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

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10th Lecture

Validity of the thermodynamic relations for the non-equilibrium Gibbs surface
Validity of the equations of state
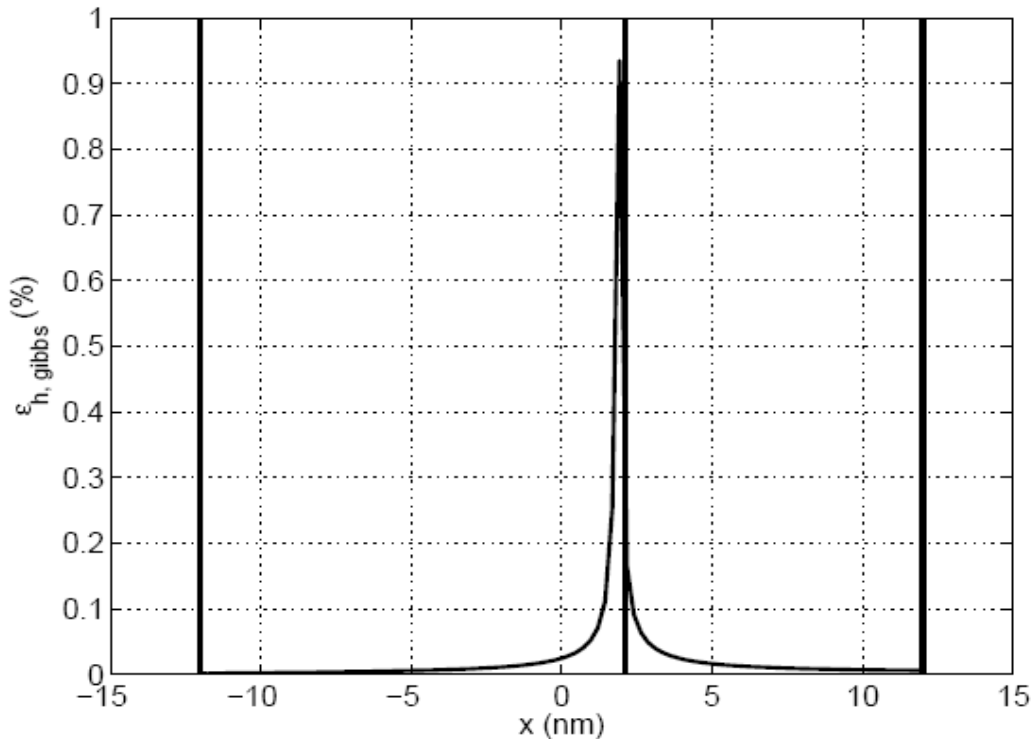From continuous to discontinuous description

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18. Validity of the thermodynamic relations for the non-equilibrium Gibbs surface

$$\hat{u} = T^s \hat{s} - \widehat{p_\parallel} + \mu_1^s \widehat{c_1} + \mu_2^s \widehat{c_2}$$

$$\varepsilon_{u,gibbs}(T,\mu_2) = \sum_{x^s} \left\{ \frac{\hat{u}(x^s) - \left[T^s \hat{s}(x^s) - \widehat{p_\parallel}(x^s) + \mu_1^s \widehat{c_1}(x^s) + \mu_2^s \widehat{c_2}(x^s) \right]}{\hat{u}(x^s)} \right\}^2$$
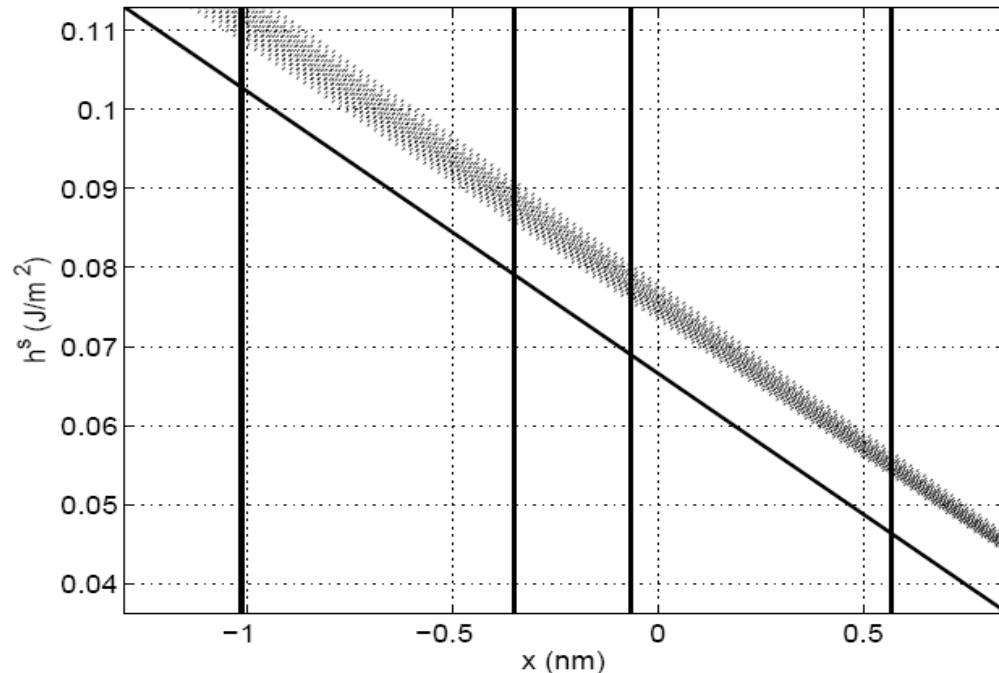

Error in percent

Non-equilibrium Gibbs surface

Error in percent

ϕ	error	$T^\ell = 1.02\,T_{eq}$		$T^\ell = 0.98\,T_{eq}$	
		for $T^s_{\{x^s\}}, \psi^s_{\{x^s\}}$	for $T^s(x^s), \psi^s(x^s)$	for $T^s_{\{x^s\}}, \psi^s_{\{x^s\}}$	for $T^s(x^s), \psi^s(x^s)$
h	$\mathcal{E}$	0.01328	-	0.033276	-
	$\epsilon_\phi(x^c)$	0.023799	0.023419	0.064597	0.065002
	$\epsilon_\phi(x^\gamma)$	0.020605	0.020737	0.056585	0.057148
	$\epsilon_\phi(x^{c1})$	0.035878	0.033571	0.085212	0.085204
	$\epsilon_\phi(x^{c2})$	0.015606	0.016541	0.047847	0.048578
u	$\mathcal{E}$	0.0071257	-	0.026714	-
	$\epsilon_\phi(x^c)$	0.016729	0.016462	0.045109	0.045392
	$\epsilon_\phi(x^\gamma)$	0.015059	0.015156	0.041048	0.041457
	$\epsilon_\phi(x^{c1})$	0.022033	0.020616	0.054286	0.05428
	$\epsilon_\phi(x^{c2})$	0.012161	0.012889	0.036244	0.036797
f	$\mathcal{E}$	0.20039	-	0.12983	-
	$\epsilon_\phi(x^c)$	7.3727	7.3666	8.7959	8.799
	$\epsilon_\phi(x^\gamma)$	1.9809	1.981	2.2605	2.2602
	$\epsilon_\phi(x^{c1})$	1.6966	1.6881	2.5586	2.5602
	$\epsilon_\phi(x^{c2})$	0.65429	0.65354	1.0109	1.0095
g	$\mathcal{E}$	0.36323	-	0.15487	-
	$\epsilon_\phi(x^c)$	272.37	272.15	73.468	73.494
	$\epsilon_\phi(x^\gamma)$	2.7241	2.7242	3.2313	3.2309
	$\epsilon_\phi(x^{c1})$	1.4054	1.3983	1.9592	1.9605
	$\epsilon_\phi(x^{c2})$	0.72857	0.72773	1.1818	1.1802

$$\hat{u} = \hat{u}_{eq}(T^s, \mu_2^s)$$

$$\varepsilon_u(T, \mu_2) = \sum_{x^s} \left\{ \frac{\hat{u}(x^s) - \hat{u}_{eq}(x_{eq}^s; T, \mu_2)}{\hat{u}(x^s)} \right\}^2$$

Equations of state

ϕ	error	$T^\ell = 1.02\, T_{eq}$		$T^\ell = 0.98\, T_{eq}$	
		for $T^s_{\{x^s\}},\psi^s_{\{x^s\}}$	for $T^s(x^s),\psi^s(x^s)$	for $T^s_{\{x^s\}},\psi^s_{\{x^s\}}$	for $T^s(x^s),\psi^s(x^s)$
h	$\mathcal{E}$	0.67514	-	0.21243	-
	$\epsilon_\phi(x^c)$	1.1052	1.1012	0.51202	0.50951
	$\epsilon_\phi(x^\gamma)$	0.0062189	0.0050111	0.074177	0.071345
	$\epsilon_\phi(x^{c1})$	8.5087	8.4753	6.4524	6.4581
	$\epsilon_\phi(x^{c2})$	3.9073	3.8963	6.1946	6.1882
u	$\mathcal{E}$	0.32181	-	0.23381	-
	$\epsilon_\phi(x^c)$	0.77685	0.77406	0.35744	0.3558
	$\epsilon_\phi(x^\gamma)$	0.0043659	0.00366	0.053575	0.051756
	$\epsilon_\phi(x^{c1})$	5.2257	5.2046	4.1104	4.1143
	$\epsilon_\phi(x^{c2})$	3.0451	3.0361	4.692	4.6875
f	$\mathcal{E}$	0.0046133	-	0.0035049	-
	$\epsilon_\phi(x^c)$	6.6737	6.67	8.0558	8.0599
	$\epsilon_\phi(x^\gamma)$	7.242	7.2428	0.37022	0.37236
	$\epsilon_\phi(x^{c1})$	15.74	15.7	25.631	25.642
	$\epsilon_\phi(x^{c2})$	13.328	13.306	20.092	20.077
g	$\mathcal{E}$	0.0017615	-	0.001069	-
	$\epsilon_\phi(x^c)$	246.55	246.41	67.29	67.32
	$\epsilon_\phi(x^\gamma)$	9.9591	9.9604	0.52885	0.53228
	$\epsilon_\phi(x^{c1})$	13.038	13.006	19.627	19.635
	$\epsilon_\phi(x^{c2})$	14.84	14.817	23.49	23.472

Conclusions for mixtures

- Verified local equilibrium numerically for the Gibbs surface

- Surface as described using excess densities can be considered as a separate thermodynamic phase

- The analysis for non equilibrium mixtures shows that one may always use the excess densities as the appropriate property of the surface

- A lot of applications

19. From continuous to discontinuous description

The continuous entropy balance equation is

$$\rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_s$$

where

$$\mathbf{J}_s = \frac{1}{T}\left(\mathbf{J}_q - \sum_{i=1}^{n-1} \psi_i \mathbf{J}_i\right)$$

$$\sigma_s = \mathbf{J}_q \cdot \nabla \frac{1}{T} - \sum_{i=1}^{n-1} \mathbf{J}_i \cdot \nabla \frac{\psi_i}{T} - \pi_{\alpha\beta} \frac{1}{T}\frac{\partial \mathbf{v}_\alpha}{\partial x_\beta}$$

To simplify the analysis we will consider only fluxes and gradients in the direction normal to a flat surface.

It is now convenient to use fluxes that are independent of *x*.

Such constant fluxes are the energy flux J_e and

the mass fluxes $\mathbf{J}_{\xi_i} \equiv \rho_i \, \mathbf{v}_i \text{ and } \mathbf{J}_m \equiv \rho \, \mathbf{v}$

We have: $\mathbf{J}_q \equiv \mathbf{J}_e - \rho \, \mathbf{v} \, e - p \, \mathbf{v} - \pi \cdot \mathbf{v} = \mathbf{J}_e - \mathbf{J}_m \, (e + p \, v) - \Pi \cdot \mathbf{v}$

$$\mathbf{J}_i \equiv \rho_i \, (\mathbf{v}_i - \mathbf{v}) = \mathbf{J}_{\xi_i} - \xi_i \, \mathbf{J}_m$$

Substituting this in the entropy production one obtains after some considerable algebra:

$$\sigma_s = \mathbf{J}_e \cdot \nabla \frac{1}{T} - \sum_{i=1}^{n} \mathbf{J}_{\xi_i} \cdot \nabla \frac{\mu_i}{T} - \mathbf{J}_m \cdot \nabla \frac{\mathbf{v}^2/2 - \mathbf{g} \cdot \mathbf{r}}{T} - \frac{\partial}{\partial x_\alpha} \frac{\pi_{\alpha\beta} \mathbf{v}_\beta}{T}$$

Using that the total mass flux is the sum of the separate mass fluxes we will combine the second and the third term. It is then convenient to introduce $\tilde{\mu}_i \equiv \mu_i + \mathbf{v}^2/2 - \mathbf{g} \cdot \mathbf{r}^s$.

Using the constant nature of the fluxes the entropy production may be written in the following form:

$$\sigma_s = \frac{\partial}{\partial x}\left[J_e \frac{1}{T} - \sum_{i=1}^{n} J_{\xi_i} \frac{\tilde{\mu}_i}{T} - \frac{\pi_{\perp\beta} v_\beta}{T} \right]$$

Integrating this from one side of the surface to the other one gets

$$\widehat{\sigma}_s = J^\ell_{s,tot\,\perp} - J^g_{s,tot\,\perp}$$

$$= J_{e,\perp}\left(\frac{1}{T^\ell} - \frac{1}{T^g} \right) - \sum_{i=1}^{n} J_{\xi_i,\perp}\left(\frac{\tilde{\mu}^\ell_i}{T^\ell} - \frac{\tilde{\mu}^g_i}{T^g} \right) - \left(\frac{\pi^\ell_{\perp\beta} v^\ell_\beta}{T^\ell} - \frac{\pi^g_{\perp\beta} v^g_\beta}{T^g} \right)$$

for stationary states.

The last term is related to the phenomenon of finite slip along the surface. We shall neglect viscous stresses so that this term is zero.

It is now appropriate to re-introduce the measurable heat fluxes

$$\mathbf{J}'_q \equiv \mathbf{J}_q - \sum_{i=1}^{n} h_i \mathbf{J}_i = \mathbf{J}_e - \sum_{i=1}^{n} \tilde{h}_i \mathbf{J}_{\xi_i}$$

where $\quad \tilde{h}_i \equiv h_i + \mathbf{v}^2/2 - \mathbf{g} \cdot \mathbf{r}^s = \tilde{\mu}_i + T s_i$

The measurable heat flux is discontinuous at the surface

$$J_q'^{,g} - J_q'^{,\ell} = \sum_{i=1}^{n} J_{\xi_i} (\tilde{h}_i^{\ell} - \tilde{h}_i^{g})$$

In terms of the measurable heat fluxes the excess entropy production becomes:

$$\hat{\sigma}_s = J_q'^{,g} \left(\frac{1}{T^{\ell}} - \frac{1}{T^g} \right) - \sum_{i=1}^{n} J_{\xi_i} \frac{1}{T^{\ell}} \left(\tilde{\mu}_i^{\ell} - \tilde{\mu}_i^{g} + s_i^{g}(T^{\ell} - T^g) \right)$$

$$\hat{\sigma}_s = J_q'^{,\ell} \left(\frac{1}{T^{\ell}} - \frac{1}{T^g} \right) - \sum_{i=1}^{n} J_{\xi_i} \frac{1}{T^g} \left(\tilde{\mu}_i^{\ell} - \tilde{\mu}_i^{g} + s_i^{\ell}(T^{\ell} - T^g) \right)$$

Note the difference in the chemical forces.

The resulting force-flux relations are

$$\frac{1}{T^\ell} - \frac{1}{T^g} = R^g_{qq} J'^{,g}_q - \sum_{i=1}^n R^g_{qi} J_{\xi_i}$$

$$\frac{1}{T^\ell}\left(\tilde{\mu}^\ell_j - \tilde{\mu}^g_j + s^g_{j,eq}(T^\ell - T^g)\right) = R^g_{jq} J'^{,g}_q - \sum_{i=1}^n R^g_{ji} J_{\xi_i}$$

on the vapor side, and

$$\frac{1}{T^\ell} - \frac{1}{T^g} = R^\ell_{qq} J'^{,\ell}_q - \sum_{i=1}^n R^\ell_{qi} J_{\xi_i}$$

$$\frac{1}{T^g}\left(\tilde{\mu}^\ell_j - \tilde{\mu}^g_j + s^\ell_{j,eq}(T^\ell - T^g)\right) = R^\ell_{jq} J'^{,\ell}_q - \sum_{i=1}^n R^\ell_{ji} J_{\xi_i}$$

We note that to linear order

$$\frac{1}{T^\ell}\left(\tilde{\mu}^\ell_j - \tilde{\mu}^g_j + s^g_j(T^\ell - T^g)\right) = \frac{1}{T^\ell}\left(\tilde{\mu}^\ell_j - \tilde{\mu}^g_j\left(T^\ell\right)\right)$$

$$\frac{1}{T^g}\left(\tilde{\mu}^\ell_j - \tilde{\mu}^g_j + s^\ell_j(T^\ell - T^g)\right) = \frac{1}{T^g}\left(\tilde{\mu}^\ell_j\left(T^g\right) - \tilde{\mu}^g_j\right)$$

Mention the sign difference between the thesis and the book

The relation between the measurable heat fluxes on the liquid and the vapor side can be written to linear order as:

$$J_q'^{,g} - J_q'^{,\ell} = \sum_{i=1}^{n} J_{\xi_i} \left(\tilde{h}_{i,eq}^{\ell} - \tilde{h}_{i,eq}^{g} \right)$$

Together with $\tilde{\mu}_{i,eq}^{g} = \tilde{\mu}_{i,eq}^{\ell}$ and $\tilde{h}_{i,eq}^{g} - \tilde{h}_{i,eq}^{\ell} = h_{i,eq}^{g} - h_{i,eq}^{\ell}$ it follows that:

$$R_{qq}^{\ell} = R_{qq}^{g}$$

$$R_{qi}^{\ell} = R_{qi}^{g} + \left(h_{i,eq}^{g} - h_{i,eq}^{\ell} \right) R_{qq}^{g}$$

$$R_{iq}^{\ell} = R_{iq}^{g} + \left(h_{i,eq}^{g} - h_{i,eq}^{\ell} \right) R_{qq}^{g}$$

$$R_{ji}^{\ell} = R_{ji}^{g} + \left(h_{i,eq}^{g} - h_{i,eq}^{\ell} \right) R_{jq}^{g} + \left(h_{j,eq}^{g} - h_{j,eq}^{\ell} \right) R_{iq}^{g} + \left(h_{i,eq}^{g} - h_{i,eq}^{\ell} \right) \left(h_{j,eq}^{g} - h_{j,eq}^{\ell} \right) R_{qq}^{g}$$

Using the Onsager reciprocal relations it follows that both resistivity matrices are symmetric.

Remarks

- Considering only transport normal to a flat surface simplifies the analysis considerably.
- For 2-dimensionally isotropic surface, which is thin compared to the curvature radii this makes no difference.
- The more general case is considered in Glavatskiy's thesis.
- Remains the calculation of the transfer resistivities for the surface.
- The results depend on the alphas and should be compared to experiments, MD simulations or kinetic theory. This determines the alphas.
- We used kinetic theory as the only available source of relevant data.