Non-Equilibrium Thermodynamics of Heterogeneous Systems: The square gradient model

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Thermodynamic properties of the Gibbs surface
The temperature of the surface
Dependence of excess densities on choice of dividing surface

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9. Thermodynamic properties of the Gibbs surface

Excess densities are defined by:

$$c^{\mathbf{exc}} \equiv \int [c(x) - c^{\mathbf{l}}(x)\,\theta(x - x^{\mathbf{s}}) - c^{\mathbf{g}}(x)\,\theta(x^{\mathbf{s}} - x)]dx$$

$$\gamma^{\mathbf{exc}} \equiv -\int \left[p_{\|}(x) - p_{\|}^{\ell}(x)\,\theta(x - x^{\mathbf{s}}) - p_{\|}^{g}(x)\,\theta(x^{\mathbf{s}} - x) \right] dx$$

$$u^{\mathbf{exc}} \equiv \int [c(x)\,U(x) - c^{\mathbf{l}}(x)\,U^{\mathbf{l}}(x)\,\theta(x - x^{\mathbf{s}}) - c^{\mathbf{g}}(x)\,U^{\mathbf{g}}(x)\,\theta(x^{\mathbf{s}} - x)]dx$$

$$g^{\mathbf{exc}} \equiv \int [c(x)\,\mu(x) - c^{\mathbf{l}}(x)\,\mu^{\mathbf{l}}(x)\,\theta(x - x^{\mathbf{s}}) - c^{\mathbf{g}}(x)\,\mu^{\mathbf{g}}(x)\,\theta(x^{\mathbf{s}} - x)]dx$$

One can do this for every density per unit of volume.

The excess densities are per unit of surface area.

The numerical analysis will be restricted to stationary states.

What about the thermodynamics?

In equilibrium the thermodynamic relations given by Gibbs for an arbitrary choice of the dividing surface are:

$$\gamma_{eq}^{\mathrm{s}} = f_{eq}^{\mathrm{s}} - \mu_{eq}^{\mathrm{s}}(T_{eq}^{\mathrm{s}})c_{eq}^{\mathrm{s}}$$

$$u_{eq}^{\mathrm{s}} = f_{eq}^{\mathrm{s}} + T_{eq}s_{eq}^{\mathrm{s}} = T_{eq}s_{eq}^{\mathrm{s}} + \gamma_{eq}^{\mathrm{s}} + \mu_{eq}(T_{eq})c_{eq}^{\mathrm{s}}$$

$$h_{eq}^{\mathrm{s}} = u_{eq}^{\mathrm{s}} - \gamma_{eq}^{\mathrm{s}} = T_{eq}s_{eq}^{\mathrm{s}} + \mu_{eq}(T_{eq})c_{eq}^{\mathrm{s}}$$

$$g_{eq}^{\mathrm{s}} = h_{eq}^{\mathrm{s}} - T_{eq}s_{eq}^{\mathrm{s}} = \mu_{eq}(T_{eq})c_{eq}^{\mathrm{s}}$$

These excess densities depend only on the temperature T_{eq} and the location of the dividing surface x^s.

For a heterogeneous system in a stationary state we must derive these relations. This would establish local equilibrium for the Gibbs surface. It would also clarify how to chose the excess densities in a stationary state such that they satisfy the thermodynamic relations given by Gibbs.

In the continuous description we have:

$$p_{\parallel}(x)V(x) = f(x) - g(x)$$

$$u(x) = f(x) + T(x)s(x) = T(x)s(x) + p_{\parallel}(x)V(x) + g(x)$$

$$h(x) = u(x) - p_{\parallel}(x)V(x) = T(x)s(x) + g(x)$$

$$g(x) = h(x) - T(x)s(x)$$

Applying the excess density procedure to these equations we obtain

$$\gamma^{\text{exc}} = f^{\text{exc}} - g^{\text{exc}}$$

$$u^{\text{exc}} = f^{\text{exc}} + (Ts)^{\text{exc}} = (Ts)^{\text{exc}} + \gamma^{\text{exc}} + g^{\text{exc}}$$

$$h^{\text{exc}} = u^{\text{exc}} - \gamma^{\text{exc}} = (Ts)^{\text{exc}} + g^{\text{exc}}$$

$$g^{\text{exc}} = h^{\text{exc}} - (Ts)^{\text{exc}}$$

for an arbitrary choice of the dividing surface.

Remains to make the proper identifications!

We identify the temperature and chemical potential with:

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

$$\mu^{\text{s}} \equiv \mu_{eq}(T^{\text{s}})$$

By defining

$$\gamma^{\text{s}} \equiv \gamma^{\text{exc}}, \quad c^{\text{s}} \equiv c^{\text{exc}}, \quad u^{\text{s}} \equiv u^{\text{exc}}, \quad h^{\text{s}} \equiv h^{\text{exc}}$$

$$s^{\text{s}} \equiv s^{\text{exc}}, \quad g^{\text{s}} \equiv \mu_{eq}(T^{\text{s}})c^{\text{exc}}, \quad f^{\text{s}} \equiv f^{\text{exc}} - g^{\text{exc}} + \mu_{eq}(T^{\text{s}})c^{\text{exc}}$$

and substituting these definitions in the equations on the previous page we obtain the relations given by Gibbs:

$$\gamma^{\text{s}} = f^{\text{s}} - \mu_{eq}(T^{\text{s}})c^{\text{s}} = f^{\text{s}} - \mu^{\text{s}}c^{\text{s}}$$

$$u^{\text{s}} = f^{\text{s}} + T^{\text{s}}s^{\text{s}} = T^{\text{s}}s^{\text{s}} + \gamma^{\text{s}} + \mu_{eq}(T^{\text{s}})c^{\text{s}} = T^{\text{s}}s^{\text{s}} + \gamma^{\text{s}} + \mu^{\text{s}}c^{\text{s}}$$

$$h^{\text{s}} = u^{\text{s}} - \gamma^{\text{s}} = T^{\text{s}}s^{\text{s}} + \mu_{eq}(T^{\text{s}})c^{\text{s}} = T^{\text{s}}s^{\text{s}} + \mu^{\text{s}}c^{\text{s}}$$

$$g^{\text{s}} = h^{\text{s}} - T^{\text{s}}s^{\text{s}} = \mu_{eq}(T^{\text{s}})c^{\text{s}} = \mu^{\text{s}}c^{\text{s}}$$

This shows the validity of local equilibrium

10. Properties of the temperature of the surface

It is nice to have established local equilibrium for the Gibbs surface in this way. It would strengthen the understanding if stronger properties could be derived, however.

Consider the following definitions of the surface temperature:

- $T^{es} = T^s$(equimolar surface)

- $T^{st} = T^s$(surface of tension)

- T_γ^s: calculate the surface tension and look up in the table of equilibrium values what the equilibrium temperature is.

- $T_{\gamma,eq}^s$: The surface temperature obtained from the daring proposition

$$\gamma\left(T_{\gamma,eq}^s\right) = m\int\left[\left(\frac{dc\left(x\right)}{dx}\right)^2 - \left(\frac{dc^l\left(x\right)}{dx}\right)^2\theta\left(x - x^s\right)\right.$$

$$\left. - \left(\frac{dc^g\left(x\right)}{dx}\right)^2\theta\left(x^s - x\right)\right]dx$$

• The equality of the first two verifies whether the surface temperature depends on the choice of the dividing surface.

• The third verifies whether equations of state remain valid.

• The fourth verifies whether the structure of the equilibrium interfacial region is the same as in equilibrium.

	T_γ^s	$T_{\gamma,eq}^s$	T^{es}	T^{st}	$T^g(x^{es})$	$T^l(x^{es})$
PG98	560.6651	560.6650	560.6651	560.6651	558.4364	561.0823
PG99	561.1563	561.1563	561.1563	561.1563	560.0528	561.3672
PG101	562.1447	562.1447	562.1447	562.1447	563.2270	561.9293
PG102	562.6421	562.6420	562.6421	562.6421	564.7860	562.2065
TL98	553.1456	553.1451	553.0787	553.0804	565.9413	551.9061
TL99	557.3527	557.3525	557.3364	557.3369	563.8449	556.8704
TL101	566.0117	566.0114	565.9966	565.9977	559.3648	566.1843
TL102	570.4054	570.4043	570.3482	570.3541	557.0069	570.4118

The agreement is astoundingly good!

Some general conclusions for non-equilibrium states:

• The surface temperature and chemical potentials are independent of the choice of the dividing surface.

• The equations of state for the surface are valid.

• The two surface temperatures determined using the surface tension differ not more than 2 parts in a million for all perturbations.

• This implies that the molar density profiles in stationary states are in extremely good approximation the same as the equilibrium profile for the surface temperature. They may be shifted up or down a bit but for the rest they are the same.

Conclusions continued

•The profiles of all the thermodynamic densities through the surface are the same as the equilibrium profiles at the temperature and chemical potentials of the surface. They are generally shifted up or down a bit.

• For the molar density and the internal energy this implies for instance:

$$c^{\text{l}} - c^{\text{g}} = c^{\text{l}}_{eq}(T^{\text{s}}) - c^{\text{g}}(T^{\text{s}})$$

$$c^{\text{l}}u^{\text{l}} - c^{\text{g}}u^{\text{g}} = c^{\text{l}}_{eq}(T^{\text{s}})u^{\text{l}}_{eq}(T^{\text{s}}) - c^{\text{g}}_{eq}(T^{\text{s}})u^{\text{g}}_{eq}(T^{\text{s}})$$

• One may in fact even use these properties to calculate the temperature of the surface with a reasonable accuracy.

Conclusions continued

• The temperature difference across the surface is very substantial.

• The temperature difference of the surface and the liquid is 10 to 20 % of the total difference across the surface.

• All these differences are generally larger than the inaccuracy in the determination of the surface temperature.

11. Dependence of the excess densities on the choice of the dividing surface

• We have now established that the surface temperature, chemical potential and normal velocity are independent of the choice of the dividing surface.

• The important question now is whether the excess densities satisfy a similar property or not.

• We will find that they depend very much on this choice.

• Important is that these differences have no measurable effects.

• How do we choose the dividing surface?

Possible choices of the dividing surface

We have already explained the equimolar surface

$$0 = \int [c(x) - c^{\mathrm{l}}(x)\,\theta(x - x^{\mathrm{es}}) - c^{\mathrm{g}}(x)\,\theta(x^{\mathrm{es}} - x)]dx$$

No excess density.

The surface of tension is defined by:

$$0 = \int (x - x^{\mathrm{st}})\,[p_{\parallel}(x) - p_{\parallel}^{\mathrm{l}}(x)\,\theta(x - x^{\mathrm{st}}) - p_{\parallel}^{\mathrm{g}}(x)\,\theta(x^{\mathrm{st}} - x)]dx$$

A property of interest is the distance between these two dividing surfaces, the so-called Tolman length: $\delta^{\mathrm{st}} \equiv x^{\mathrm{st}} - x^{\mathrm{es}}$

Typical values for water at an equilibrium pressure of 200 bar are:

State	x^{es}	x^{st}	$\delta^{\mathrm{st}} = x^{\mathrm{st}} - x^{\mathrm{es}}$
Equilibrium	0.0000	−0.0258	−0.0258
Case PG98	−0.1203	−0.1499	−0.0296

The value is in nm and the liquid is on the right hand side.

The distance of an arbitrary dividing surface to the equimolar surface is given by: $\delta^{\mathrm{s}} \equiv x^{\mathrm{s}} - x^{\mathrm{es}}$

All such distances are a function of the temperature alone in a one-component system.

Excess densities for different dividing surfaces are related by:

$$u^{\mathrm{s}} = u^{\mathrm{es}} + \int_{x^{\mathrm{es}}}^{x^{\mathrm{s}}} \left(c^{\mathrm{l}}\left(x \right) u^{\mathrm{l}}\left(x \right) - c^{\mathrm{g}}\left(x \right) u^{\mathrm{g}}\left(x \right) \right) dx$$

$$= u^{\mathrm{es}} + \delta^{\mathrm{s}} \left(c^{\mathrm{l}}\left(x^{\mathrm{es}} \right) u^{\mathrm{l}}\left(x^{\mathrm{es}} \right) - c^{\mathrm{g}}\left(x^{\mathrm{es}} \right) u^{\mathrm{g}}\left(x^{\mathrm{es}} \right) \right)$$

to linear order in the distance.

Similar relations are valid for the other thermodynamic densities.

As the distance between dividing surfaces is in practice always very small, it is normally enough not to go beyond linear order.

Equimolar surface

	x^{es}	γ^{es}	u^{es}	f^{es}	s^{es}	h^{es}	g^{es}
	nm	mJ/m^2	mJ/m^2	mJ/m^2	μJ/K m^2	mJ/m^2	mJ/m^2
EQ	0.0000	7.89510	85.5004	7.8951	138.17	77.605	0.0000
PG98	-0.1203	8.03148	85.2016	12.117	137.64	77.170	4.0852
PG99	-0.0607	7.96333	85.3480	10.012	137.90	77.385	2.0492
PG101	0.0620	7.82677	85.6583	5.7635	138.45	77.832	-2.0633
Pg102	0.1253	7.75832	85.8213	3.6167	138.74	78.063	-4.1416
TL98	0.5237	9.09685	90.9243	-7.1863	147.95	81.827	-16.283
TL99	0.2744	8.49571	88.1952	0.4412	143.00	79.699	-8.0545
TL101	-0.3042	7.29962	82.8788	15.091	133.53	75.579	7.7916
TL102	-0.6447	6.71485	80.3785	21.933	129.16	73.664	15.218

Surface of tension

	x^{st}	c^{st}	γ^{st}	u^{st}	f^{st}	s^{st}	h^{st}	g^{st}
	nm	μmol/m^2	mJ/m^2	mJ/m^2	mJ/m^2	μ J/m^{2}K	mJ/m^2	mJ/m^2
EQ	-0.0258	-0.64280	7.89510	89.1927	42.350	83.402	81.298	34.455
PG98	-0.1499	-0.73912	8.03148	89.4138	51.752	74.602	81.382	43.721
PG99	-0.0885	-0.69133	7.96333	89.3034	47.077	78.967	81.340	39.114
PG101	0.0381	-0.59349	7.82677	89.0811	37.568	87.909	81.254	29.741
PG102	0.1033	-0.54344	7.75832	88.9682	32.731	92.484	81.210	24.973
TL98	0.5082	-0.40248	9.09685	93.4151	13.906	113.98	84.318	4.8086
TL99	0.2541	-0.51614	8.49571	91.2750	27.799	99.227	82.779	19.304
TL101	-0.3365	-0.78624	7.29962	87.2205	57.694	66.230	79.921	50.395
TL102	-0.6852	-0.95145	6.71486	85.4247	74.029	47.345	78.710	67.314

• It is interesting to look at these tables of excess densities for the equimolar surface and the surface of tension.

• Even though the distance between them is only 0.025 nm, the excesses are often substantially different. Gamma is the same, u and h are 7% different, the others are completely different.

• This makes it extra astounding that local equilibrium is satisfied so convincingly.

As we have already established that the profiles of the various densities in a stationary state are the same as the equilibrium profiles at the temperature of the surface with a possible small shift of the whole profile it follows that:

$$c^{\text{s}}(T^{\text{s}}) = \delta^{\text{s}}(T^{\text{s}})[c^{\text{l}}_{eq}(T^{\text{s}}) - c^{\text{g}}_{eq}(T^{\text{s}})]$$

$$u^{\text{s}}(T^{\text{s}}, c^{\text{s}}(T^{\text{s}})) = u^{\text{es}}(T^{\text{s}}) + \delta^{\text{s}}(T^{\text{s}}) \left[c^{\text{l}}_{eq}(T^{\text{s}})u^{\text{l}}_{eq}(T^{\text{s}}) - c^{\text{g}}_{eq}(T^{\text{s}})u^{\text{g}}_{eq}(T^{\text{s}})\right]$$

$$= u^{\text{es}}(T^{\text{s}}) + c^{\text{s}}(T^{\text{s}}) \left[\frac{c^{\text{l}}_{eq}(T^{\text{s}})u^{\text{l}}_{eq}(T^{\text{s}}) - c^{\text{g}}_{eq}(T^{\text{s}})u^{\text{g}}_{eq}(T^{\text{s}})}{c^{\text{l}}_{eq}(T^{\text{s}}) - c^{\text{g}}_{eq}(T^{\text{s}})}\right]$$

And similar expressions for the other thermodynamic densities.

• It is clear that it is very important and useful to tabulate all the equilibrium properties of the surface, and the corresponding properties in the adjacent media, as a function of the temperature.