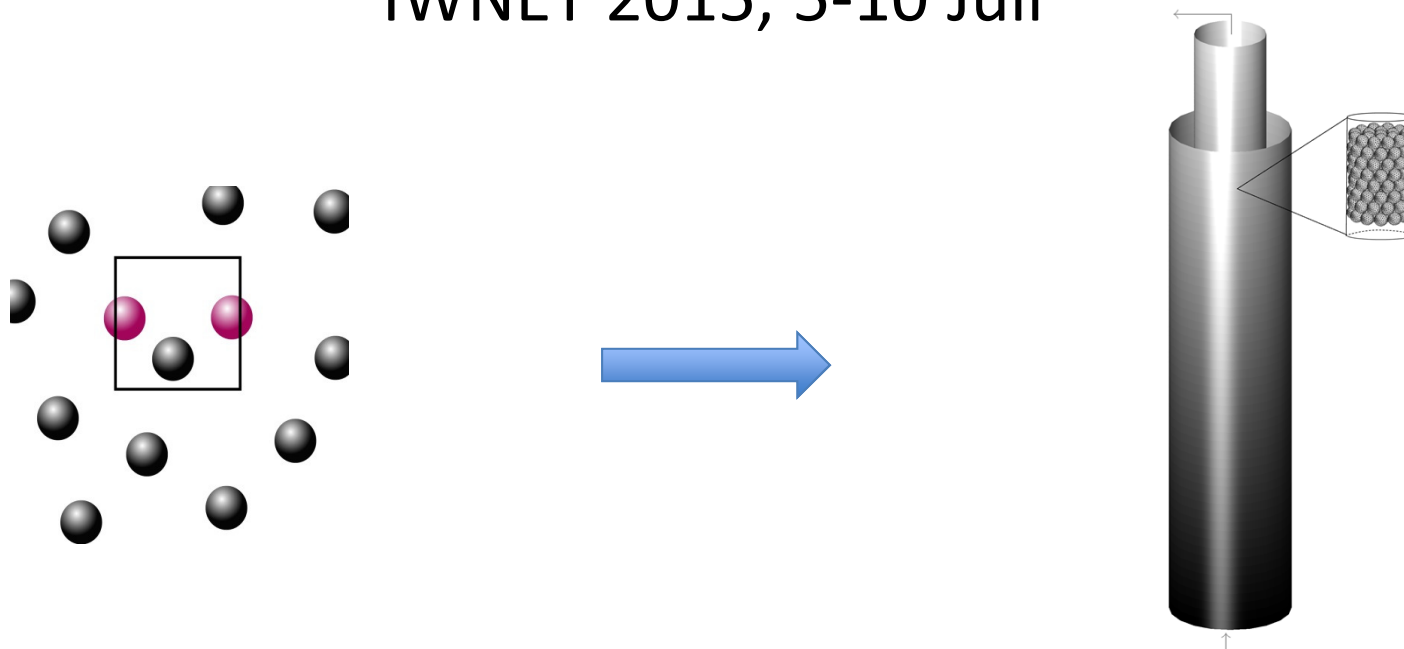


# Small and large system thermodynamics

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IWNET 2015, 5-10 Juli



«From molecule to process»

# The small system team

Thuat Trinh



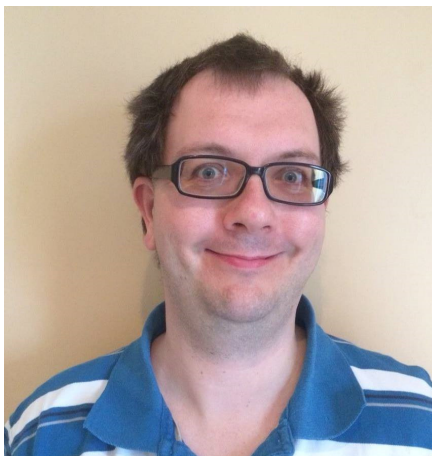
Signe Kjelstrup



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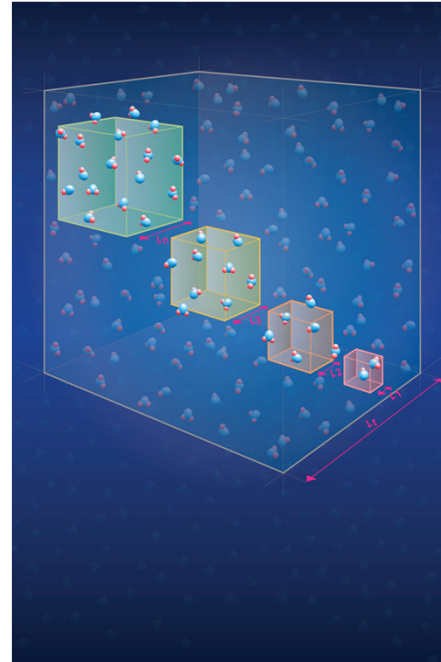


Jean-Marc Simon



# What are the thermodynamic factors?

$$\frac{1}{\Gamma_{jk}(T, V, \mu_l)} \equiv \frac{k_B T}{N_j} \left( \frac{\partial N_k}{\partial \mu_j} \right)_{T, V, \mu_{l \neq j}}$$



Reservoir:  
T, V and  $N_j$  constant

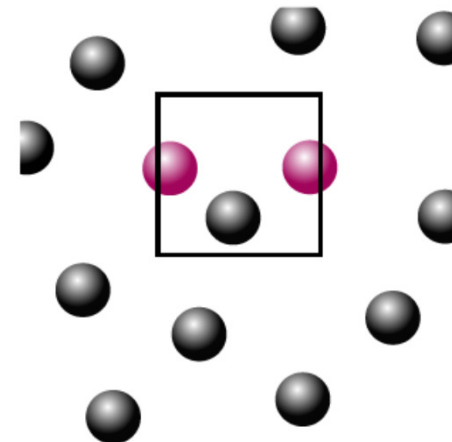
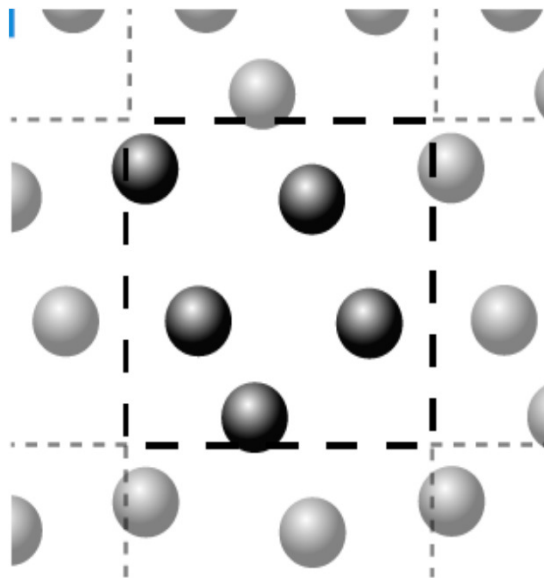
Test volume has  
T, V,  $\mu_j$  constant

For the small volumes: 
$$\frac{1}{\Gamma_{jk}} = \left[ \frac{\langle N_j N_k \rangle - \langle N_j \rangle \langle N_k \rangle}{\langle N_j \rangle} \right]_{T, V, \mu}$$

Can be shown using the grand canonical ensemble

Periodic (large) system (reservoir): Has no surface energy

The test volume (not periodic): Has surface energy

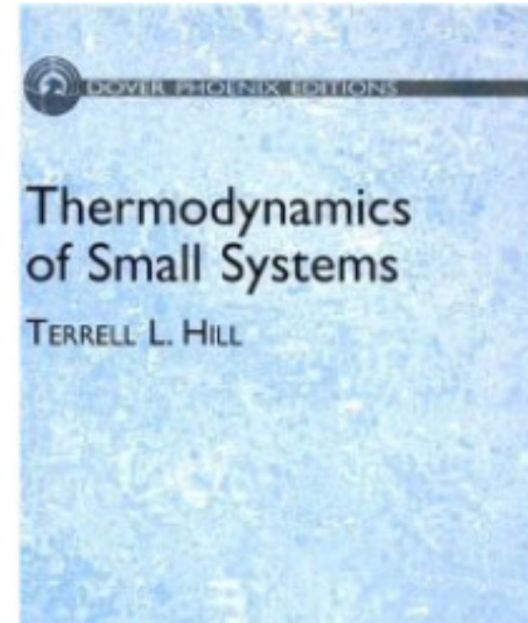


The test volume is according to Hill a «small system»

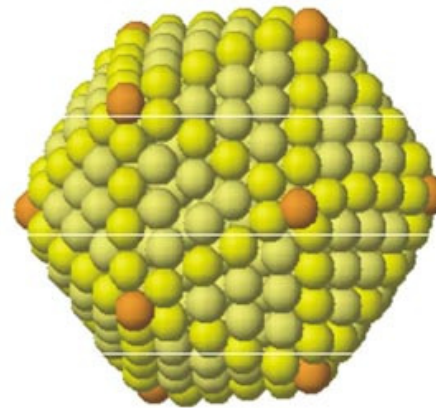
Schnell et al. Mol. Phys. 110, 1069(2011 )

# Small systems in equilibrium

- Do thermodynamic equations apply?
- Is there a link between the nanoscale and macroscale?
- If so, can we make systematic use of it?



1963





# Hill's thermodynamics for small systems

## Use N replicas of the small system

Gibbs relation with  $V$ ,  $T$  and  $N_j$  controlled

$$dU_t^C = TdS_t^C - p^C NdV + \sum_{j=1}^n \mu_j^C NdN_j + X^C dN$$

$X^C dN$ : work to be added to a system of replica, when the number of replicas  $N$  changes

$$X^C = \left( \frac{\partial U_t^C}{\partial N} \right)_{S_t^C, V, N_j}$$

$X^C$  is the replica energy



$$dU_t^C = TdS_t^C - p^C NdV + \sum_{j=1}^n \mu_j^C NdN_j + X^C dN$$

Using extensivity in N gives  $U_t^C = TS_t^C + X^C N$

Define averages by  $U_t^C \equiv \bar{U}^C N$  and  $S_t^C \equiv S^C N$

It follows that  $X^C = \bar{U}^C - TS^C = F^C$

The replica energy is equal to the Helmholtz energy per replica

$C$  is short for canonical

Substituting  $U_t^C \equiv \bar{U}^C N$  and  $S_t^C \equiv S^C N$  in

$$dU_t^C = TdS_t^C - p^C NdV + \sum_{j=1}^n \mu_j^C NdN_j + X^C dN$$

gives  $d\bar{U}^C = TdS^C - p^C dV + \sum_{j=1}^n \mu_j^C dN_j$

Substitution of  $X^C = \bar{U}^C - TS^C = F^C$  gives

$$dF^C = -S^C dT - p^C dV + \sum_{j=1}^n \mu_j^C dN_j$$

It follows that

$$S^C(V, T, N_j) = -\left(\frac{\partial F^C}{\partial T}\right)_{V, N_j}, \quad p^C(V, T, N_j) = -\left(\frac{\partial F^C}{\partial V}\right)_{T, N_j}$$

$$\mu_j^C(V, T, N_l) = \left(\frac{\partial F^C}{\partial N_j}\right)_{V, T, N_{k \neq j}}$$



# Hill's thermodynamics for small systems

## Use N replicas of the small system

Gibbs relation with  $V$ ,  $T$  and  $\mu_j$  controlled

$$dU_t^{GC} = TdS_t^{GC} - p^{GC}NdV + \sum_{j=1}^n \mu_j dN_{j,t}^{GC} + X^{GC} dN$$

The replica energy is now  $X^{GC} = \left( \frac{\partial U_t^{GC}}{\partial N} \right)_{S_t^{GC}, V, N_{j,t}^{GC}} \equiv -\hat{p}(V, T, \mu_j)V$

Extensivity gives  $\bar{U}^{GC} = TS^{GC} + \sum_{j=1}^n \mu_j \bar{N}_j^{GC} - \hat{p}V$

GC is short for grand canonical

Inverse matrix of thermodynamic factors:  $(\Gamma^{-1})_{jk}^{GC}(V, T, \mu_j) \equiv \frac{k_B T}{\bar{N}_j^{GC}} \left( \frac{\partial \bar{N}_j^{GC}}{\partial \mu_k} \right)_{V, T, \mu_{m \neq k}}$

Substituting the averages into

$$dU_t^{GC} = TdS_t^{GC} - p^{GC}NdV + \sum_{j=1}^n \mu_j dN_{j,t}^{GC} + X^{GC}dN$$

$$\text{gives } d\bar{U}^{GC} = TdS^{GC} - p^{GC}dV + \sum_{j=1}^n \mu_j d\bar{N}_j^{GC}$$

Substituting  $\bar{U}^{GC} = TS^{GC} + \sum_{j=1}^n \mu_j \bar{N}_j^{GC} - \hat{p}V$  gives

$$d\hat{p}V = S^{GC}dT + p^{GC}dV + \sum_{j=1}^n \bar{N}_j^{GC}d\mu_j$$

It follows that  $S^{GC}(V, T, \mu_l) = \left( \frac{\partial \hat{p}V}{\partial T} \right)_{V, \mu_l}$ ,  $p^{GC}(V, T, \mu_l) = \left( \frac{\partial \hat{p}V}{\partial V} \right)_{T, \mu_l}$

$$\bar{N}_j^{GC}(V, T, \mu_l) = \left( \frac{\partial \hat{p}V}{\partial \mu_j} \right)_{V, T, \mu_{k \neq j}}$$

Differential and  
integral pressure

# Statistical mechanics of small systems

Hamiltonian for  $N$  particles

$$H(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{j=1}^N \frac{|\mathbf{p}_j|^2}{2m_j} + V(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{p}_1, \dots, \mathbf{p}_N)$$

The canonical partition function is

$$\begin{aligned} Q(V, T, N_j) &= \frac{1}{h^{3N}} \prod_{k=1}^n \frac{1}{N_k!} \int dp_1 \dots dp_N \int_V dr_1 \dots dr_N \exp(-\beta H) \\ &= \prod_{k=1}^n \frac{1}{N_k! \Lambda_k^{3N_k}} \int_V dr_1 \dots dr_N \exp(-\beta V) \end{aligned}$$

where  $\beta \equiv 1/k_B T$  and  $\Lambda_k \equiv h / \sqrt{2\pi m_k k_B T}$

Helmholtz energy per replica  $F^C(V, T, N_j) = -k_B T \ln Q(V, T, N_j)$

The grand canonical partition function is

$$\Xi(V, T, \mu_j) = \sum_{N_1=1}^{\infty} \dots \sum_{N_n=1}^{\infty} \exp[\beta(\mu_1 N_1 + \dots + \mu_n N_n)] Q(V, T, N_j)$$

The integral pressure is

$$\hat{p}(V, T, \mu_j) V = -k_B T \ln \Xi(V, T, \mu_j)$$

Calculation of the partition functions makes it possible to obtain the thermodynamic properties of small systems.

**Exercises:** calculate the canonical and grand canonical partition functions for a multi-component ideal gas in a cubic box, where particles of component  $k$  can be adsorbed at the surface with a binding energy  $E_k^s$ . Calculate the resulting thermodynamic quantities.

## Excercise: controlled variables $V, T, N_j$

The canonical partition function for 1 particle of component  $k$  is

$$Q_{1,k}(V, T) = \frac{V}{\Lambda_k^d} + \frac{O}{\Lambda_k^{d-1}} \exp(\beta E_k^s) = \left( \frac{L}{\Lambda_k} \right)^d + c_d^s \left( \frac{L}{\Lambda_k} \right)^{d-1} \exp(\beta E_k^s)$$

The canonical partition function for the whole system is

$$Q(V, T, N_l) = \prod_{k=1}^n \frac{1}{N_k!} Q_{1,k}^{N_k}(V, T)$$

The Helmholtz energy is

$$\begin{aligned} F^C(V, T, N_1, \dots, N_n) &= -k_B T \ln Q(V, T, N_l) \\ &= -k_B T \sum_{k=1}^n \ln \left( \frac{1}{N_k!} Q_{1,k}^{N_k}(V, T) \right) = \sum_{k=1}^n F_k^C(V, T, N_k) \end{aligned}$$



Using Stirling this gives

$$\begin{aligned} F_k^C(V, T, N_k) &= k_B T \ln(N_k!) - N_k k_B T \ln Q_{1,k}(V, T) \\ &= N_k k_B T \ln\left(\frac{N_k}{e}\right) + \frac{1}{2} k_B T \ln(2\pi N_k) - N_k k_B T \ln Q_{1,k}(V, T) \\ &= N_k k_B T \left[ \ln\left(\frac{\Lambda_k^d N_k}{V e}\right) + \frac{1}{2} \frac{\ln(2\pi N_k)}{N_k} - \ln\left(1 + c_d^s \frac{\Lambda_k}{L} \exp(\beta E_k^s)\right) \right] \\ &\simeq N_k k_B T \left[ \ln\left(\frac{\Lambda_k^d N_k}{V e}\right) + \frac{1}{2} \frac{\ln(2\pi N_k)}{N_k} - c_d^s \frac{\Lambda_k}{L} \exp(\beta E_k^s) \right] \end{aligned}$$

It is clear that for large  $L$  the Helmholtz energy is linear in  $1/L$

Using the Helmholtz energy we can calculate  $p^C$  and  $\mu_k^C$

$$p^C(V, T, N_l) = - \left( \frac{\partial F^C}{\partial V} \right)_{T, N_l} \simeq k_B T \sum_{k=1}^n n_k \left[ 1 - c_d^s \frac{1}{d} \frac{\Lambda_k}{L} \exp(\beta E_k^s) \right]$$

$$\begin{aligned} \mu_j^C(V, T, N_l) = - \left( \frac{\partial F^C}{\partial N_j} \right)_{V, T, N_l} &\simeq k_B T \ln(n_j \Lambda_j^d) + \frac{k_B T}{2N_j} - c_d^s k_B T \frac{\Lambda_j}{L} \exp(\beta E_j^s) \\ &\quad - c_d^s \sum_{k=1}^n n_k \frac{\Lambda_k}{L} \frac{\partial E_k^s}{\partial n_j} \exp(\beta E_k^s) \end{aligned}$$

Similarly we can calculate  $S^C$  and  $\Gamma_{jk}^C$ , were we have given terms to linear order in  $1/L$ . There are higher order contributions in  $1/L$ .

Note that there are contributions containing derivatives of the binding energy to the surface.

## Excercise: controlled variables $V, T, \mu_j$

The grand canonical partition function is

$$\begin{aligned}\Xi(V, T, \mu_1, \dots, \mu_n) &= \prod_{k=1}^n \sum_{N_k=0}^{\infty} \exp(\beta \mu_k N_k) \frac{1}{N_k!} Q_{1,k}^{N_k}(V, T) \\ &= \exp \left[ \sum_{k=1}^n \exp(\beta \mu_k) Q_{1,k}(V, T) \right]\end{aligned}$$

This gives, to linear order in  $1/L$ , for the **integral pressure**

$$\begin{aligned}\hat{p}(V, T, \mu_1, \dots, \mu_n) &= \frac{k_B T}{V} \ln \Xi = \frac{k_B T}{V} \sum_{k=1}^n \exp(\beta \mu_k) Q_{1,k}(V, T) \\ &= k_B T \sum_{k=1}^n \frac{\exp(\beta \mu_k)}{\Lambda_k^d} \left[ 1 + c_d^s \frac{\Lambda_k}{L} \exp(\beta E_k^s) \right]\end{aligned}$$

and for the **differential pressure (they are different!!!)**

$$p^{GC}(V, T, \mu_1, \dots, \mu_n) = \left( \frac{\partial \hat{p} V}{\partial V} \right)_{T, \mu_j} = k_B T \sum_{k=1}^n \frac{\exp(\beta \mu_k)}{\Lambda_k^d} \left[ 1 + c_d^s \frac{d-1}{d} \frac{\Lambda_k}{L} \exp(\beta E_k^s) \right]$$

The derivatives of  $\hat{p}$  give the entropy and the particle number densities.

$$s(V, T, \mu_j) = \frac{S(V, T, \mu_j)}{V} = \left( \frac{\partial \hat{p}(V, T, \mu_j)}{\partial T} \right)_{V, \mu_j}$$

$$\bar{n}_j^{GC}(V, T, \mu_l) = \frac{\bar{N}_j^{GC}(V, T, \mu_l)}{V} = \left( \frac{\partial \hat{p}(V, T, \mu_l)}{\partial \mu_j} \right)_{V, T, \mu_{k \neq j}}$$

The inverse matrix of thermodynamic factors is given by the second derivative of  $\hat{p}$  with respect to  $\mu$ .

The explicit calculation leads to an expansion in  $1/L$ .

End exercises

# Small system method

The probability to be close to the surface differs from that far away

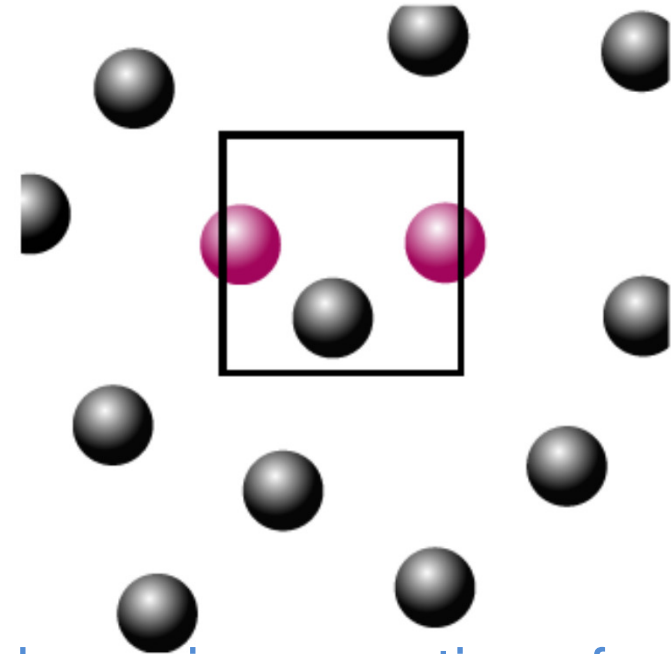


Surface energies:  $E_k^s(T, \mu_j)$

A general feature we find for the thermodynamic properties of small systems in molecular dynamics simulations is ( $V=L^d$ )

$$\alpha = \frac{A}{V} = \alpha_0 + \alpha_1 \left( \frac{\Lambda}{L} \right) + \alpha_2 \left( \frac{\Lambda}{L} \right)^2 + \dots$$

This makes it possible to obtain the thermodynamic limit from simulations of small systems



## In the Small System Method we use this feature

We simulate a system of a few thousand particles. In small sub-volumes with a volume  $V$ , the temperature  $T$  and the chemical potentials  $\mu_j$  are determined by the large box.

For the inverse thermodynamic factors one has:

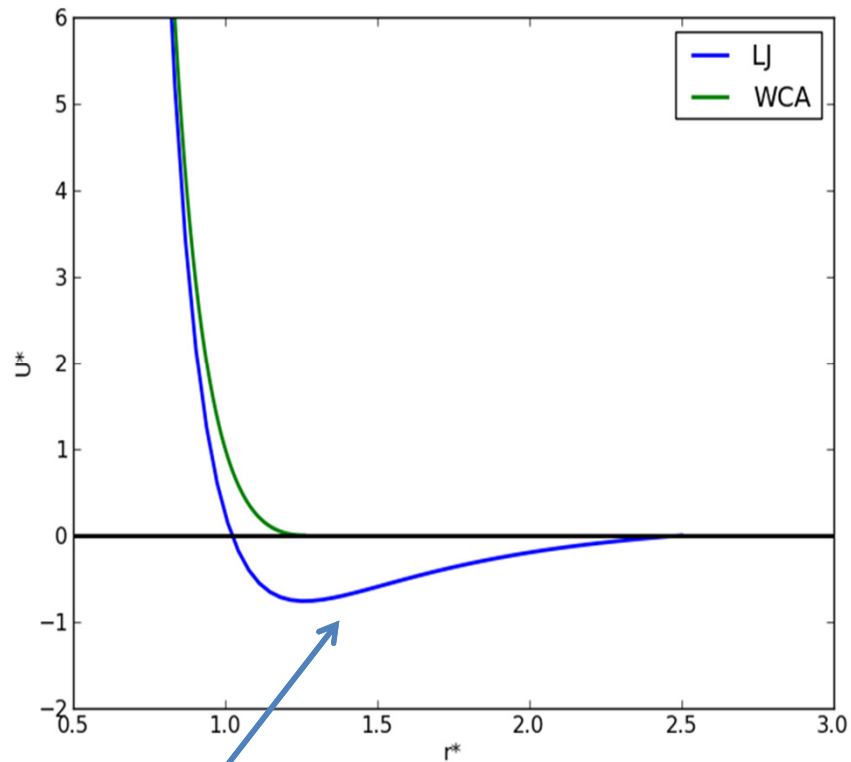
$$\left[ \frac{1}{\Gamma_{jk}} \right]_{T,V,\mu} = \left[ \frac{1}{\Gamma_{jk}} \right]_{T,V,\mu}^{\infty} + C_1 \frac{1}{L} + C_2 \left( \frac{1}{L} \right)^2 \dots$$

This gives the inverse thermodynamic factors in the thermodynamic limit as a function of  $T, V, \mu_j$ .

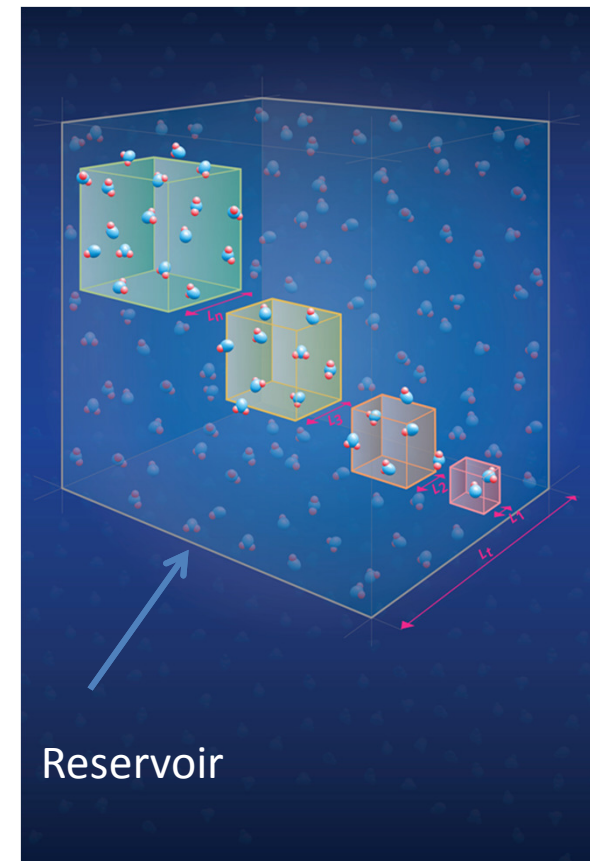
Kirkwood, Buff, JCP19 (1951)774 explain how to obtain the relevant quantities from  $\Gamma_{jk}$  in other ensembles.



# Interaction potential, example

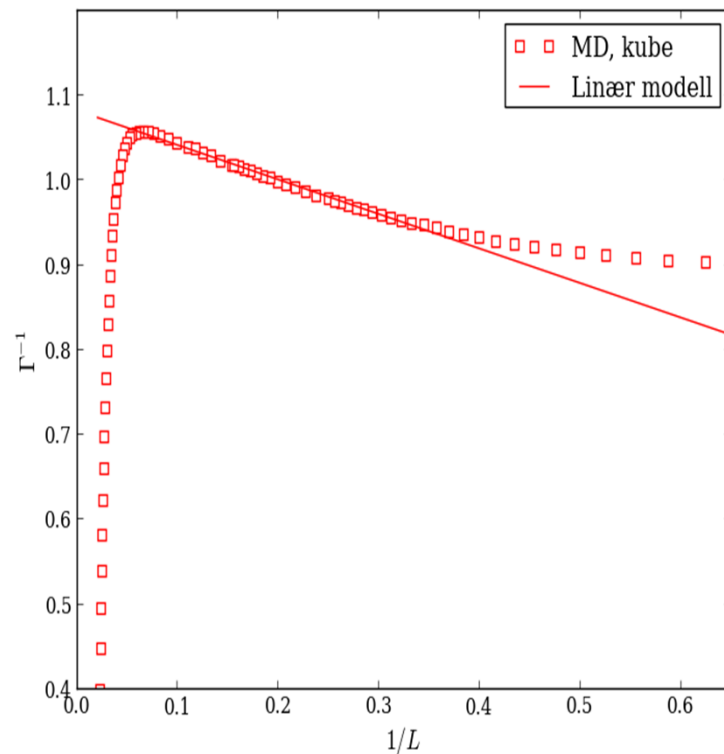


Lennard-Jones pair-potential



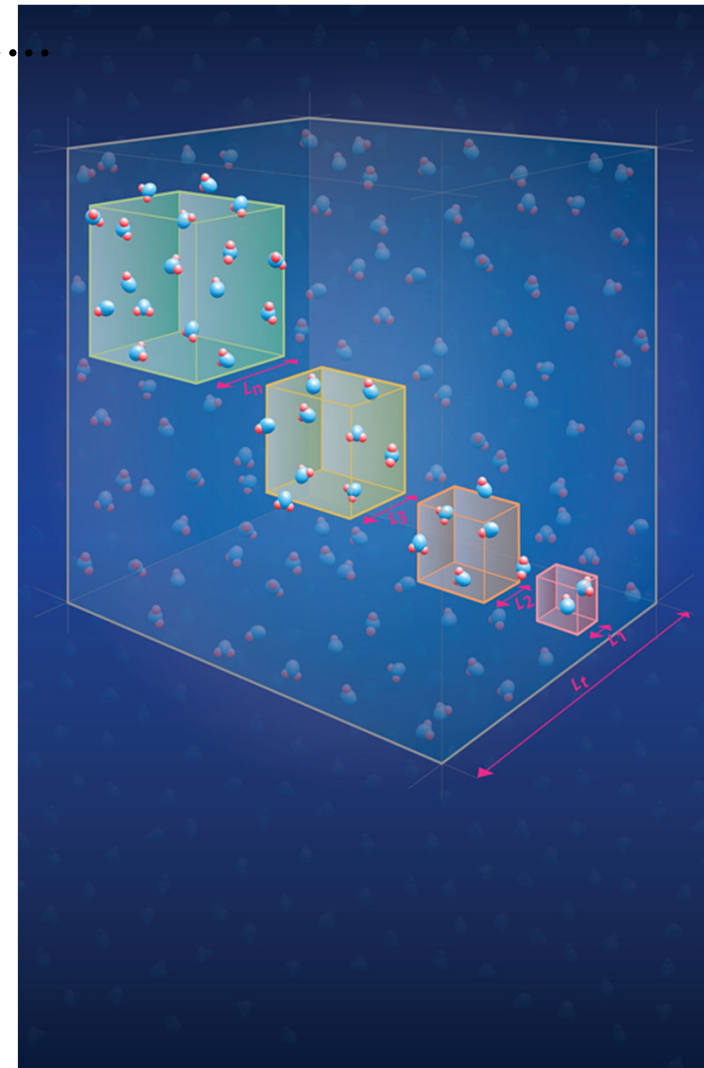
# Testing the formula from statistical mechanics

$$\left[ \frac{1}{\Gamma_{jk}} \right]_{T,V,\mu} = \left[ \frac{1}{\Gamma_{jk}} \right]_{T,V,\mu}^{\infty} + C_1 \frac{1}{L} + C_2 \left( \frac{1}{L} \right)^2 \dots$$

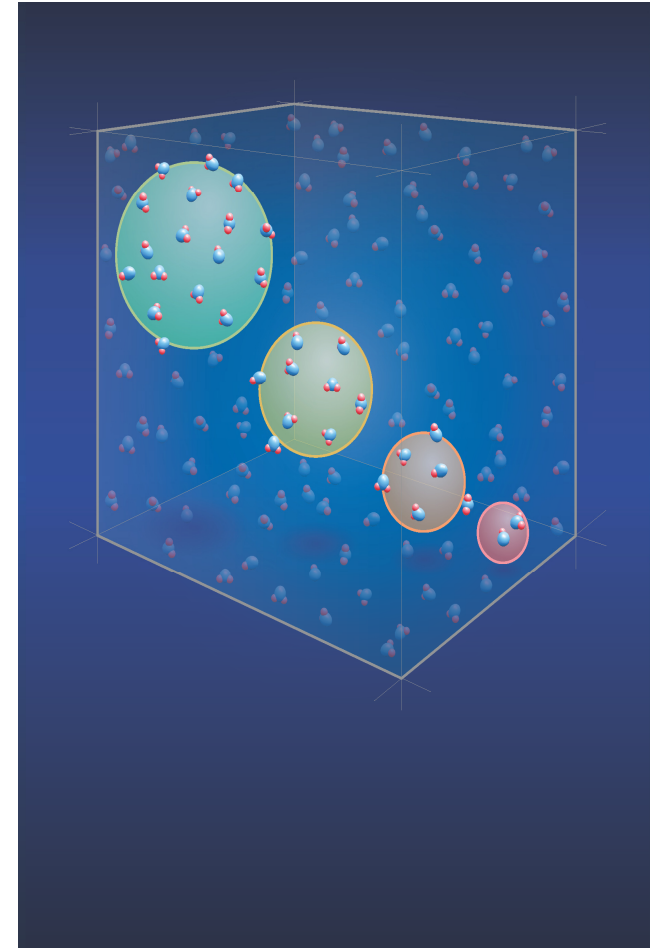
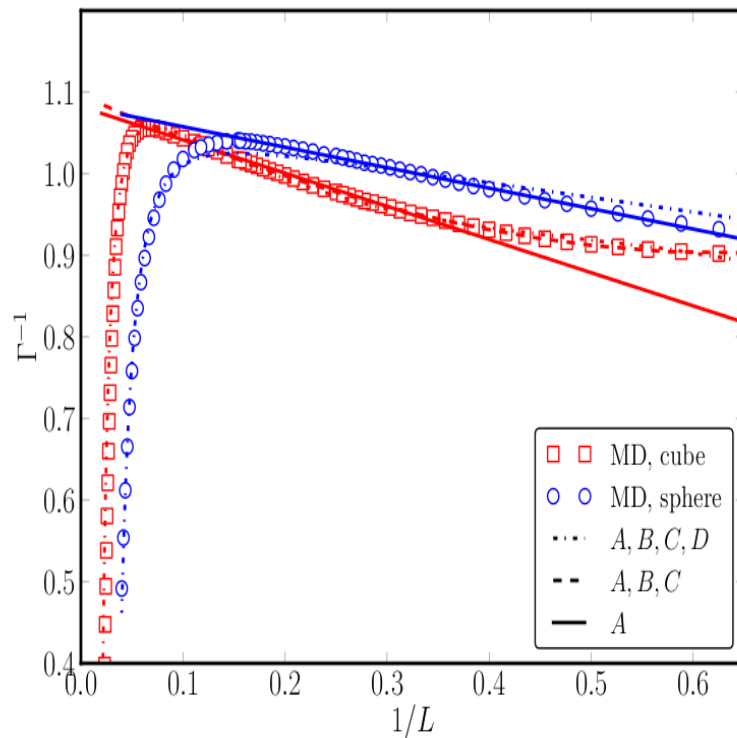


L J-particles,  $T^* = 2.0$ ,  $\rho^* = 0.1$

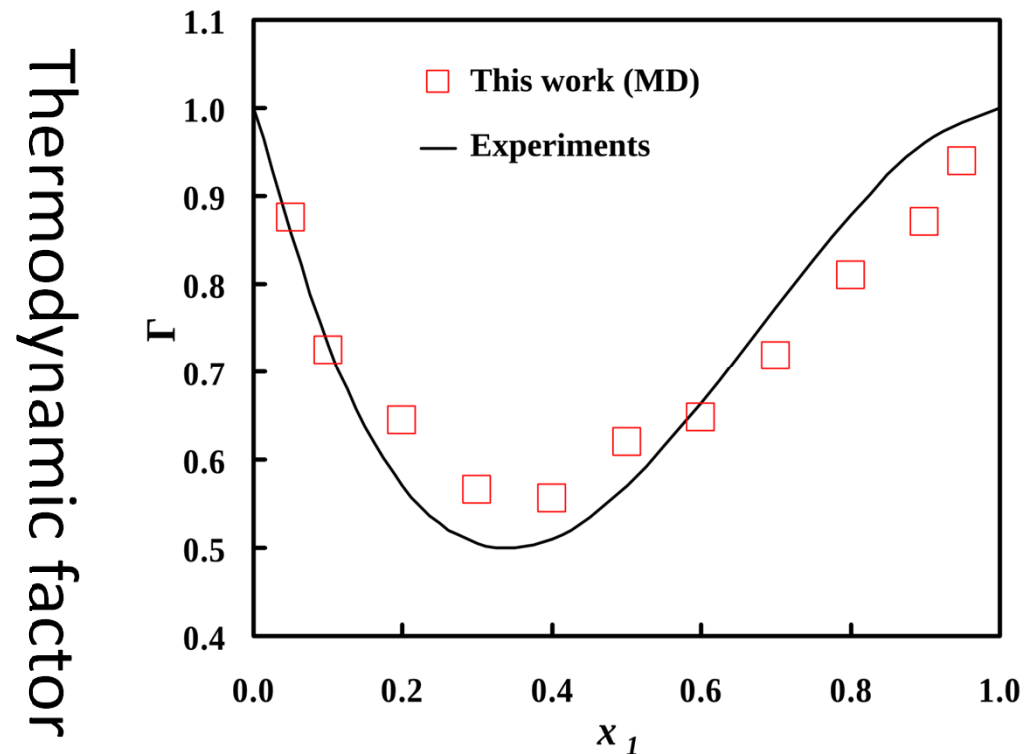
Schnell et al. Mol Phys. 2011, CPLEters, 2011



# Comparing cubic and spherical sub-volumes



Experiments give the Fick diffusion coefficient. MD simulations give the Maxwell-Stefan diffusion coefficients. Their ratio gives the thermodynamic factor:



Molfraction acetone in tetrachloromethane

**Excellent agreement**

Liu et al, J. Phys. Chem B 115, 12921 (2011)

# Small System's Method

## Recipy

1. Choose the reservoir with a given  $\mu, V, T$
2. Choose shape and size of test volume
3. Count fluctuations in  $N$  in the test volume and find the limit value (infinite  $L$ ) by extrapolation

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\infty}} + \frac{A}{L} + \frac{B}{L^2} + \frac{C}{L^3} \dots$$

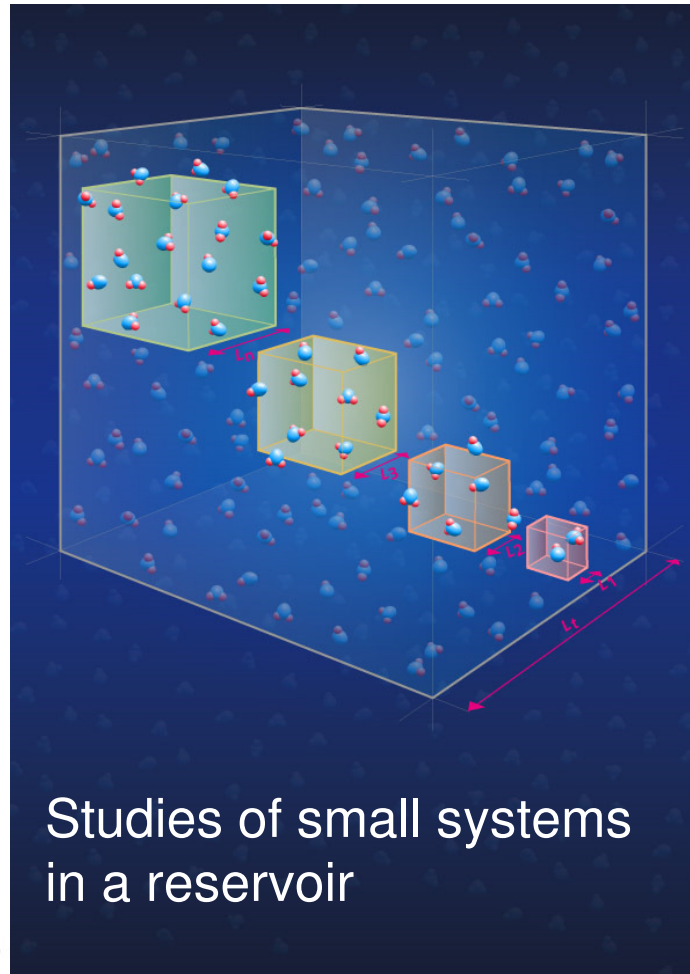
4. Control: The result must not depend on the reservoir size

# Conclusions

- It is possible to describe the properties of small systems using thermodynamics
- The **Small System Method** gives a scaling law for properties on the nanoscale as a function of  $1/L$
- Bulk properties can be found in a rapid manner using linear extrapolation.



# Kirkwood–Buff Integrals for Finite Volumes



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## Kirkwood-Buff integrals of radial distribution functions

$$G_{\alpha\beta}^{\infty} = \int_0^{\infty} (g_{\alpha\beta}(r) - 1) \mathbf{dr}$$

Why are these integrals so important?

Kirkwood and Buff showed that many thermodynamic properties, like the thermodynamic factors, compressibility, activity coefficients, partial molar volumes can be calculated in terms of the KB integrals

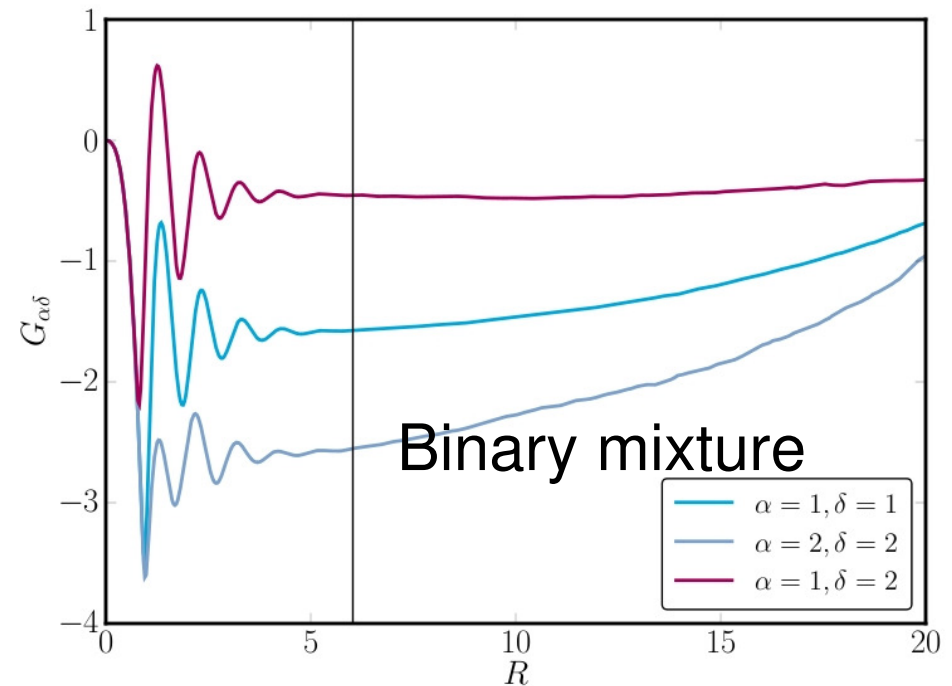
What is difficult in their calculation?

(1) Kirkwood, J. G.; Buff, F. P. *The Statistical Mechanical Theory of Solutions I*. *J. Chem. Phys.* **1951**, *19*, 774–777.

(2) Ben-Naim, A. *Molecular Theory of Solutions*: Oxford University Press: Oxford, U.K., 2005.

## Kirkwood-Buff integrals of radial distribution functions

$$\begin{aligned}
 G_{\alpha\delta} &= V \frac{\langle N_\alpha N_\delta \rangle - \langle N_\alpha \rangle \langle N_\delta \rangle}{\langle N_\alpha \rangle \langle N_\delta \rangle} - \frac{\delta_{\alpha\delta}}{c_\alpha} \\
 &= 4\pi \int_0^\infty [g_{\alpha\delta}^{\mu VT}(r) - 1] r^2 dr \\
 &\approx 4\pi \int_0^R [g_{\alpha\delta}^{NVT}(r) - 1] r^2 dr
 \end{aligned}$$



Convergence problems due to the fact that the pair correlation functions do not properly approach 1 for large  $r$  when  $V$  is finite

# Kirkwood–Buff Integrals for Finite Volumes

$$\begin{aligned}
 G_{\alpha\beta}^V &\equiv \frac{1}{V} \int_V \int_V (g_{\alpha\beta}(r_{12}) - 1) \, d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= V \frac{\langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle \langle N_\beta \rangle}{\langle N_\alpha \rangle \langle N_\beta \rangle} - \frac{\delta_{\alpha\beta}}{c_\alpha} = \left( \frac{1}{\Gamma_{\alpha\beta}^V} - \delta_{\alpha\beta} \right) \frac{V}{\langle N_\beta \rangle}
 \end{aligned}$$

When the volume size  $\gg$  correlation length this reduces to

$$G_{\alpha\beta}^\infty = \int_0^\infty (g_{\alpha\beta}(r) - 1) \, d\mathbf{r}$$

P. Krüger, S.K. Schnell, D. Bedeaux, S. Kjelstrup, T.J.H. Vlugt, J.M. Simon, *J. Phys. Chem. Lett.* **4**, 235 (2013)

Innovation and Creativity

Standard approximation:  $\tilde{G}_{\alpha\beta}^R \equiv \int_0^{2R} 4\pi r^2 (g_{\alpha\beta}(r) - 1) dr$

The **small volume correction** (Peter Krüger, Jean-Marc Simon)

$$\begin{aligned} G_{\alpha\beta}^V &\equiv G_{\alpha\beta}^R = \frac{1}{V} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 [g_{\alpha\beta}(r_{12}) - 1] = \frac{1}{V} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 h_{\alpha\beta}(r_{12}) \\ &= \frac{1}{V} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \int_0^\infty dr \delta(r - r_{12}) h_{\alpha\beta}(r) = \int_0^{2R} dr w(r, R) h_{\alpha\beta}(r) \end{aligned}$$

Where we choose  $V$  to be a **hypersphere with radius  $R$**  and where

$$w(r, R) \equiv \frac{1}{V} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \delta(r - r_{12})$$

# $w(r,x)$ for hyperspheres in 1 to 3 dimensions

$d$	KB	$w$	$w - x(\partial w/\partial x)$
1	1	$1 - x$	1
2	$2\pi r$	$4r(\arccos(x) - x(1 - x^2)^{1/2})$	$4r(\arccos(x) + x(1 - x^2)^{1/2})$
3	$4\pi r^2$	$4\pi r^2(1 - 3x/2 + x^3/2)$	$4\pi r^2(1 - x^3)$

<sup>a</sup> $x = r / (2R)$ .  $w$  and  $-x(\partial w/\partial x)$  are strictly zero for  $x \geq 1$ . The functions that correspond to  $w$  in the usual KB theory (eq 4) are listed under "KB".

P. Krüger, S.K. Schnell, D. Bedeaux, S. Kjelstrup, T.J.H. Vlugt, J.M. Simon,  
J. Phys. Chem. Lett. **4**, 235 (2013)

One may show that:  $G_{\alpha\beta}^R - G_{\alpha\beta}^\infty \sim \frac{A}{V} \sim \frac{1}{R}$

This suggests to Taylor expand in  $1/R$  to get a better approximation.  
This leads to:

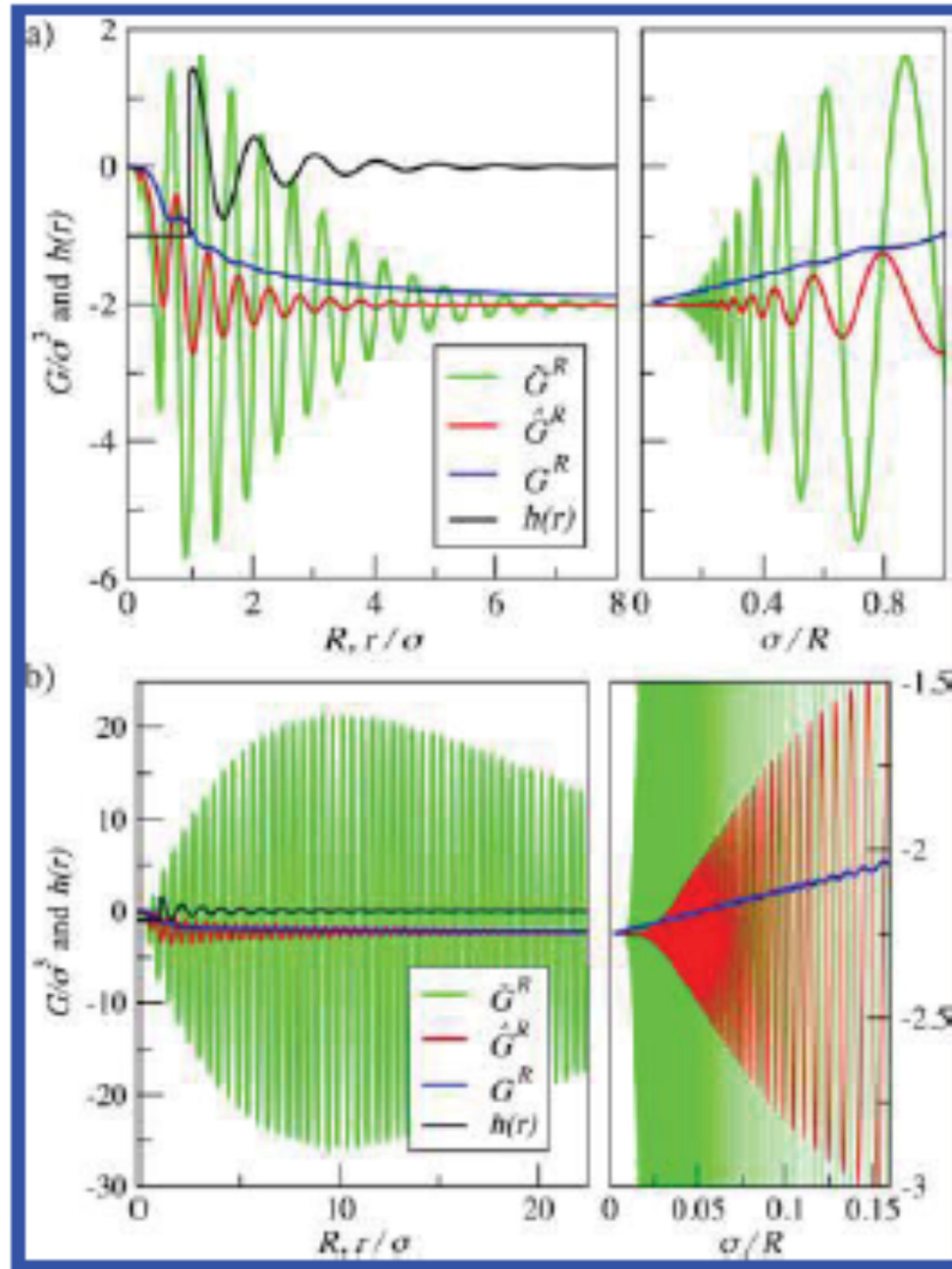
$$\hat{G}_{\alpha\beta}^R \equiv \int_0^{2R} dr \left[ w(r, x) - x \frac{\partial w(r, x)}{\partial x} \right] h_{\alpha\beta}(r_{12})$$

Using as trial correlation function:

$$h(r) = \begin{cases} \frac{3/2}{r/\sigma} \exp\left(\frac{1-r/\sigma}{\chi}\right) \cos\left[2\pi\left(\frac{r}{\sigma} - \frac{21}{20}\right)\right], & r/\sigma \geq \frac{19}{20} \\ -1, & r < \frac{19}{20}\sigma \end{cases}$$

we compare:  $\tilde{G}_{\alpha\beta}^R$ ,  $G_{\alpha\beta}^R$  and  $\hat{G}_{\alpha\beta}^R$  for  $\chi=2$  and  $\chi=20$





The **green** curve gives  $\tilde{G}_{\alpha\beta}^R$  which has huge oscillations and converges very slowly

The **red** curve gives  $\hat{G}_{\alpha\beta}^R$  which has much smaller oscillations and converges rapidly

The **blue** curve gives  $G_{\alpha\beta}^R$  which has very small oscillations and with a  $1/R$  extrapolation which gives the correct value

The black curve gives  $h(r)$



# Conclusion

$$G_{\alpha\beta}^R$$

gives an efficient way to calculate Kirkwood-Buff integrals using the  $1/R$  extrapolation

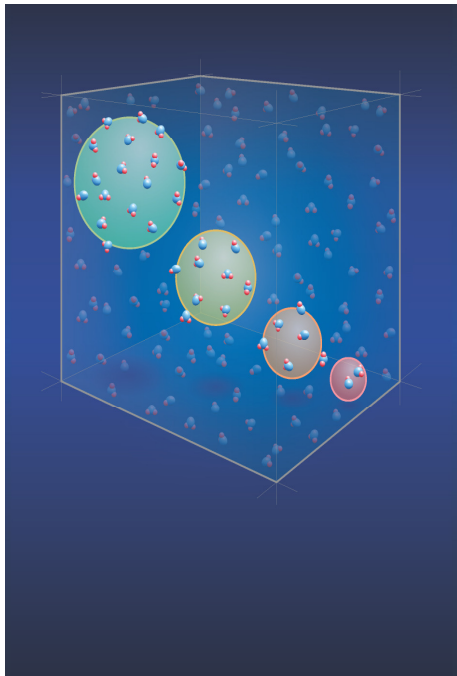
# Chemical reactions

**Dissociation of hydrogen  $\text{H}_2 \leftrightarrow 2\text{H}$**

# Chemical reactions

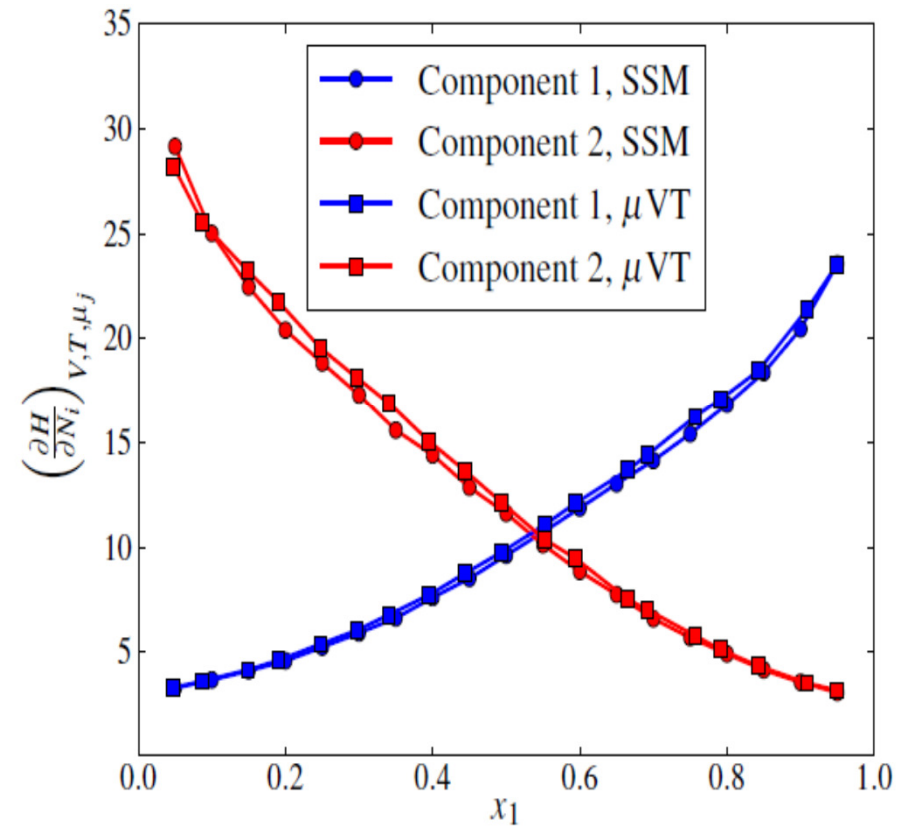
**Partial molar enthalpies, constant  $T, V, \mu_j$**

$$H_i(L) = \left( \frac{\partial H}{\partial N_i} \right)_{T, V, \mu_j} = \left[ \frac{\langle UN_i \rangle - \langle U \rangle \langle N_i \rangle + k_B T \langle N_i \rangle}{\langle N_i^2 \rangle - \langle N_j \rangle^2} \right]_{T, V, \mu_i}$$



$$\frac{1}{H_i} = \frac{1}{H_i^\infty} \left[ 1 + \frac{A}{L} + \dots \right]_{T, V, \mu_j}$$

# Partial molar enthalpies, constant $T$ , $V$ and $\mu$

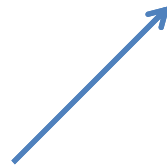


Results from SSM (circles) and direct Monte Carlo simulations (squares)

**Aim:**

**Partial molar enthalpy at constant  $T$ ,  $p$  and  $N_j$ :**

$$\left[ H_i^\infty \right]_{T,V,\mu_j} \Rightarrow \left[ H_i^\infty \right]_{T,p,N_j}$$



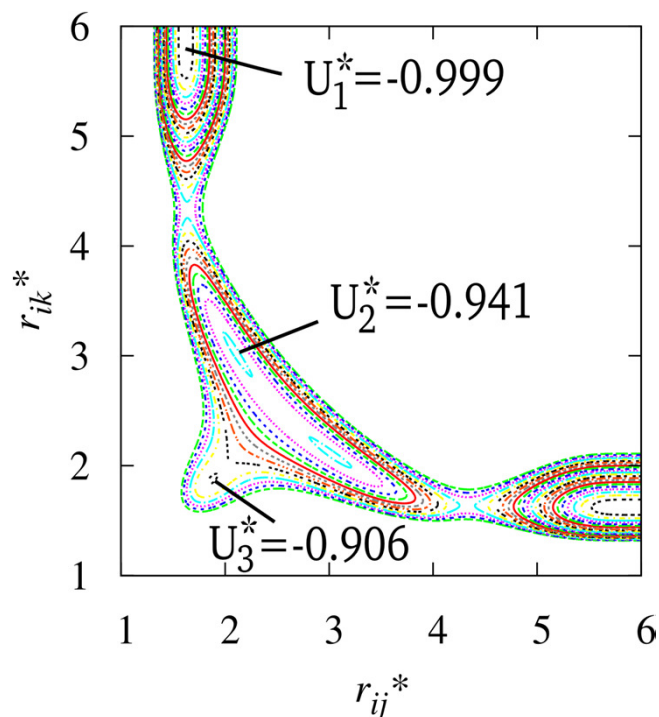
Legendre transform

Schnell, Skorpa, Bedeaux, Kjelstrup, Vlugt, Simon, JCP, **141**, 144501 (2014)

# Dissociation of hydrogen $\text{H}_2 \leftrightarrow 2\text{H}$

Density 156 K: 0.0011 / 0.0191 g (cm)<sup>-3</sup>

$$U(r_1, r_2, \dots, r_N) = \sum_{i < j} u_{(2)}(r_{ij}) + \sum_{i < j < k} u_{(3)}(r_i, r_j, r_k)$$

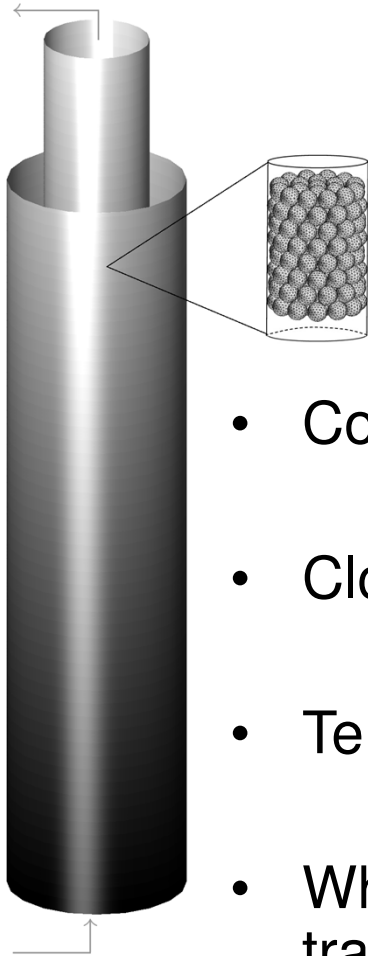


## Energy surface of $U$ for H-H...H

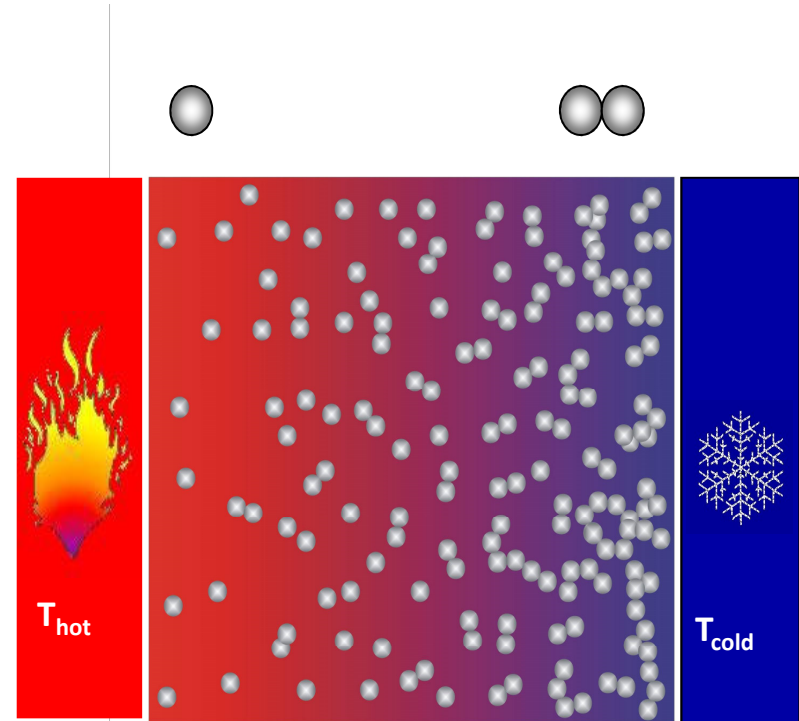
- F.H. Stillinger and T.A. Weber, JPC, 1988
- Diedrich and Anderson, Science 1992, JPC 1994
- D. Kohen, J.C. Tully, F.H. Stillinger, Surface Science, 1998

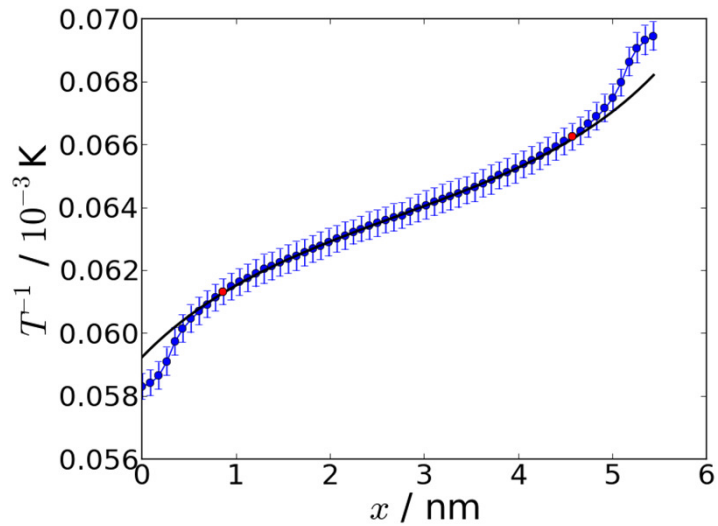
Skorpa, Simon, Bedeaux, Kjelstrup, PCCP, 2014, 16, 19681 and 16, 1227

# Away from equilibrium



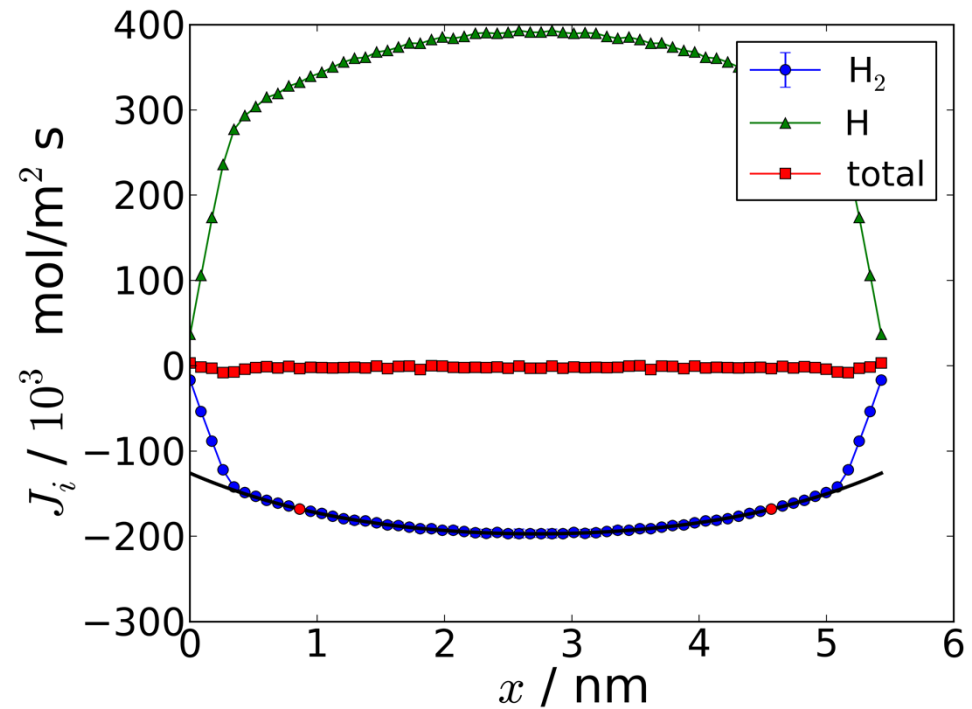
- Constant pressure
- Closed system
- Temperature gradient
- What are the transport properties?





Transport of H og H<sub>2</sub>  
due to a temperature  
gradient!

$$J_{\text{H}} = -2J_{\text{H}_2}$$





# Laws of transport

- Heat transport

$$J'_q = - \left[ \lambda_{J_{H_2}=0} \right] \frac{dT}{dx} + q^* J_{H_2}$$

Heat of transfer

- Mass transport

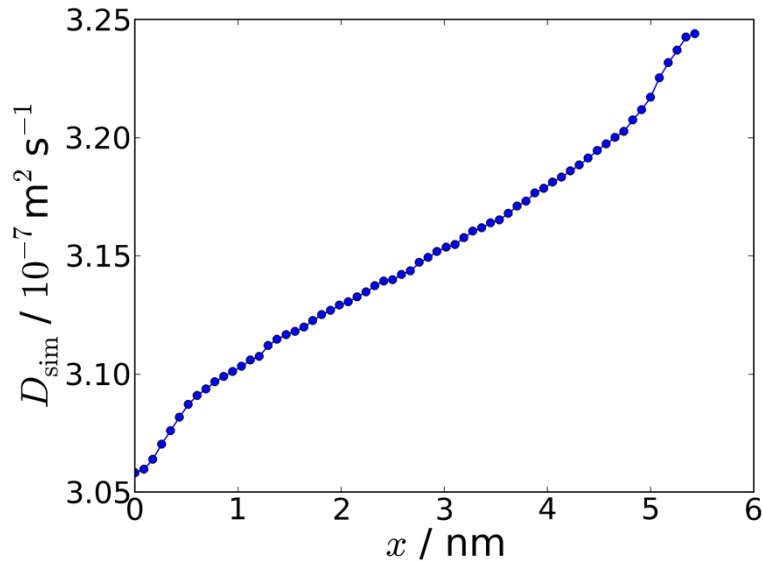
$$J_{H_2} = -\Gamma^{-1} \frac{q^* D}{T} \frac{dT}{dx} - D \frac{d}{dx} c_{H_2}$$

Diffusion constant

Bird, Stewart , Lightfoot, *Transport Phenomena*, 2nd. Ed. 2007:

«The Dufour energy flux  $q$  is quite complex of nature and usually of minor importance»

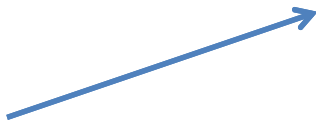
# Diffusion in a reacting mixture



Kinetic gas theory  
 $D \approx 10^{-6} \text{ m}^2 / \text{s}$

	H <sub>2</sub>	F <sub>2</sub>
Penetration depth	10 Å	4 Å
Mean free path	12 Å	3-6 Å

# Heat conduction and heat of transfer

$$J'_q = -[\lambda_{J=0}] \frac{dT}{dx} + q^* J_{H_2}$$


$\lambda_{J=0}$ W/K	$\lambda_{\Delta G/T=\text{konstant}}$ W/K	$q^*$ kJ/mol	$\Delta_r H$ kJ/mol
1.5	4.4	-3000	424



Compare Bird, Stewart, Lightfoot, *Transport Phenomena*, 2nd. Ed. 2007!

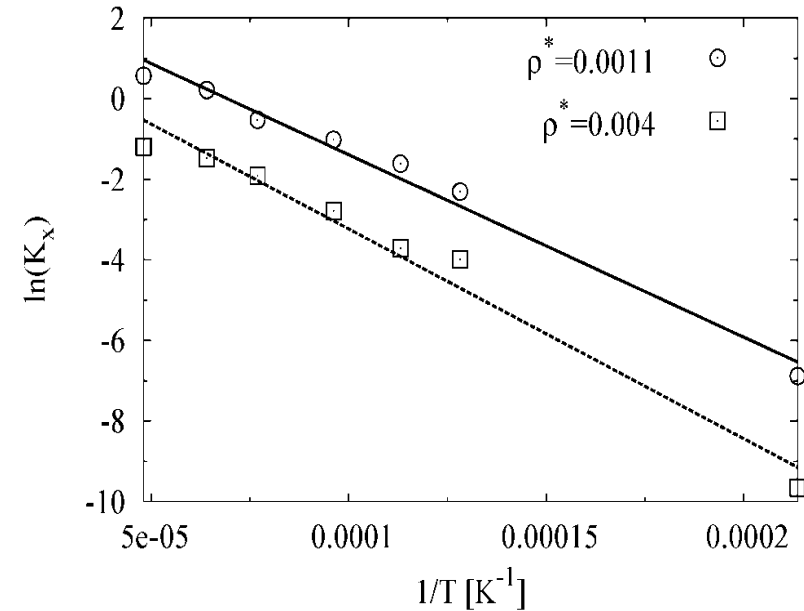
# Conclusions

- It is possible to describe the properties of small systems using thermodynamics
- The Small System Method gives a scaling law for properties from the nano to the macroscopic scale
- A bulk property can thus be found in a rapid manner.
- Non-equilibrium thermodynamics can be used to define the laws of transport. The mechanism can be understood from simulations.

# Dissociation of hydrogen $\text{H}_2 \leftrightarrow 2\text{H}$

Mol fractions  $\rightarrow K_x \rightarrow$  reaction enthalpy

$T^*$	$x_H$	$K_x$
0.15	0.405	0.28
0.20	0.647	1.18
0.25	0.730	1.97
0.30	0.939	4.09
0.40	0.964	5.50



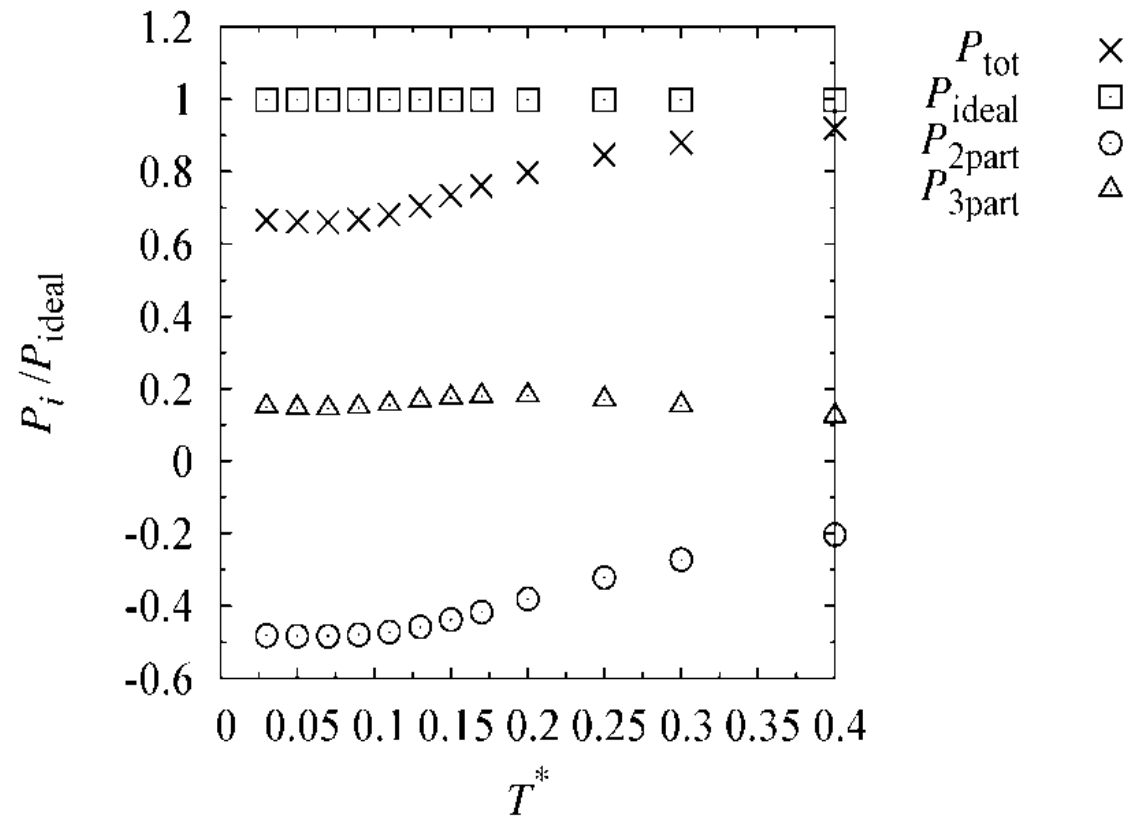
$$K_x = \frac{x_H^2}{x_{\text{H}_2}}$$

$$\Delta H = 430 \text{ kJ mol}^{-1}$$

Ideal mixture

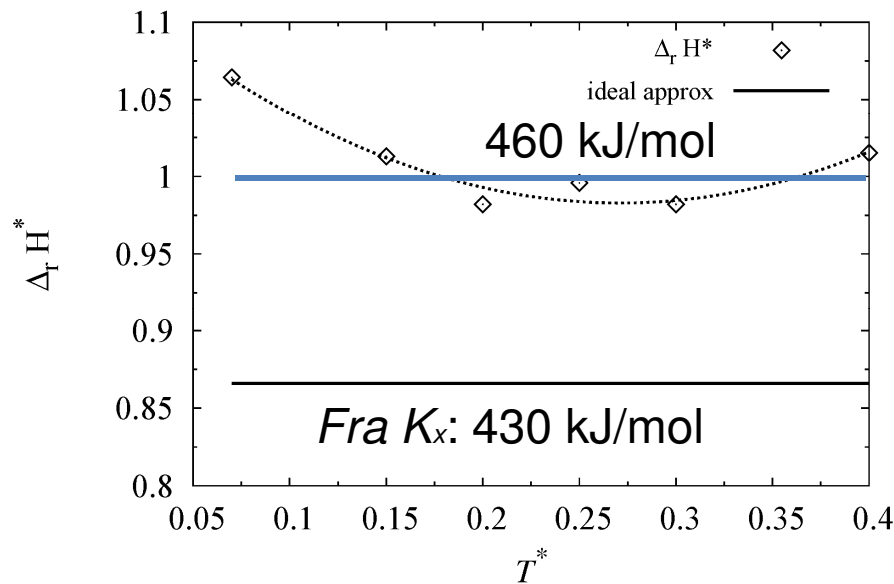
Skorpa et al. PCCP, 2014

# But the mixture is not ideal!



# Equilibrium constant from reaction enthalpy

$$\int_{K_{th}=K_x}^{K_{th}(T)} d \ln K_{th} = \int_{T_x}^T \frac{\Delta H}{R} d\left(\frac{1}{T}\right)$$



Density: 0.0003

$$K_{th} = K_x \frac{p}{p^0} \frac{\gamma_{H_2}^2}{\gamma_{H_2}}$$

$$\Delta_r H = \sum_{prod} \nu_i H_i - \sum_{react} \nu_i H_i$$

# Thermodynamic equilibrium constant

Average reaction enthalpy:

460 kJ/mol

Temperature dependent reaction enthalpy

$$\Delta_r H (\rho^*=0.0003)=0.0003T^2-8.9T+4.9 \times 10^5$$

$T^*$	$K_{th}$	$(\gamma_H)^2 / \gamma_{H_2}$
0.15	700	1.2
0.20	4 300	1.0
0.25	12 300	1.3
0.30	25 100	1.0
0.40	60 900	1.3

$T^*$	$K_{th}$	$(\gamma_H)^2 / \gamma_{H_2}$
0.15	600	1.0
0.20	3 200	0.8
0.25	8 000	0.9
0.30	16 600	0.7
0.40	37 900	0.8



**SSM gives very good accuracy. Only one simulation**



# Implementing the code LAMMPS Molecular Dynamics Simulator

<http://lammps.sandia.gov/index.html>

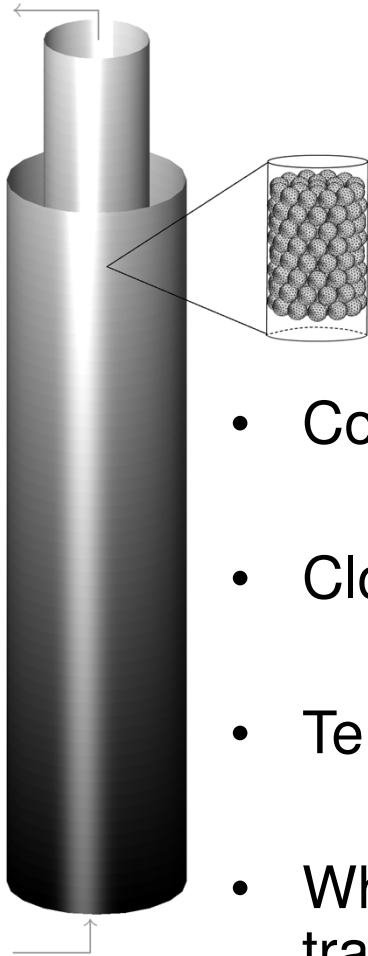
## Results NOTUR

- **Stand alone code:**

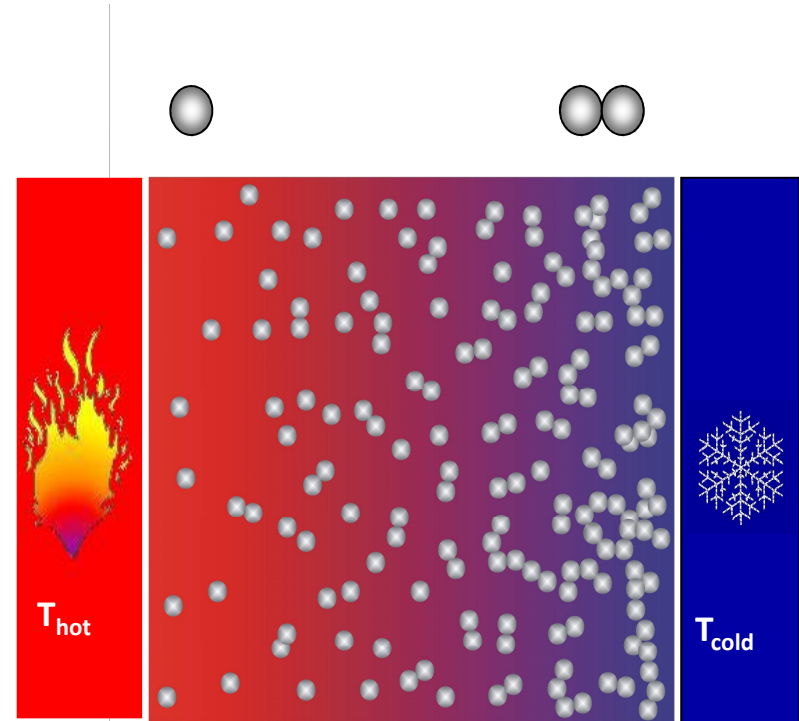
- Python: 10 hours /16 kernels
- C++: 5 minutes / single kernel
- C++/OMP: **4 minutes /16 kernels**
- Time profile: 95% for reading, 5% for computing

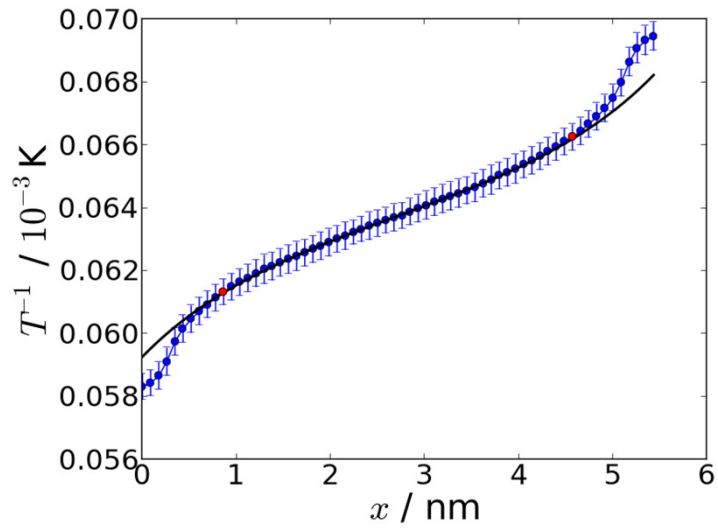
Trinh, Nagel, Holvik, Kjelstrup, in prep.

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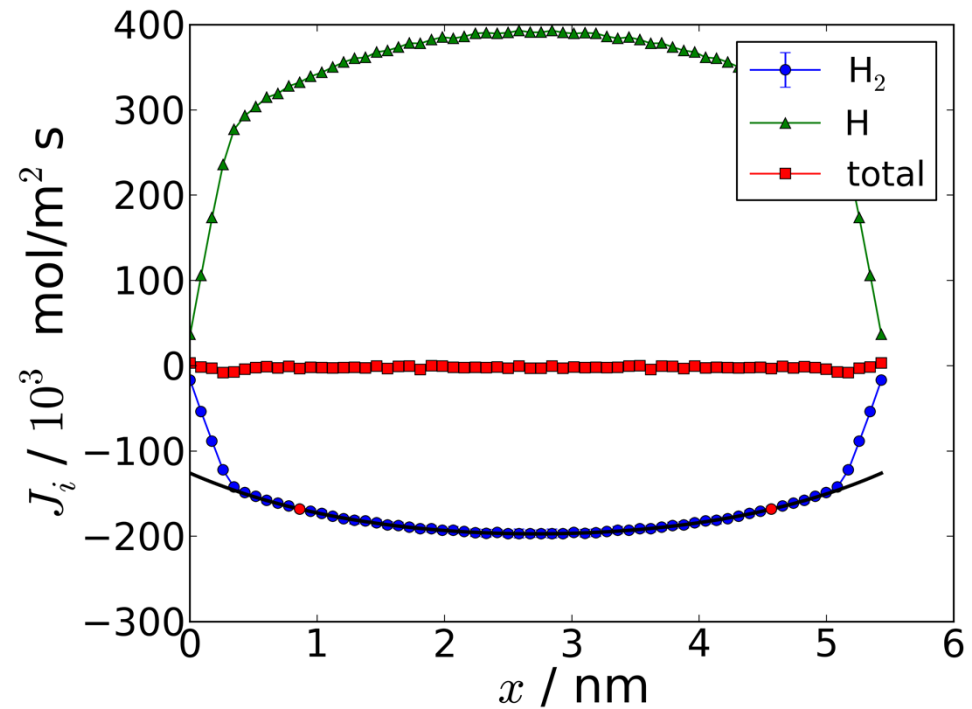
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Transport of H og H<sub>2</sub> due to a temperature gradient!

$$J_{\text{H}} = -2J_{\text{H}_2}$$



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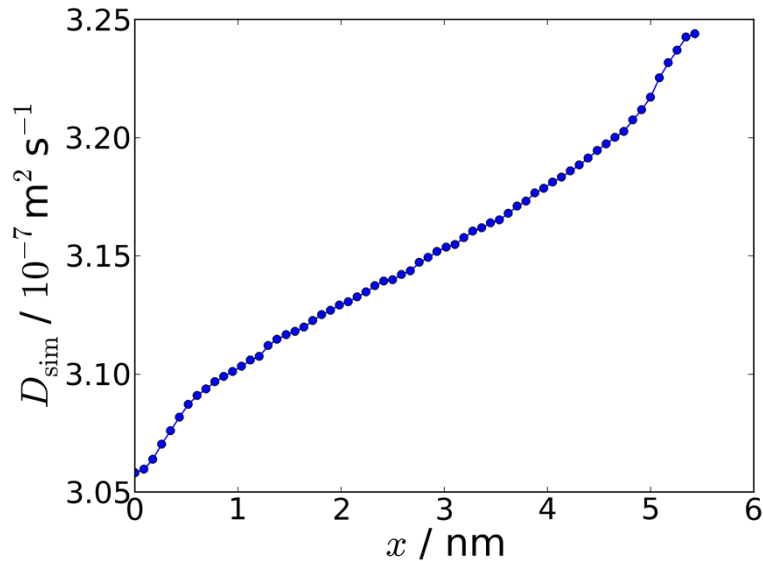
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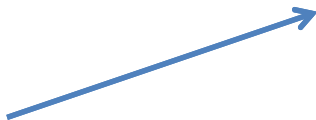
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# Conclusions

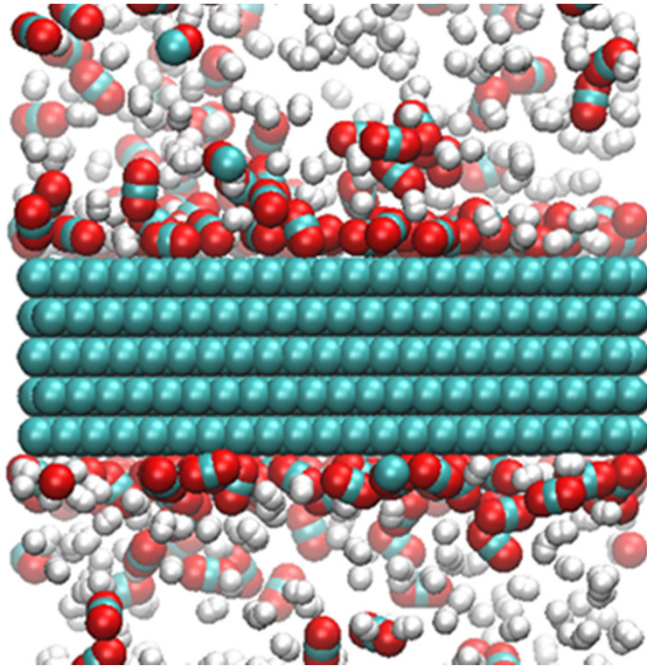
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# **CO<sub>2</sub> adsorption on graphite**



# CO<sub>2</sub> adsorption on graphite

CO<sub>2</sub> : Rigid rotor TraPPE force field



Interaction potential

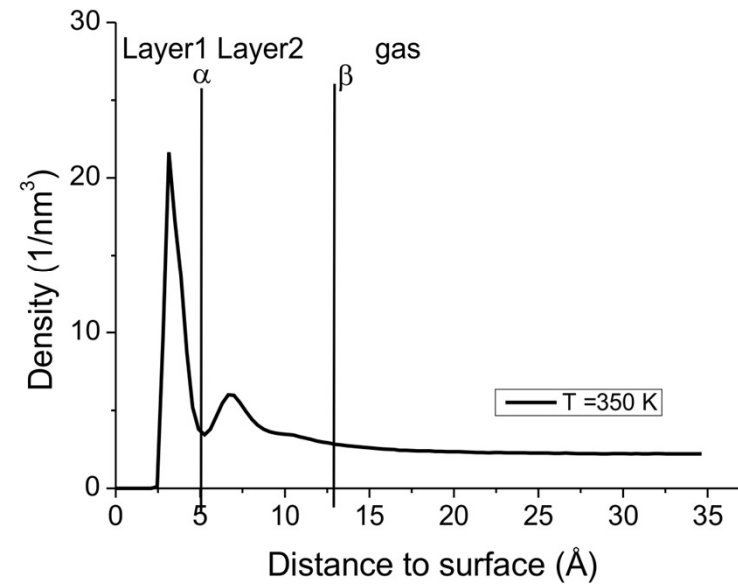
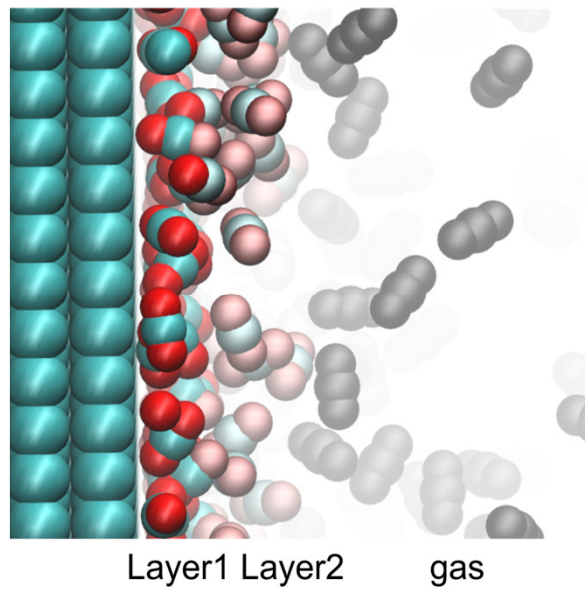
$$V(\text{CO}_2 - \text{CO}_2) = V^{LJ} + V^{\text{Columbic}}$$

$$V(\text{C} - \text{CO}_2) = V^{LJ}$$

**Table 1. LJ potential parameters used in simulation**

Atom	$\sigma$ (Å)	$\epsilon/k_B$ (K)	charge (e)
C (in CO <sub>2</sub> )	2.80	27	0.7
O (in CO <sub>2</sub> )	3.05	79	-0.35
C (graphite)	3.34	26	0

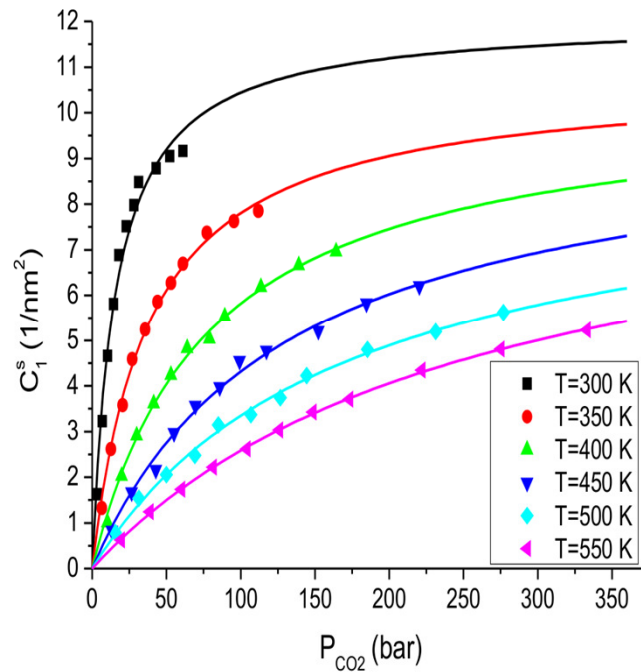
## Equilibrium adsorbate – gas



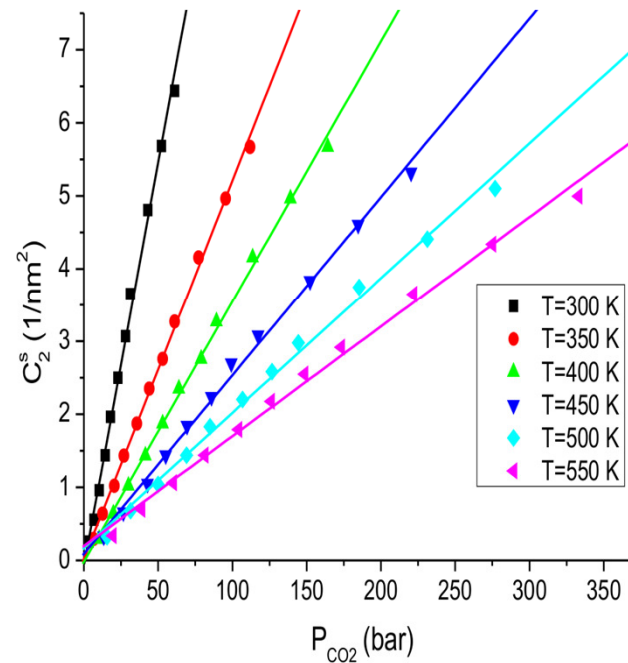
**Two surface layers!**

# Adsorption isotherms for layer 1 and 2

Fully covered surface at 350 K: 12.5 molekul/(nm)<sup>2</sup>



Langmuir- isotherm for layer 1.

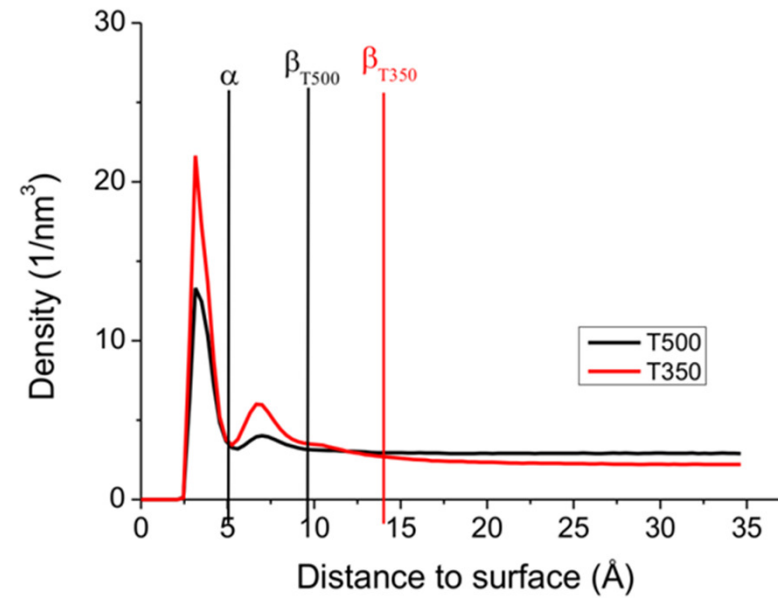
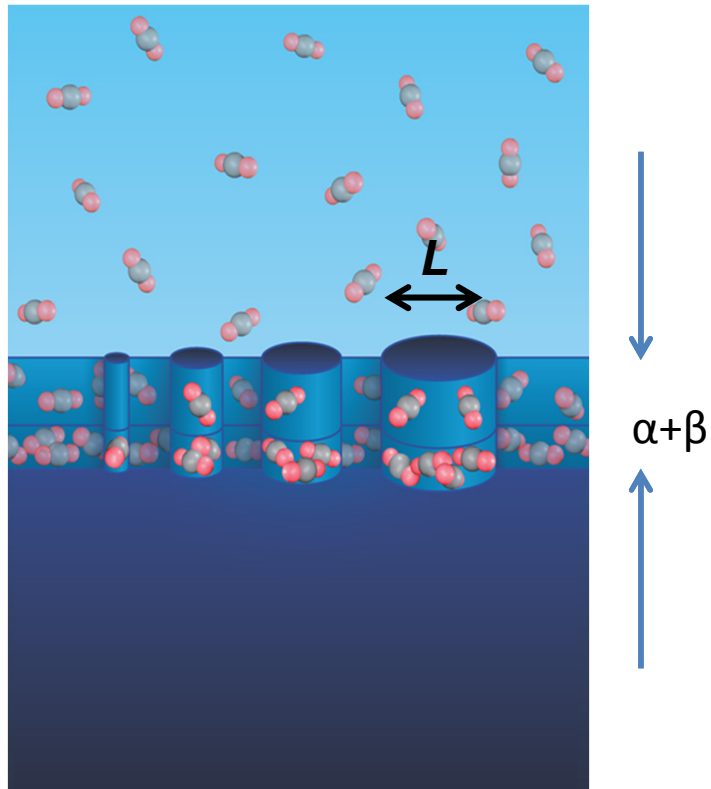


Henry's law applies to layer 2

**Choose Henry's law standard state!**

# CO<sub>2</sub> adsorption on graphite

## cylindrical test volume

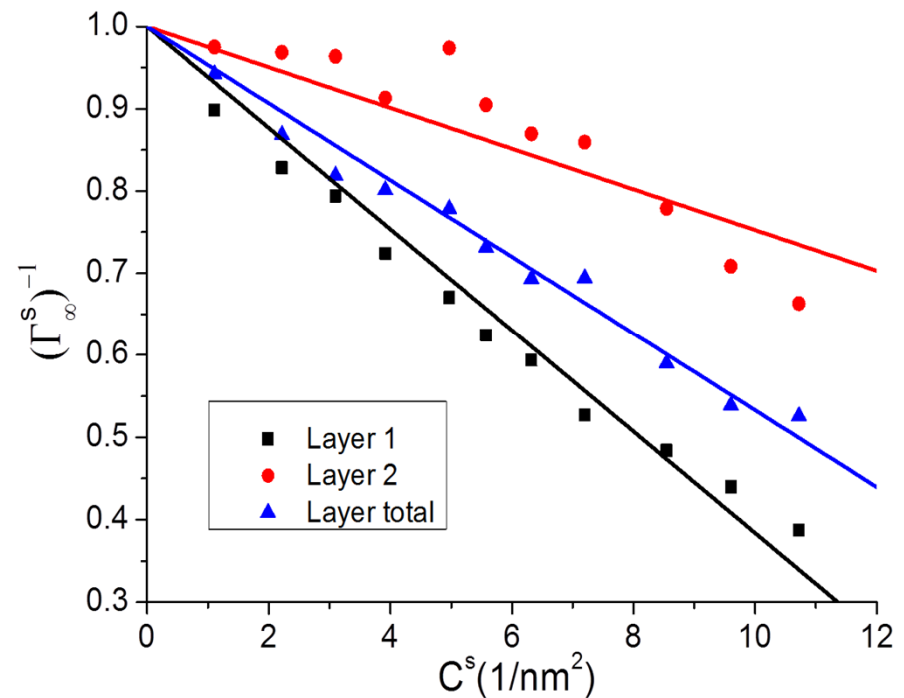
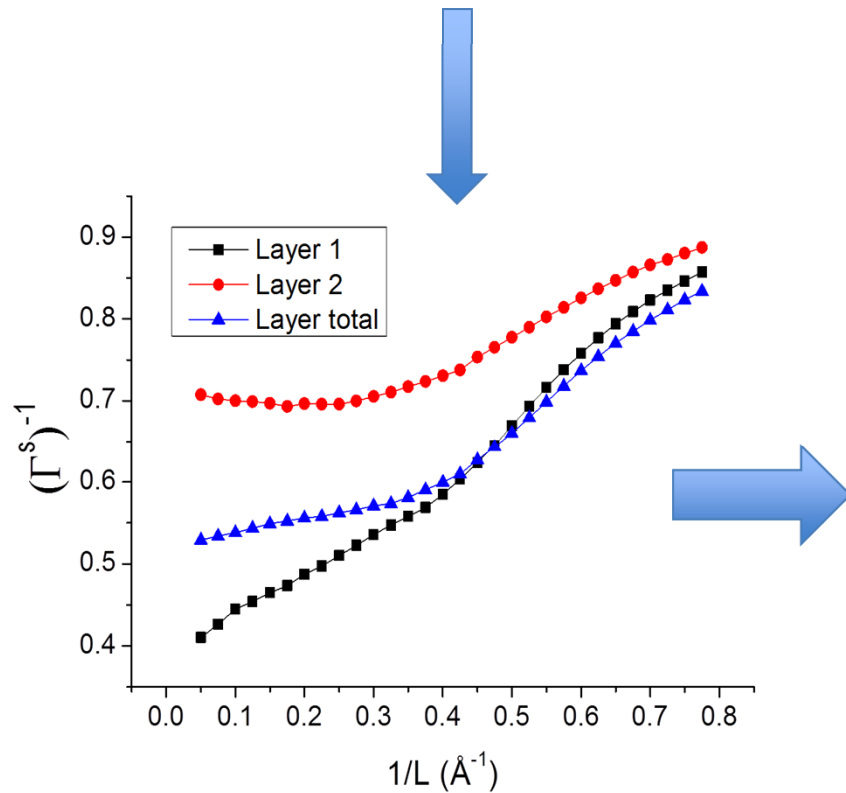
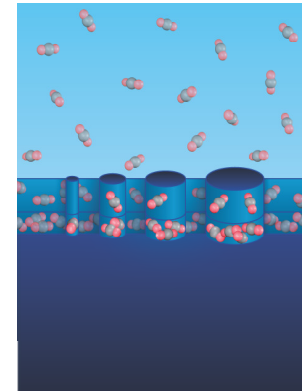


Reservoir:  
168 Å x 216 Å x 336 Å

$$\frac{1}{\Gamma^s} = \frac{1}{\Gamma_\infty^s} \left[ 1 + \frac{B}{L} \right]$$

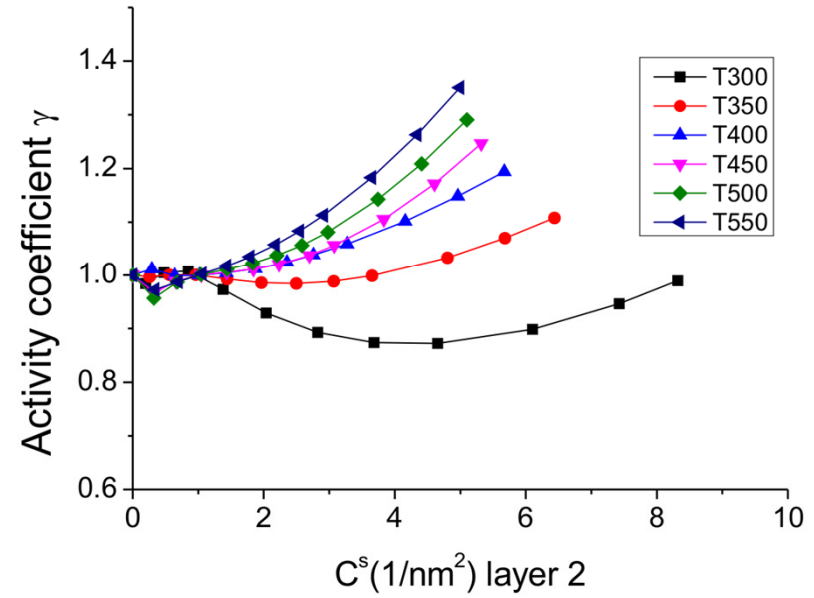
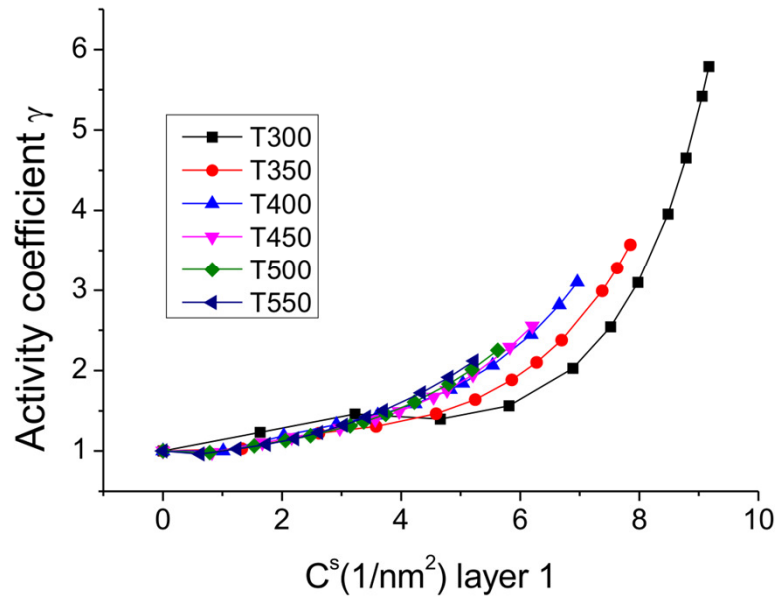
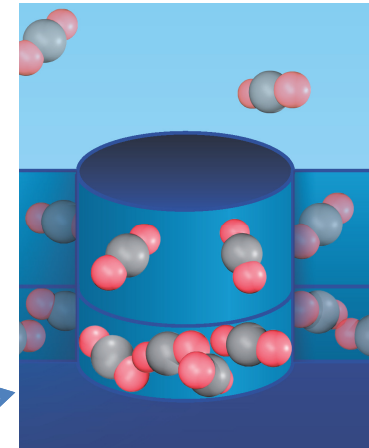
# Thermodynamic factor, CO<sub>2</sub> on graphite

$$\frac{1}{\Gamma^s} = \frac{1}{\Gamma_\infty^s} \left[ 1 + \frac{B}{L} \right]$$

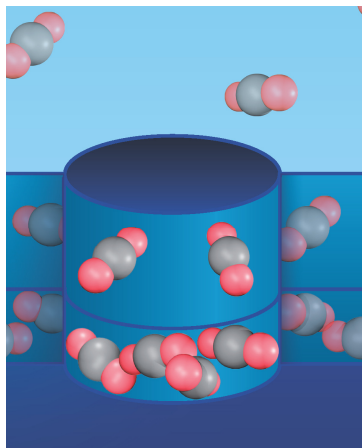


# Activity coefficients for CO<sub>2</sub> in layers 1 and 2

$$\gamma_i^s = 1 + aC_i^s + b(C_i^s)^2$$



## CO<sub>2</sub> adsorption on graphite



Standard chemical potential, enthalpy and entropy for layers 1 og 2

298 K	Total layer	Layer 1	Layer 2		CO <sub>2</sub> gas
$\mu^0$ kJ/mol	-47 $\pm 1$	-47 $\pm 1$	-42 $\pm 1$		-54.11
$S^0$ J/K mol	157 $\pm 3$	145 $\pm 3$	155 $\pm 3$		213.78
$H^0$ kJ/mol	0 $\pm 1$	-4 $\pm 1$	3 $\pm 1$		9.36

$$S_i^0 = - \left[ \frac{\partial \mu_i^0}{\partial T} \right]_p$$

$$H_i^0 = \mu_i^0 + TS_i^0$$

$$\Delta_{ads} H = -10 \pm 1 \text{ kJ / mol}$$

Trinh et al , PCCP, 2014

# Conclusions

- It is possible to describe the properties of small systems using thermodynamics by introducing the reversible work related to change in system size
- The Small System Method gives a scaling law for properties on the micro and macroscopic scales
- A bulk property can thus be found in a rapid manner.
- Non-equilibrium thermodynamics can be used to define the laws of transport. The mechanism can be understood from simulations.