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

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1st Lecture

The van der Waals and alternative equations of state.

The van der Waals square gradient model of a two-phase single-component fluid-fluid interface.

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The first part of this lecture series will focus on the description of the liquid-vapor interface in a one-component fluid.

I will use the 23rd chapter of a book I have written together with Signe Kjelstrup:

Signe Kjelstrup and Dick Bedeaux, Series on Advances in Statistical Mechanics-Vol. 16, Non-Equilibrium Thermodynamics of Heterogeneous Systems, World Scientific, Singapore, 2008.

This chapter is based on earlier work I did with Eivind Johannessen and Audun Røsjorde on the non-equilibrium van der Waals square gradient model:

- D. Bedeaux, E. Johannessen, A. Røsjorde,
The Non-equilibrium van der Waals Square Gradient Model I: The Model and its Numerical Solution, Physica A 330 (2003) 329-353.
- E. Johannessen and D. Bedeaux,
The Non-equilibrium van der Waals Square Gradient Model II: Local Equilibrium of the Gibbs Surface, Physica A 330 (2003) 354-372.
- E. Johannessen and D. Bedeaux,
The Non-equilibrium van der Waals Square Gradient Model III: Heat and Mass Transfer Coefficients, Physica A 336 (2004) 252-270

The book describes much of what we did on the description of transport through and into interfaces

Non-Equilibrium Thermodynamics
of Heterogeneous Systems

The purpose of this book is to encourage the use of non-equilibrium thermodynamics to describe transport in complex, heterogeneous media. With large coupling effects between the transport of heat, mass, charge and chemical reactions at surfaces, it is important to know how one should properly integrate across systems where different phases are in contact. No other book gives a prescription of how to set up flux equations for transports across heterogeneous systems.

The authors apply the thermodynamic description in terms of excess densities, developed by Gibbs for equilibrium, to non-equilibrium systems. The treatment is restricted to transport into and through the surface. Using local equilibrium together with the balance equations for the surface, expressions for the excess entropy production of the surface and of the contact line are derived. The excess entropy production is as usual a sum of the product of forces with their conjugate forces, enabling the derivation of the force-flux relations for the surface, or the proper boundary conditions for transport through the surface.

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Non-Equilibrium Thermodynamics
of Heterogeneous Systems

KJELSTRUP
BEDEAUX

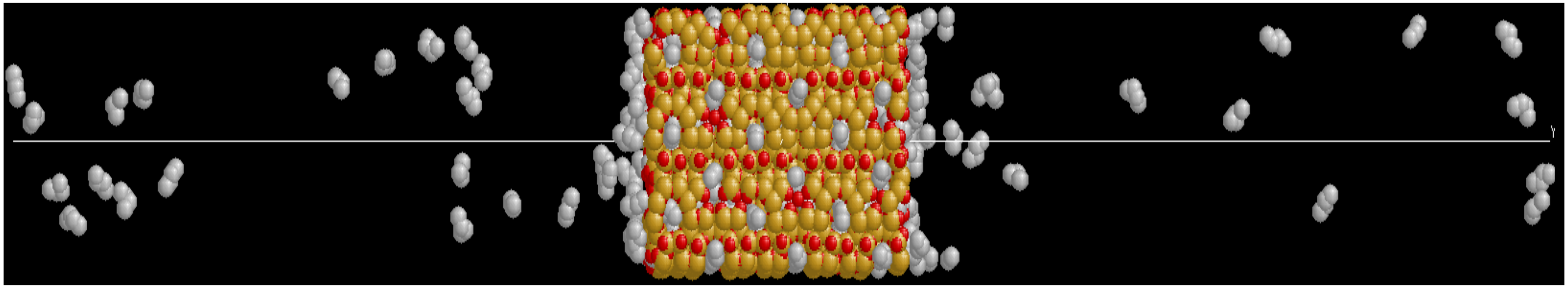
Series on Advances in Statistical Mechanics – Volume 16

Non-Equilibrium Thermodynamics
of Heterogeneous Systems

SIGNE KJELSTRUP DICK BEDEAUX

World Scientific

Signe Kjelstrup and Dick Bedeaux,
Non-Equilibrium Thermodynamics of Heterogeneous Systems; World Scientific, 2008;
Series on Advances in Statistical Mechanics, Vol. 16.



Transport of n-butane through and into a zeolite crystal.

- Molecular description
- Continuous description
- Macroscopic description with excess densities

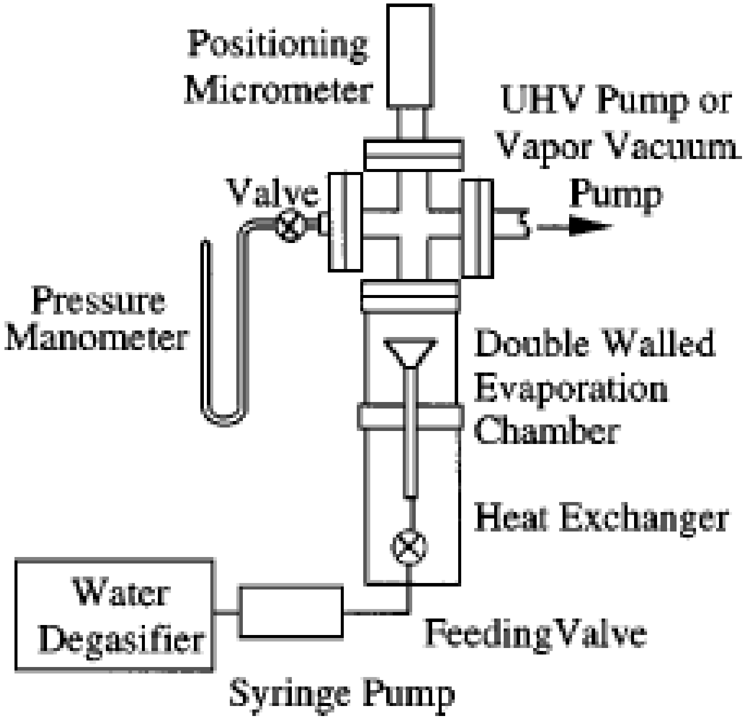
All these descriptions have their strengths and weaknesses.

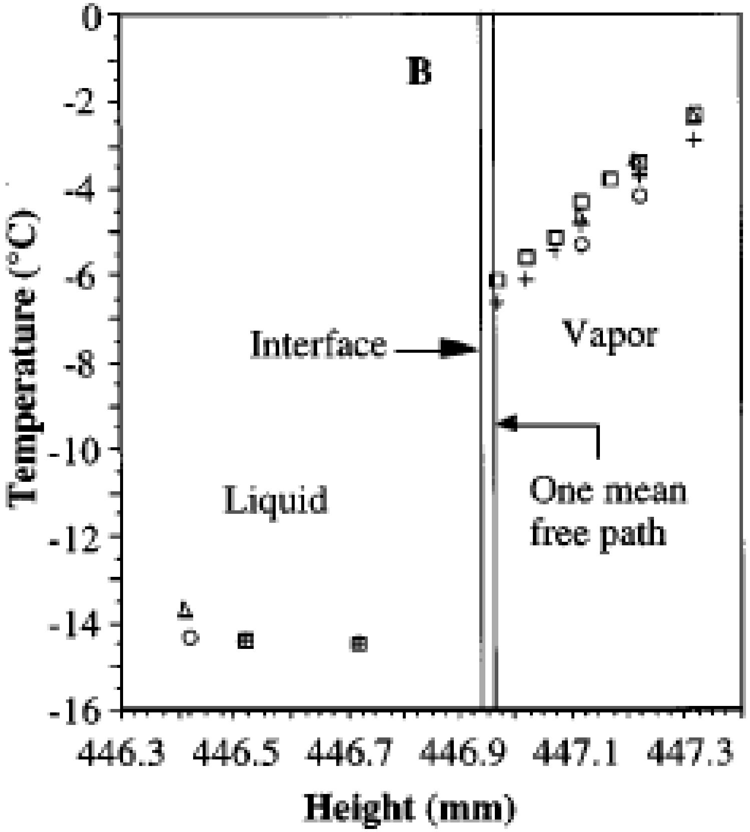
All three of them have something to add and should therefore be pursued.

How they are related is very important.

Just to show that really remarkable things happen at surfaces

Experiments Fang and Ward for the evaporation of water

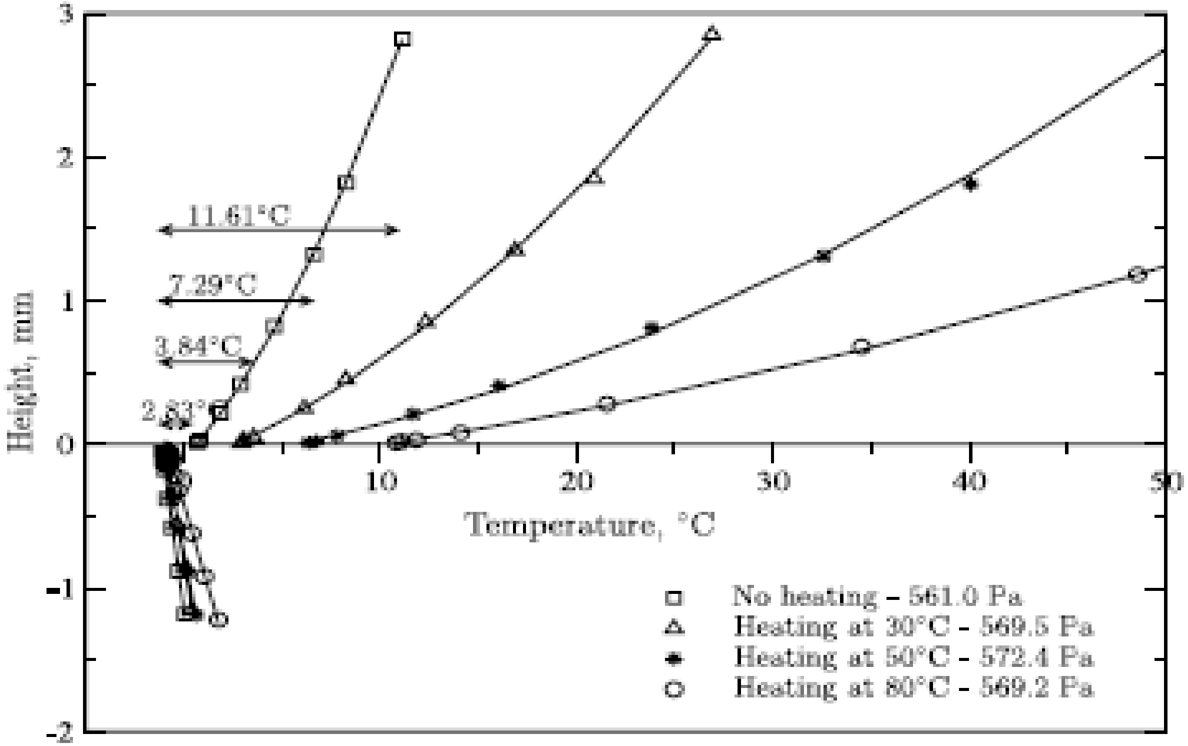




Phys. Rev. E 59 (1999) 417-428

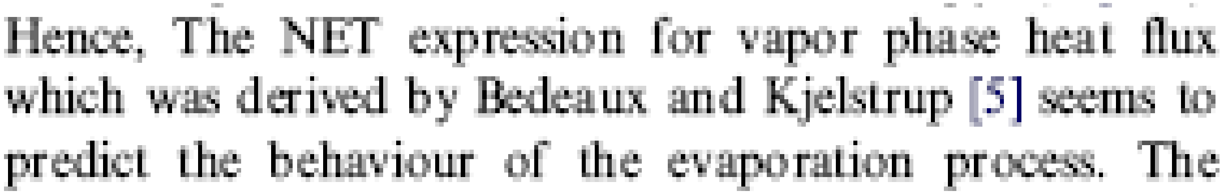
D. Bedeaux and S. Kjelstrup, Transfer Coefficients for Evaporation, Physica A, 270 (1999) 413-426,

Experiments Badam, Kumar, Durst, Danov for the evaporation of water



Exp. Thermal and Fluid Sc. 32(2007)276-292

Quote:



Hence, The NET expression for vapor phase heat flux which was derived by Bedeaux and Kjelstrup [5] seems to predict the behaviour of the evaporation process. The

1. The van der Waals equation of state

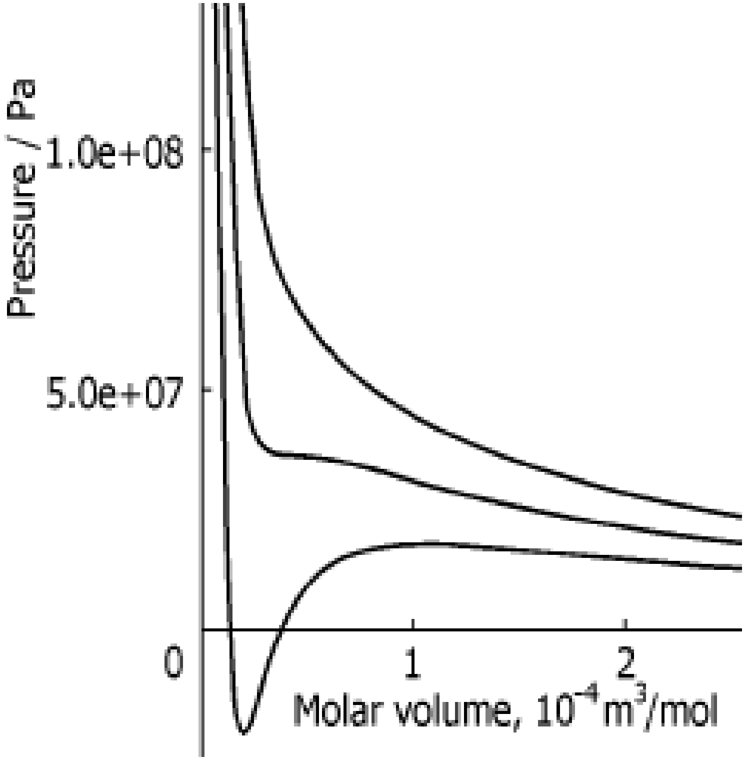
The van der Waals equation of state for one component is:

$$pw = \frac{cRT}{1-Bc} - Ac^2 = \frac{RT}{V-B} - \frac{A}{V^2}$$

The resulting critical temperature, pressure and volume per mole are: $T_c = 8A/27RB$, $p_c = A/27B^2$ and $V_c = 3B$

For water we use A=0.339 J m^{3}mol^{-2} and B=1.87 10^{-5} m^{3}mol^{-1}. These reproduce T_c=646 K and V_c=5.61 10^{-5} m^{3}mol^{-1}. The critical pressure p_c=360 bar is larger than the experimental value 220 bar.

The figure shows the resulting pressures for water



Alternative equations of state

As we see the agreement of the van der Waals equation of state is not perfect. The agreement can be improved by using either the Soave-Redlich-Kwong or the Peng-Robinson equation of state

$$p_{SRK} = \frac{RTc}{1-Bc} - \frac{Ac^2}{1-Bc} \qquad p_{PR} = \frac{RTc}{1-Bc} - \frac{Ac^2}{1+2Bc-B^2c^2}$$

For the liquid and around the critical point the agreement remains unsatisfactory, however.

Further improvement can be obtained using the so-called density functional theories (DFT).

In our papers we always used the van der Waals equation of state. We will therefore not further discuss SRK and PR.

We must find the other thermodynamic quantities for the van der Waals model. The Gibbs relation for the molar Helmholtz energy is:

$$dF_W = -S_W dT - p_W dV$$

Integrating this over the volume we obtain:

$$F_W = -RT\ln\left[\frac{e\,(V-B)}{\Lambda^3 N_A}\right] - \frac{A}{V} = -RT\ln\left[\frac{e\,(1-Bc)}{c\Lambda^3 N_A}\right] - Ac$$

We chose an integration constant such that this expression reduces to the ideal gas one for smal *c*. The mean thermal de Broglie wave length is: $\Lambda \equiv N_A h/\sqrt{2\pi MRT}$

N_A is Avogrado's number.

Differentiating with respect to *T* we find the molar entropy:

$$S_W = R\ln\left[\frac{e\,(V-B)}{\Lambda^3 N_A}\right] + \frac{3}{2}R = R\ln\left[\frac{e\,(1-Bc)}{c\Lambda^3 N_A}\right] + \frac{3}{2}R$$

A and *B* were assumed to be independent of the temperature.

The molar Helmholtz energy and enthalpy satisfy:

$$F_W = U_W - TS_W = \mu_W - p_W V \quad \text{and} \quad H_W = U_W + p_W V = \mu_W + TS_W$$

This gives for the chemical potential, enthalpy and internal energy:

$$\begin{aligned}
\mu_W &= -RT \ln\left[\frac{e\,(V-B)}{\Lambda^3 N_A}\right] + \frac{RTV}{V-B} - 2\frac{A}{V} \\
&= -RT \ln\left[\frac{e\,(1-Bc)}{c\Lambda^3 N_A}\right] + \frac{RT}{1-Bc} - 2Ac \\
H_W &= \frac{3}{2}RT - 2\frac{A}{V} + \frac{V\,RT}{V-B} = \frac{3}{2}RT - 2Ac + \frac{RT}{1-Bc} \\
U_W &= \frac{3}{2}RT - \frac{A}{V} = \frac{3}{2}RT - Ac
\end{aligned}$$

These quantities satisfy the Gibbs relation $dU_W = T\,dS_W - p_W\,dV$

and the Gibbs – Duhem relation $d\mu_W = -S_W\,dT + V\,dp_W$

2. Van der Waals square gradient model of a one-component liquid-vapor interface

In 1893 van der Waals introduced the following molar Helmholtz energy density

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

He only used it for equilibrium surfaces with *T* independent of the position and time and *c* independent of the time.

In equilibrium the concentration profile $c_{eq}(x)$ is such that

$$\mathrm{F}_{eq} \equiv \Omega \int c_{eq}(x) F(c_{eq}(x), T_{eq}) dx$$

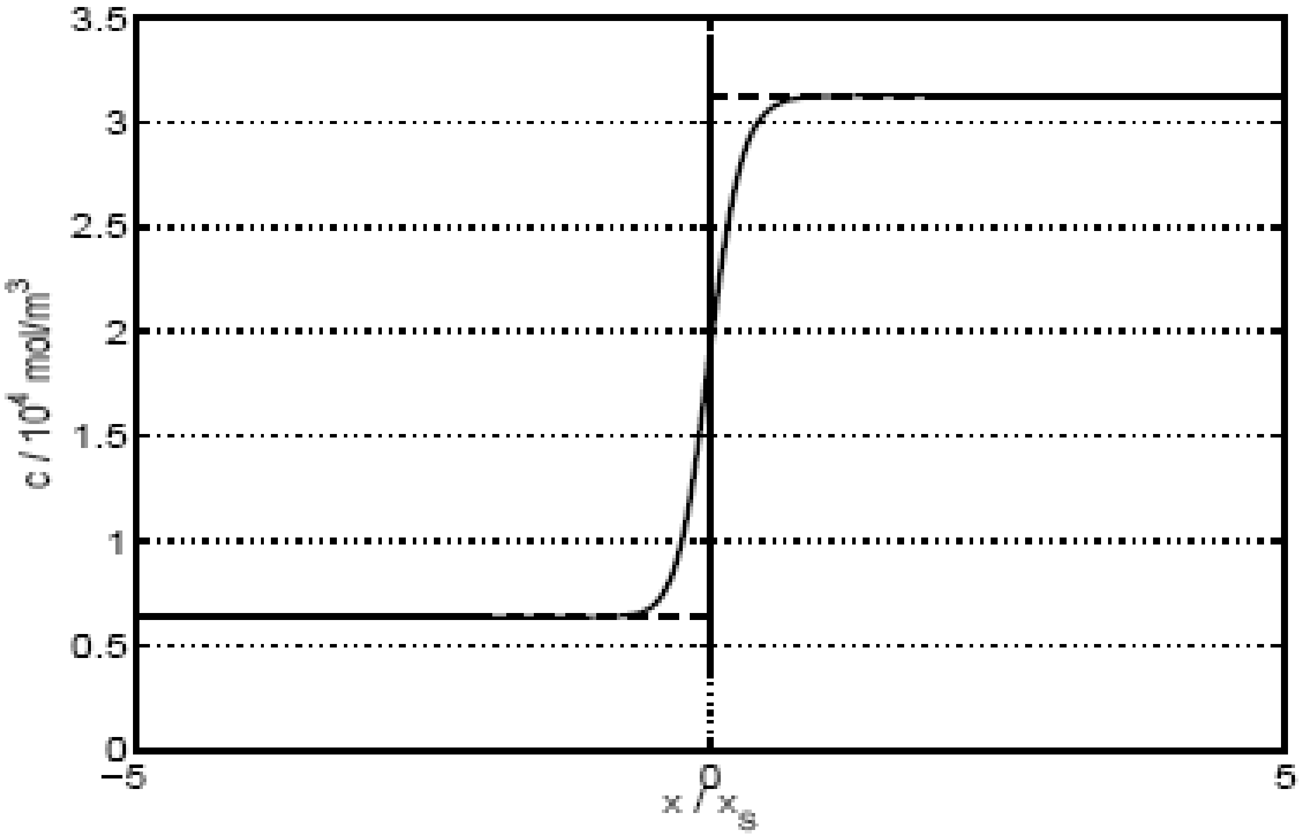
has a minimum for a given total mole number

$$\mathrm{N}_{eq} \equiv \Omega \int c_{eq}(x) dx$$

The resulting Euler-Lagrange equation is:

$$\frac{\partial\left[c_{eq}(x)F_{eq}(c_{eq}(x))\right]}{\partial c_{eq}(x)} - m\frac{d^2 c_{eq}(x)}{dx^2} + \mu = 0$$

The figure gives the density profile for water for a pressure of 200 bar and a temperature of 561.65 K. x_s is a scaling length, to be defined later, which is of the order of the diameter of the molecules.



We will use the molar Helmholtz energy that van der Waals introduced as a function of position and time dependent density and temperatue profiles

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

For the chemical potential and the pressure normal to the surface we use

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

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

In equilibrium these quantities are both independent of *x* and *t*

We refer to the book by Rowlinson and Widom for a discussion of these choices.

J.S. Rowlinson, B. Widom, Molecular Theory of Capillarity, Clarendon Press, Oxford, 1982

We define the parallel pressure by

$$p_{\|}(x,t) \equiv c(x,t)\left[\mu(x,t) - f(x,t)\right]$$

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

The molar entropy by

$$S(x,t) \equiv \left(\frac{\partial F}{\partial T}\right)_v = \left(\frac{\partial F_W}{\partial T}\right)_v = S_W\left(c(x,t),T(x,t)\right)$$

The molar internal energy by

$$U(x,t) \equiv F(x,t) + T(x,t)\,S(x,t)$$

$$= T(x,t)\,S(x,t) - p_{\|}(x,t)V(x,t) + \mu(x,t)$$

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

The molar enthalpy by

$$H(x,t) \equiv U(x,t) + p_{\|}(x,t)V(x,t) = T(x,t)S(x,t) + \mu(x,t)$$

$$= H_W\left(c(x,t),T(x,t)\right) - m\frac{d^2c(x,t)}{dx^2}$$

- An important aspect in the choice of the above definitions is that all the normal thermodynamic relations are valid if one uses the parallel pressure.

One of the reasons van der Waals introduced the square gradient terms was to obtain a finite surface tension.

Minus the excess of the parallel pressure gives the surface tension. As the parallel and the normal pressure are the same away from the surface, one finds in equilibrium:

$$\gamma_{eq} = -\int \left[p_{||,eq}(x) - p_{\perp,eq}(x) \right] dx$$

Substituting the expressions given above he found:

$$\gamma_{eq} = m \int \left(\frac{dc_{eq}(x)}{dx} \right)^2 dx$$

Van der Waals used this expression to calculate the equilibrium surface tension.

- An interesting question is whether these expressions, and in particular the 2nd one, are still valid away from equilibrium?

Remarks

- The expressions for the parallel and normal pressure in a 1-component system were derived elegantly by Yang, Fleming and Gibbs.
- The expression for the entropy, which does not have a gradient contribution, was motivated by van der Waals.
- All the thermodynamic relations are the same as in the homogeneous phases, if one uses the parallel pressure rather than the homogeneous pressure.
- In our analysis we need all these thermodynamic variables.
- In the litterature about the use of the square gradient model for the non-equilibrium case one seems to avoid the use of most of these thermodynamic variables, see e.g. Hohenberg and Halperin.

A. J. M. Yang, P. D. Fleming, and J. H. Gibbs, J. Chem. Phys. **64**, 3732 (1976).

P.C. Hohenberg, B.J. Halperin, Rev. Mod. Phys. 49 (1977) 435