= -\frac{1}{T} \nabla \cdot \mathbf{J}_q - \frac{1}{T} \pi_{\alpha\beta} v_{\beta\alpha} + \sum_{i=1}^{n-1} \frac{\psi_i}{T} \nabla \cdot \mathbf{J}_k \\ &= -\nabla \cdot \frac{1}{T} \left(\mathbf{J}_q - \sum_{i=1}^{n-1} \psi_i \mathbf{J}_k \right) + \mathbf{J}_q \cdot \nabla \frac{1}{T} - \frac{1}{T} \pi_{\alpha\beta} v_{\beta\alpha} - \sum_{i=1}^{n-1} \mathbf{J}_k \cdot \nabla \frac{\psi_i}{T}\end{aligned}$$

Comparing this with the entropy balance equation one finds the entropy flux and production

$$\begin{aligned}\mathbf{J}_s &= \frac{1}{T} \left(\mathbf{J}_q - \sum_{i=1}^{n-1} \psi_i \mathbf{J}_k \right) \\ \sigma_s &= \mathbf{J}_q \cdot \nabla \frac{1}{T} - \frac{1}{T} \pi_{\alpha\beta} v_{\beta\alpha} - \sum_{i=1}^{n-1} \mathbf{J}_k \cdot \nabla \frac{\psi_i}{T}\end{aligned}$$

8th Lecture

8.2. In a stationary binary mixture the balance laws reduce to

$$\begin{aligned}0 &= \frac{\partial \rho v}{\partial x} \\ \frac{\partial \rho v \xi_1}{\partial x} &= -\frac{\partial J_1}{\partial x} \\ \frac{\partial \rho v^2}{\partial x} &= -\frac{\partial p_{\perp}}{\partial x} \\ \frac{\partial \rho v u}{\partial x} &= -\frac{\partial J_q}{\partial x} - p \frac{\partial v}{\partial x} + v \frac{\partial \gamma_{xx}}{\partial x}\end{aligned}$$

where we used that all fluxes and gradients are in the x -direction and where $v = v_x$. It follows immediately that ρv , $J_1 + \rho \xi_1 v$ and $p_{\perp} + \rho v^2$ are independent of x . The energy balance equation can be written as

$$\frac{\partial (J_q + \rho v u)}{\partial x} = -p \frac{\partial v}{\partial x} + v \frac{\partial \gamma_{xx}}{\partial x} = -\frac{\partial p v}{\partial x} + v \frac{\partial p_{\perp}}{\partial x}$$

It follows that

$$\frac{\partial (J_q + \rho v u + p v)}{\partial x} = v \frac{\partial p_{\perp}}{\partial x} = -v \frac{\partial \rho v^2}{\partial x} = -\frac{\partial \frac{1}{2} \rho v^3}{\partial x}$$

Consequently $J_e \equiv J_q + \rho e v + p v = J_q + \rho(u + \frac{1}{2}v^2)v + p v$ is independent of x .

8.2. Using $\varepsilon_k \equiv \sqrt{\kappa_{\rho_1 \rho_1} / \kappa_{\rho_2 \rho_2}} - 1$, $\kappa_{\rho_1 \rho_2} = \sqrt{\kappa_{\rho_1 \rho_1} \kappa_{\rho_2 \rho_2}}$ and $\kappa = \kappa_{\rho_2 \rho_2}$, we can write

$$\begin{aligned}\kappa_{\rho\rho}(\rho, \xi) &= \kappa [\varepsilon_k^2 \xi^2 + 2\varepsilon_k \xi + 1] = \kappa (1 + \varepsilon_k \xi)^2 \\ \kappa_{\rho\xi}(\rho, \xi) &= \kappa [\varepsilon_k^2 \xi \rho + \varepsilon_k \rho] = \kappa \rho \varepsilon_k (1 + \varepsilon_k \xi) \\ \kappa_{\xi\xi}(\rho, \xi) &= \kappa \varepsilon_k^2 \rho^2\end{aligned}$$

Substituting these relations into the expression for the total κ gives

$$\kappa(\rho, \xi, \rho', \xi') = -\frac{\kappa}{2\rho} \left\{ (1 + \varepsilon_k \xi)^2 \rho'^2 + 2\rho \varepsilon_k (1 + \varepsilon_k \xi) \rho' \xi' + \rho^2 \varepsilon_k^2 \xi'^2 \right\}$$

If we work out q'^2 we get

$$\begin{aligned}q'^2 &= \left\{ \frac{d}{dx} [\rho(1 + \varepsilon_k \xi)] \right\}^2 = \left\{ \rho'(1 + \varepsilon_k \xi) + \rho \varepsilon_k \xi' \right\}^2 \\ &= (1 + \varepsilon_k \xi)^2 \rho'^2 + 2\rho \varepsilon_k (1 + \varepsilon_k \xi) \xi' \rho' + \rho^2 \varepsilon_k^2 \xi'^2\end{aligned}$$

This proves that

$$\kappa(\rho, \xi, \rho', \xi') = -\frac{\kappa q'^2}{2\rho}$$