

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

Dick Bedeaux

Department of Chemistry, Norwegian University of Science
and Technology, Trondheim, Norway

8th Lecture

Università Degli Studi di Brescia, Italy,

13-16 September 2010

15. The numerical analysis for stationary mixtures

In a stationary state it follows from the balance equations that the following fluxes are constant:

$$\rho v, \quad J_1 + \rho \xi v, \quad \rho v^2 + p + \gamma_{xx} - \rho g x, \quad J_e \equiv J_q + \rho e v + p v$$

where $e = u + v^2/2 - g x$

The thermodynamic variables are given by:

$$f(x) = f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi')$$

$$u(x) = f_0(T, \rho, \xi) - T \frac{\partial}{\partial T} f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi')$$

$$p(x) = \rho^2 \frac{\partial}{\partial \rho} \left(f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi') \right) - \rho \frac{d}{dx} \left(\rho \frac{\partial}{\partial \rho'} \mathcal{K}(\rho, \xi, \rho', \xi') \right)$$

$$\psi(x) = \frac{\partial}{\partial \xi} \left(f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi') \right) - \frac{1}{\rho} \frac{d}{dx} \left(\rho \frac{\partial}{\partial \xi'} \mathcal{K}(\rho, \xi, \rho', \xi') \right)$$

$$\mu(x) = \frac{\partial}{\partial \rho} \left(\rho \left(f_0(T, \rho, \xi) + \mathcal{K}(\rho, \xi, \rho', \xi') \right) \right) - \frac{d}{dx} \left(\rho \frac{\partial}{\partial \rho'} \mathcal{K}(\rho, \xi, \rho', \xi') \right) - \psi(x) \xi$$

$$s(x) = -\frac{\partial}{\partial T} f_0(T, \rho, \xi) \qquad \gamma_{xx}(x) = 2 \rho \mathcal{K}(\rho, \xi, \rho', \xi')$$

Here $f_0(T, \rho, \xi) = f_0^\nu(T, c, \xi)/M(\zeta)$ is the specific Helmholtz energy of the homogeneous phase

The molar mass of the mixture is:

$$M = M_1 M_2 / (M_1 + \xi (M_2 - M_1)) = M_2 + \zeta (M_1 - M_2)$$

The molar Helmholtz energy of the homogeneous phases is given by:

$$f_0^\nu(T, c, \xi) = -RT \ln \left(\frac{e}{c N_A} \frac{w(T, \xi)}{\Lambda^3(T, \xi)} (1 - B(\zeta) c) \right) - A(T, \xi) c$$

Lambda is the mean de Broglie wavelength. For w a constant will be used.

The mixing rules for A and B are

$$\begin{aligned} A(T, \xi) &= a_{11} \zeta^2 + 2 a_{12} \zeta (1 - \zeta) + a_{22} (1 - \zeta)^2 \\ B(\zeta) &= b_1 \zeta + b_2 (1 - \zeta) \end{aligned}$$

with $a_{ij} = \sqrt{a_i a_j}$, where a_i as well as b_i is a coefficient of a pure component i . We will assume in this thesis that all a_{ij} and b_i are independent of temperature.

The gradient contribution is given by the following general expression in the mixture:

$$\mathcal{K}(\rho, \xi, \rho', \xi') \equiv \frac{1}{2\rho} \left(\kappa_{\rho\rho}(\rho, \xi) \rho'^2 + 2 \kappa_{\rho\xi}(\rho, \xi) \rho' \xi' + \kappa_{\xi\xi}(\rho, \xi) \xi'^2 \right)$$

where

$$\begin{aligned} \kappa_{\rho\rho}(\rho, \xi) &= (\kappa_{\rho_1\rho_1} - 2\kappa_{\rho_1\rho_2} + \kappa_{\rho_2\rho_2}) \xi^2 + 2(\kappa_{\rho_1\rho_2} - \kappa_{\rho_2\rho_2}) \xi + \kappa_{\rho_2\rho_2} \\ \kappa_{\rho\xi}(\rho, \xi) &= (\kappa_{\rho_1\rho_1} - 2\kappa_{\rho_1\rho_2} + \kappa_{\rho_2\rho_2}) \rho \xi + (\kappa_{\rho_1\rho_2} - \kappa_{\rho_2\rho_2}) \rho \\ \kappa_{\xi\xi}(\rho, \xi) &= (\kappa_{\rho_1\rho_1} - 2\kappa_{\rho_1\rho_2} + \kappa_{\rho_2\rho_2}) \rho^2 \end{aligned}$$

Using as mixing rule: $\kappa_{\rho_1\rho_2} = \sqrt{\kappa_{\rho_1\rho_1} \kappa_{\rho_2\rho_2}}$

The gradient contribution can be written as: $\mathcal{K}(\rho, \xi, \rho', \xi') \equiv \frac{\kappa q'^2}{2\rho}$

where $\kappa \equiv \kappa_{\rho_2\rho_2}$

$$q \equiv \rho (1 + \varepsilon_{\kappa}^m \xi)$$

$$\varepsilon_{\kappa}^m \equiv \varepsilon_{\kappa} \equiv \sqrt{\frac{\kappa_{\rho_1\rho_1}}{\kappa_{\rho_2\rho_2}}} - 1$$

q will be referred to as the order parameter.

The variables may now be written using q . This gives:

$$p(x) = p_0 - \kappa \left(\frac{1}{2} q'^2 + q q'' \right)$$

$$\mu(x) = \mu_0 - \kappa q''$$

$$\psi(x) = \psi_0 - \varepsilon_\kappa \kappa q''$$

For the equilibrium surface tension one obtains:

$$\gamma_{eq} \equiv \int dx \gamma_{xx, eq}(x) = \kappa \int dx q'_{eq}{}^2$$

It follows that $\kappa_{\rho_i \rho_i}$ is proportional to the surface tension $\gamma_{eq, i}$ of the pure component i . It follows therefore that as estimate for ε_κ one may use the relation

$$\varepsilon_\kappa \simeq \sqrt{\frac{\gamma_1}{\gamma_2}} - 1$$

In the mixture cyclohexane and n-hexane, which we will study in more detail, the components are very similar. As a consequence epsilon will be small. If the components are very different q may become equal to the density of one of the components.

As resistances in the continuous description we use:

$$r_{qq}(x) = r_{qq}^g + (r_{qq}^\ell - r_{qq}^g) q_0(x) + \alpha_{qq} (r_{qq}^\ell + r_{qq}^g) q_1(x)$$

$$r_{q1}(x) = r_{q1}^g + (r_{q1}^\ell - r_{q1}^g) q_0(x) + \alpha_{q1} (r_{q1}^\ell + r_{q1}^g) q_1(x)$$

$$r_{11}(x) = r_{11}^g + (r_{11}^\ell - r_{11}^g) q_0(x) + \alpha_{11} (r_{11}^\ell + r_{11}^g) q_1(x)$$

The modulatory curves are:

$$q_0(x) \equiv \frac{q(x) - q_{eq}^g}{q_{eq}^\ell - q_{eq}^g}, \quad q_1(x) \equiv \frac{|q'(x)|^2}{|q'_{eq}(x)|_{max}^2}$$

The first two contribution on the right hand side give a gradual transition from the resistance in one phase to the other.

The last contribution is only unequal to zero in the interfacial region. The parameters alpha must be chosen appropriately.

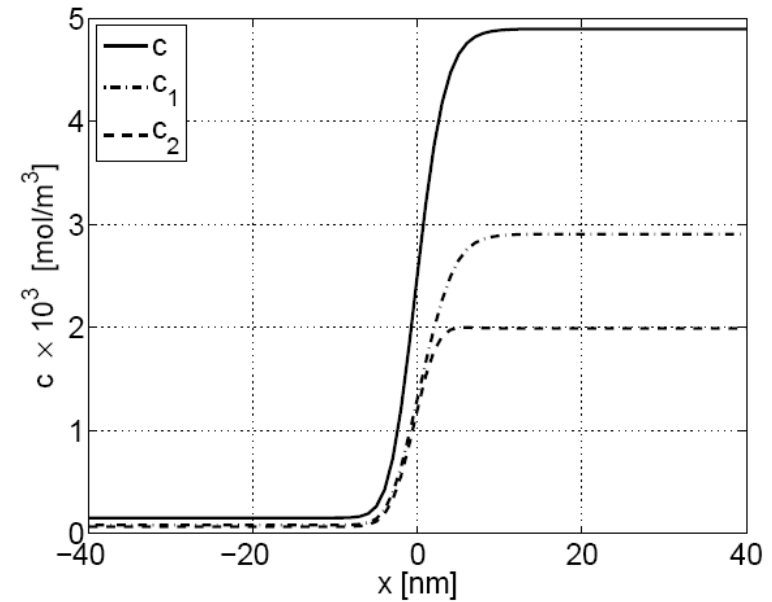
We use a comparison with results from kinetic theory to obtain these alphas.

Kinetic theory agrees only if some of the alphas are finite!

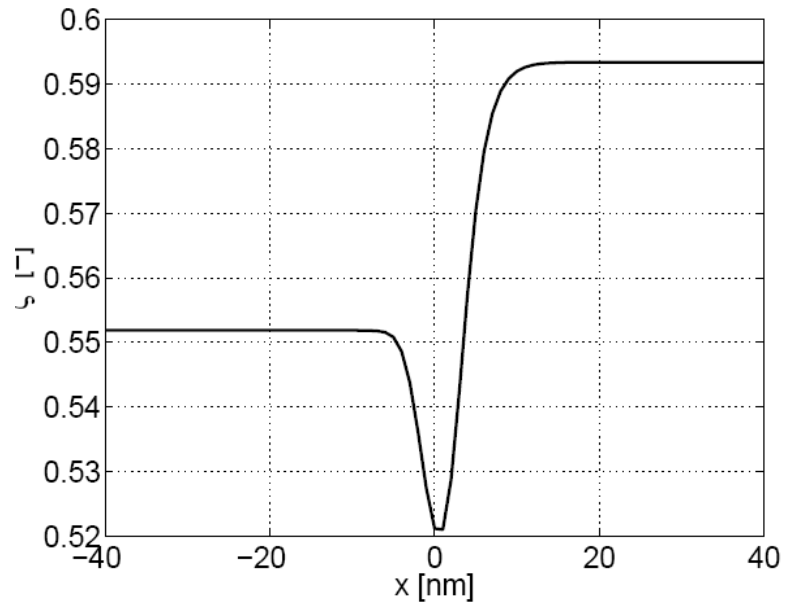
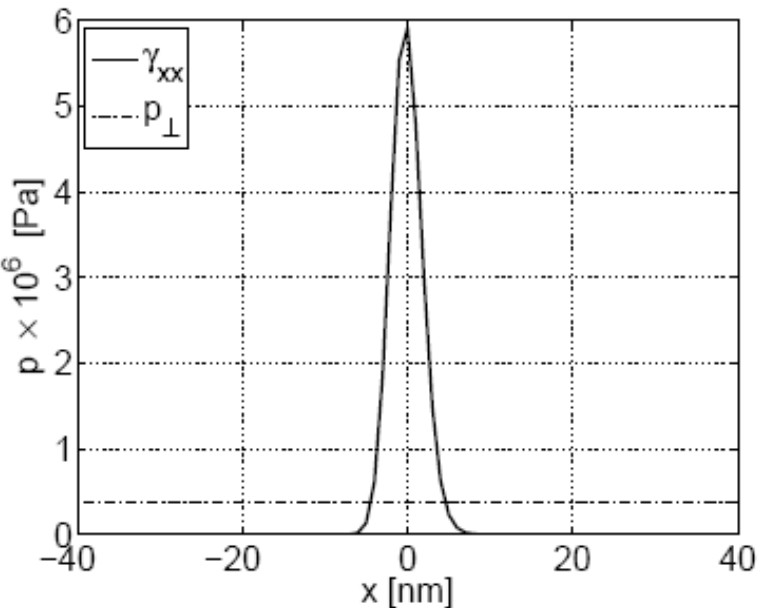
The solution procedure is described in the thesis(p.70-75). First an equilibrium state is constructed:

Table 4.3: *Coexistence data*

T_{eq}	= 330	[K]
ψ_{eq}^ν	= 700	[J/mol]
μ_{eq}^ν	= -57098	[J/mol]
p_{eq}	= 376095	[Pa]
c_{eq}^g	= 153.23	[mol/m ³]
c_{eq}^l	= 4898.26	[mol/m ³]
ζ_{eq}^g	= 0.5519	
ζ_{eq}^l	= 0.5934	

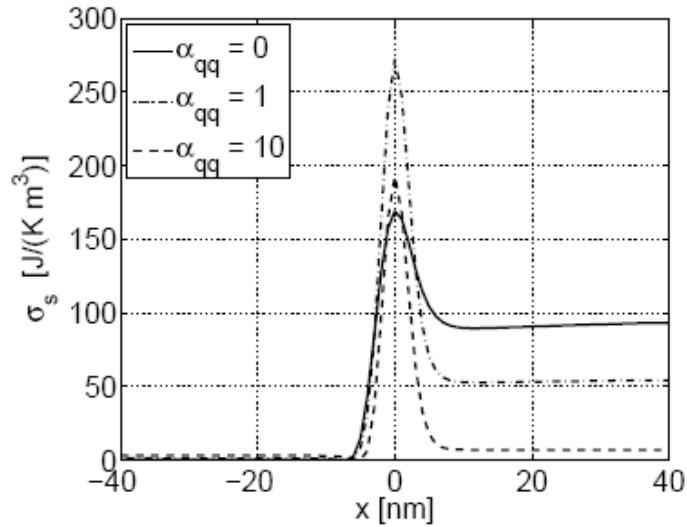


(a) Molar concentrations

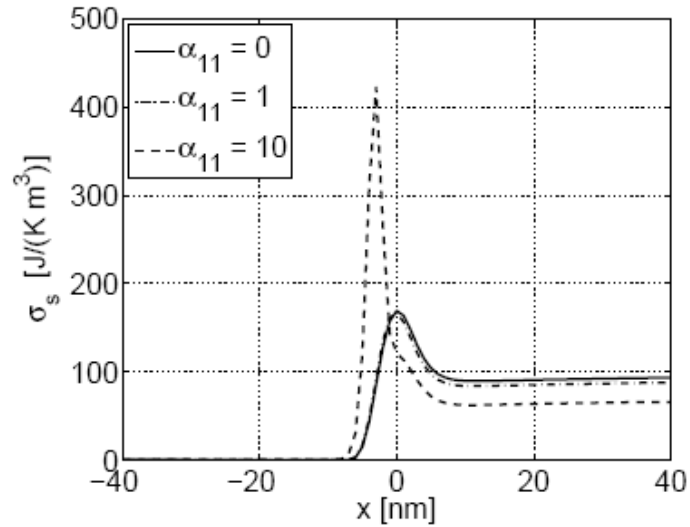


(b) Molar fraction

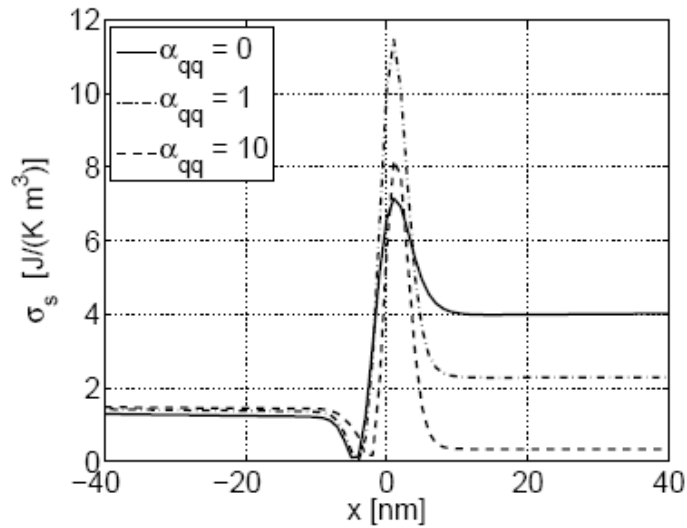
It is interesting to see the behavior of the entropy production. It is clear that the surface contributes even for $\alpha = 0$!



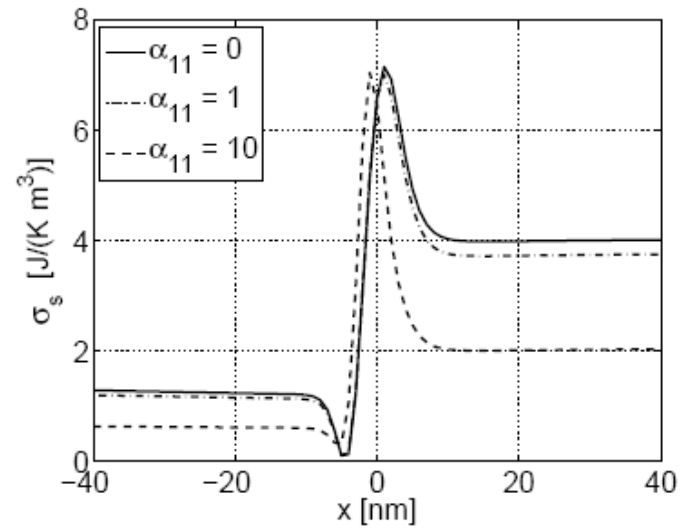
(a) $T^\ell = 1.05 T_{eq}$, $\alpha_{qq} \neq 0$



(b) $T^\ell = 1.05 T_{eq}$, $\alpha_{11} \neq 0$

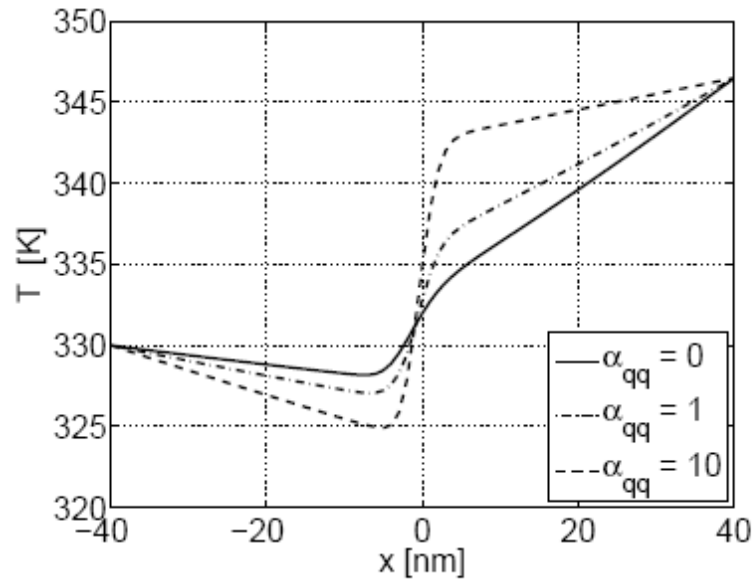


(c) $p^g = 0.95 p_{eq}$, $\alpha_{qq} \neq 0$

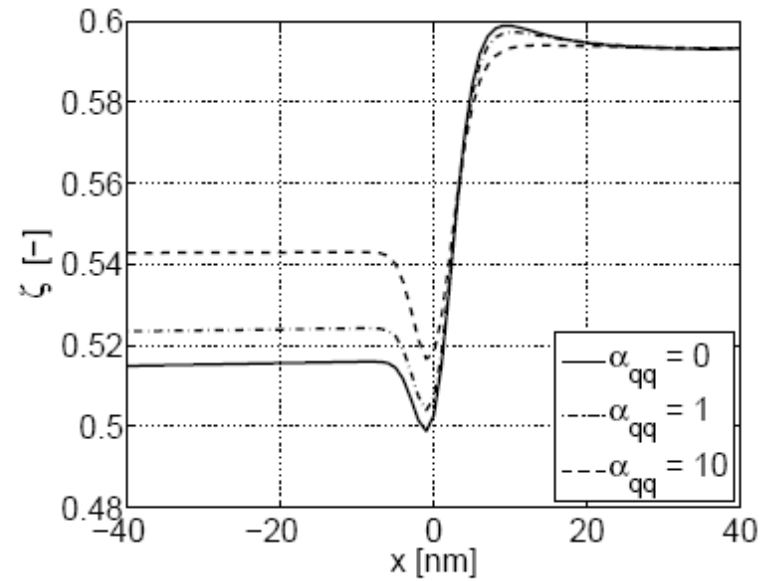


(d) $p^g = 0.95 p_{eq}$, $\alpha_{11} \neq 0$

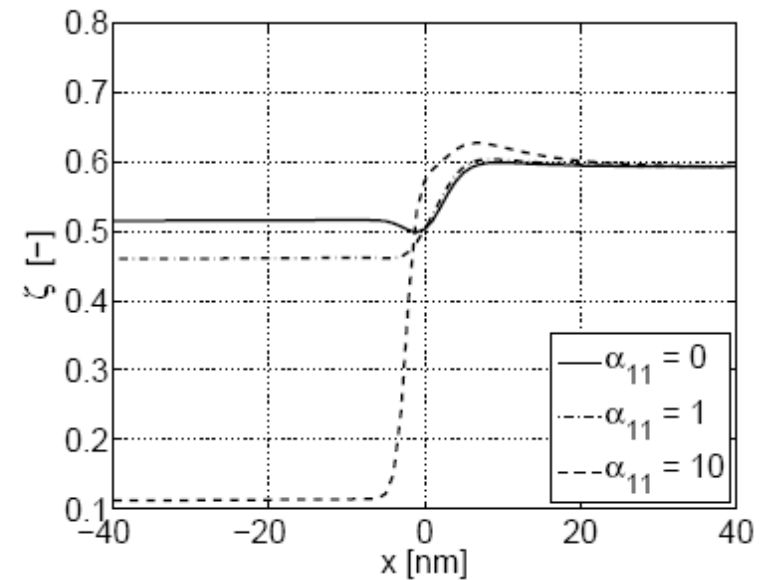
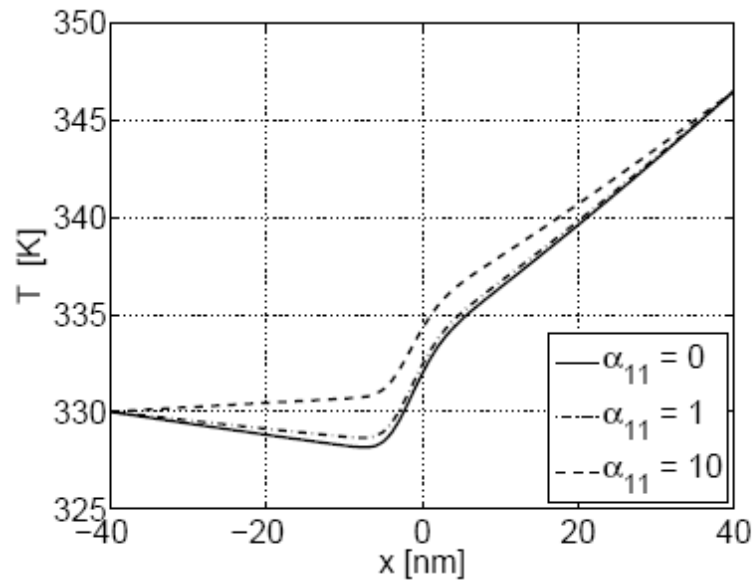
Temperature and mole fraction profiles for $T^l = 1.05 T_{eq}$



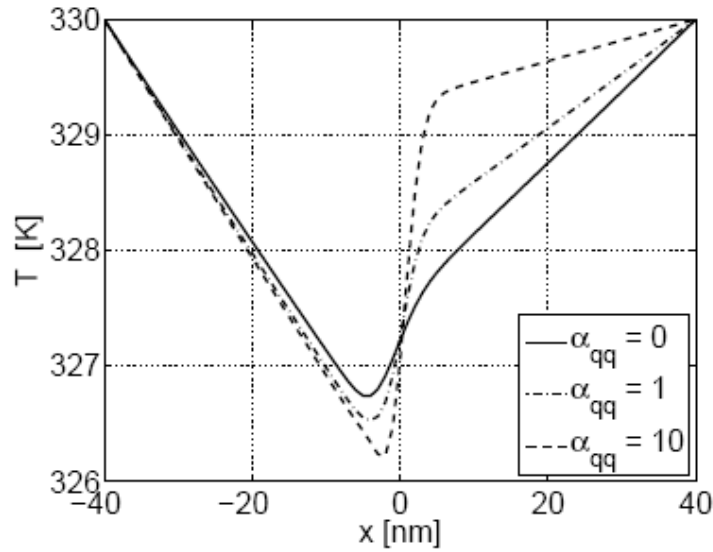
(a)



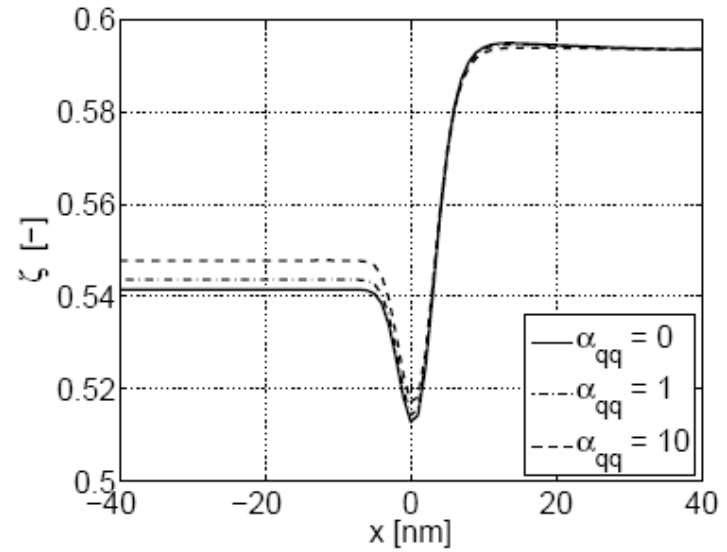
(b)



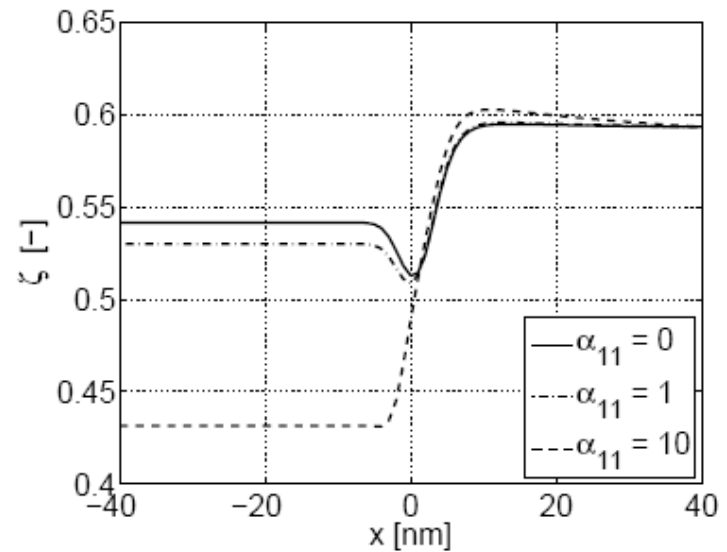
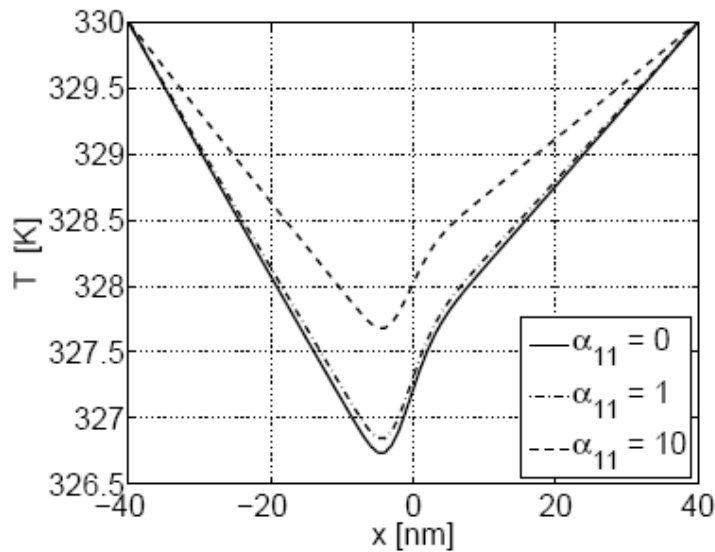
Temperature and mole fraction profiles for $p^g=0.95p_{eq}$



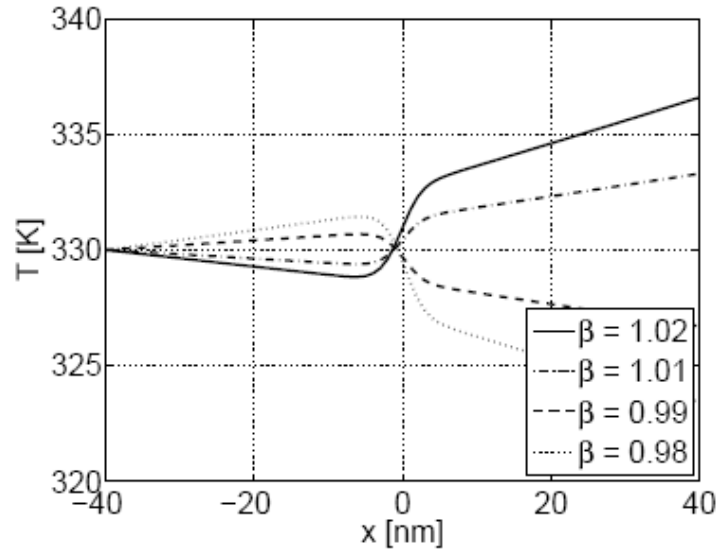
(a)



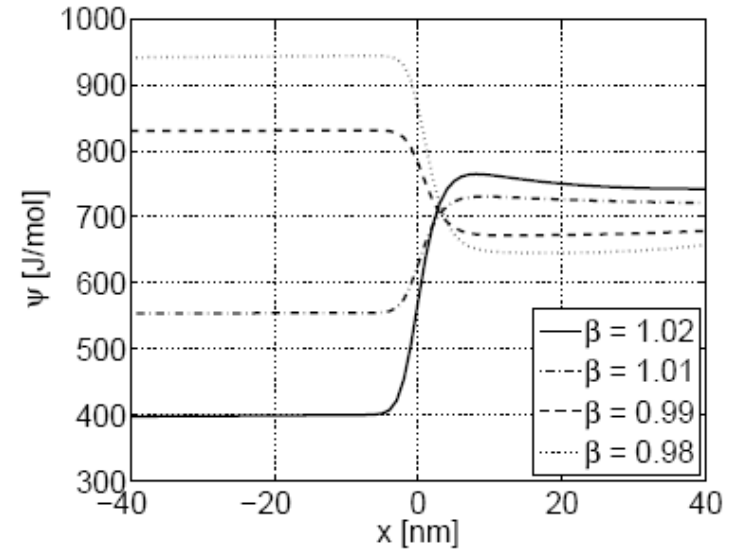
(b)



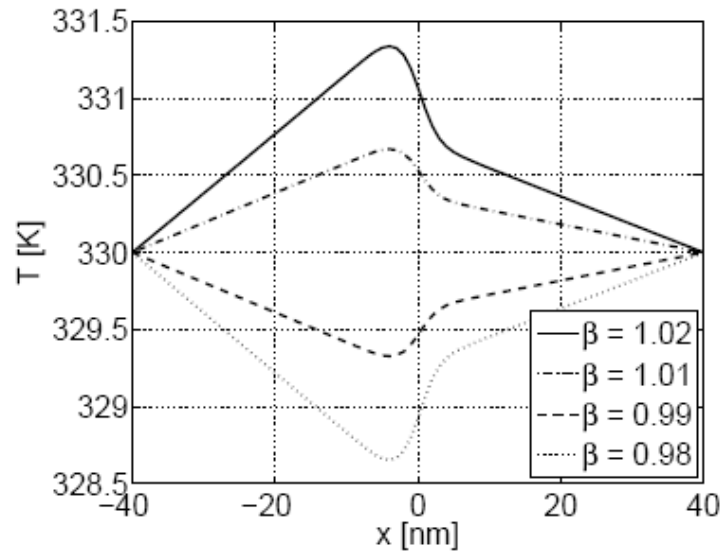
Temperature and chemical potential profiles



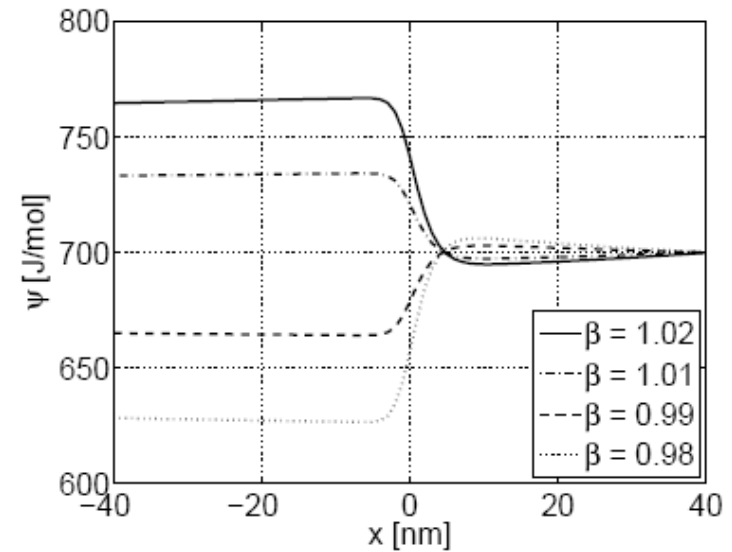
(a) $T^\ell = \beta T_{eq}$



(b) $T^\ell = \beta T_{eq}$



(c) $p^g = \beta p_{eq}$



(d) $p^g = \beta p_{eq}$