Simulations de systèmes bi-phasiques hors équilibre

Holger Maier*, Manfred J. Hampe
Fachgebiet Thermische Verfahrenstechnik
Technische Universität Darmstadt

Philippe A. Bopp
Department of Chemistry
Université Bordeaux 1
Philippe.Bopp@u-bordeaux1.fr

* PhD thesis, TU Darmstadt
now at Wacker Chemie, Burghausen / Cleveland TN

References

NEMD Simulation of the Thermocapillary Effect
Holger A. Maier
Dissertation
Fachbereich Maschinenbau
Technische Universität Darmstadt, 2011

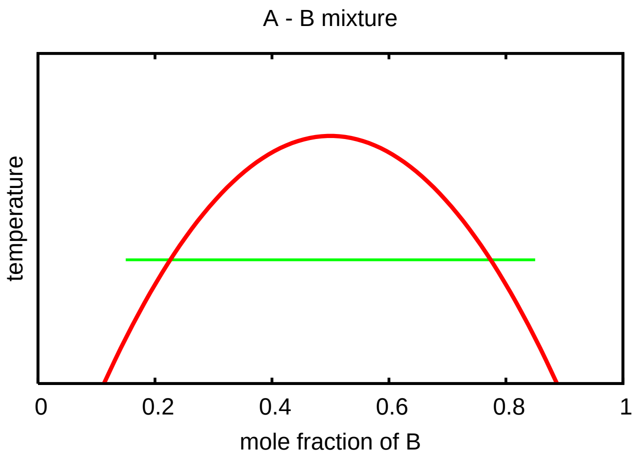
Non-Equilibrium Molecular Dynamics Simulation of the Thermocapillary Effect
H. A. Maier, Ph. A. Bopp, and M. J. Hampe
Can.J.Chem.Eng. 90, 833 (2012)

MD Simulations of the Soret Effect in Simple Partially Miscible Binary Biphasic Mixtures
H. A. Maier, M. J. Hampe, and Ph. A. Bopp
Chem.Phys.Let. 518, 55-60 (2011)

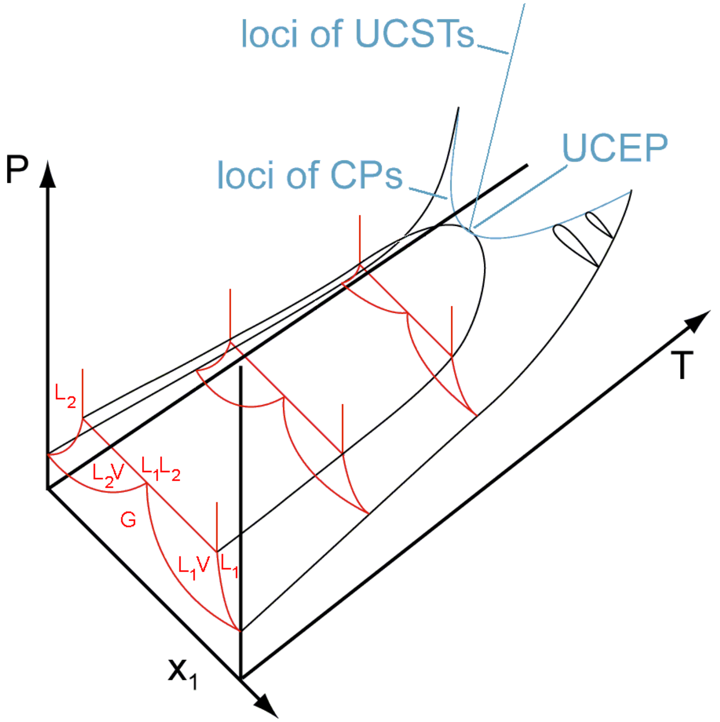
Scope and Limits of Molecular Simulations
Ph. A. Bopp, J. B. Buhn, H. A. Maier, and M. J. Hampe
Chem. Eng. Commun. 195 (11) 1437-1464 (2008)

Starting point of the investigation

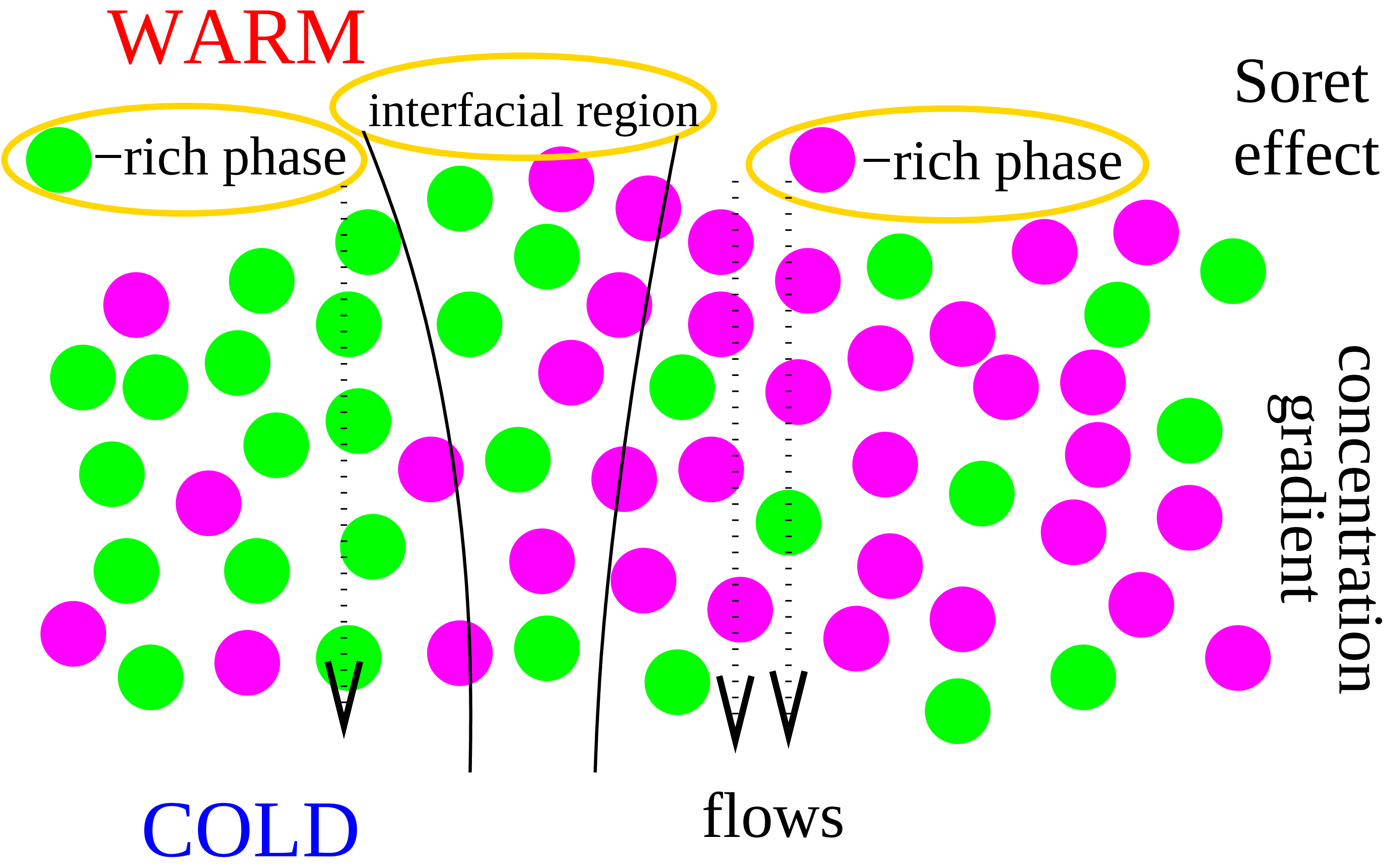
If an interface is subjected to a gradient, e.g. of temperature, motions will arise. They are believed to be an important factor in the mass transport across such interfaces, e.g. in liquid-liquid extraction in chemical engineering.



'Simple' phase diagram
for an A-B mixture



CP : Critical Points
UCST : Upper Critical Solution Temperature
UCEP : Upper Critical End Point



WARM

🟢−rich phase

interfacial region

🟣−rich phase

Soret effect

concentration gradient

flows

COLD

Marangoni Convection

- – Any variation in temperature or composition results in local variations of surface tension .... and thus induces convective motion.
  This effect is called the Marangoni convection.
- – ... temperature induced convection called thermocapillary convection
- – In terrestrial environments, Marangoni convection is usually overshadowed by buoyancy-driven flows,
  in reduced gravity ... (it) could become very important.
- – ... Marangoni effects may be an important factor ... in thin fluid layers.
- – Marangoni flows arise in applications like coating, electronic cooling, welding, wafer drying ......

from Denis Melnikov:
"Development of numerical codes for the study of Marangoni convection"
Thesis, Université Libre de Bruxelles, 2004

Aim of this work

To study the Marangoni convections **not in terms of macroscopic variables** (surface tension, viscosity, ...)
but in terms of **microscopic** ones (i.e. intermolecular interactions)

Tool: **M**olecular **D**ynamics (**MD**) computer simulations
- a type of **molecular simulations**
which allows to study structural and dynamical properties
in and out of equilibrium

The Essentials of MD Simulations

- Input: Interatomic and/or intermolecular **interactions**

Molecular Dynamics (MD) (numerical) Simulation

- Output: A sample of the classical **trajectory** of an ensemble of N ($=$ 1,000 - 100,000) such atoms or molecules in a periodic arrangement under **proper external conditions** (e.g. pressure, temperature, temperature gradient, ...)
  (Depending on the conditions (equilibrium, non-equilibrium, ...), this could be a sample of the micro-canonical, canonical, ... ensemble, or more complicated things)

- Analyze the trajectory by means of statistical mechanics
  → e.g. internal energy ΔU, (self-)diffusion D_{s}, viscosity η,
  X-ray or neutron scattering functions $S(Q)$, $S(Q,\omega)$, ...

Interactions: Spherical particles, Argon-like (*i.e. extremely simplified*)

Lennard-Jones (*for computational ease*)

$$U_{ij}(r_{ij}) = 4\epsilon_{ij} \cdot \left((\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6} \right)$$

for the A-A, B-B, and A-B interactions.

In most cases

$$U_{\mathrm{A-A}} = U_{\mathrm{B-B}} \neq U_{\mathrm{A-B}}$$

to make the system symmetric, $U_{\mathrm{A-B}}$ controls the miscibility.

(*Rule of thumb:*
$U_{\mathrm{A-B}}$ *strong, deep compared to* $U_{\mathrm{A-A}}$ *and* $U_{\mathrm{B-B}}$ $\rightarrow$ *very miscible*
$U_{\mathrm{A-B}}$ *weak, shallow compared to* $U_{\mathrm{A-A}}$ *and* $U_{\mathrm{B-B}}$ $\rightarrow$ *little or not miscible*)

Masses: $m_{\mathrm{A}} = m_{\mathrm{B}} = m_{\mathrm{Ar}} = 40$ amu (which simplifies the dynamics)

Not so '**extremely simplified**'

– Shape (multi-center LJ, Buckingham, ...)

– Longs range interactions (electrostatic ....)

– Deformation of molecules (flexible models)

– Polarizability

– .....

– Different masses, moments of inertia (→ flexible models!)

How 'important' all this is will also depend on the thermodynamic state to be studied

These difficulties are e.g. illustrated by the fact that there are probably well over 100 'water models' (i.e. inter- (and intra-) molecular potentials and geometries for H_2O) in the literature:
(e.g. TIPS, TIP3P, TIP4P, TIP..., SPC, SPC/E, CF1, CF2, BJH, MCY, ST2 ....)

- Equilibrium MD (EMD) (usual)
- Non-Equilibrium MD (NEMD):

Non-stationary
Stationary

Non-stationary: Perturb the system at some time t_0 and watch relaxation (usually many times, and take averages)

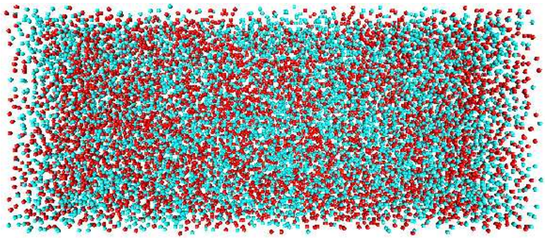
Stationary: Perturb the system continuously (e.g. heat and cool) so that its global state is independent of time:

$$\frac{\partial}{\partial t} = 0$$

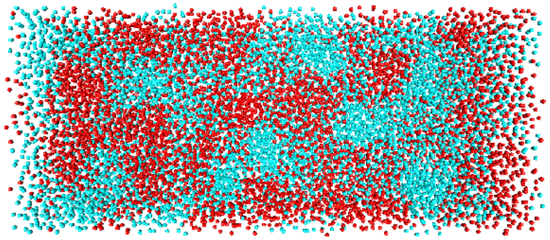
We will use here stationary non-equilibrium MD simulations

First: An MD Demixing 'Experiment'

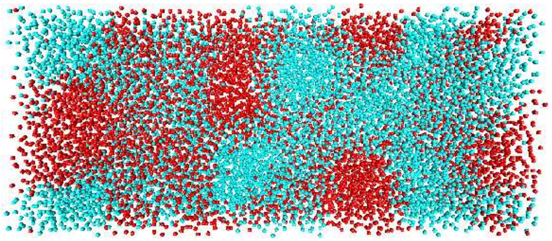
$t = 0$ ns



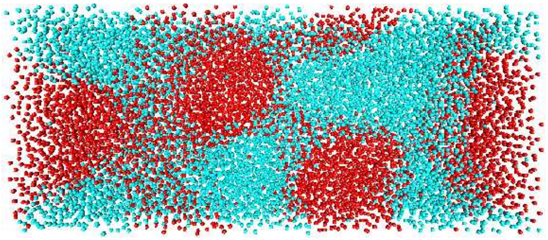
$t = 0.16$ ns



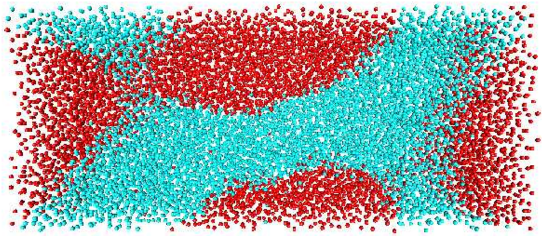
$t = 0.36$ ns



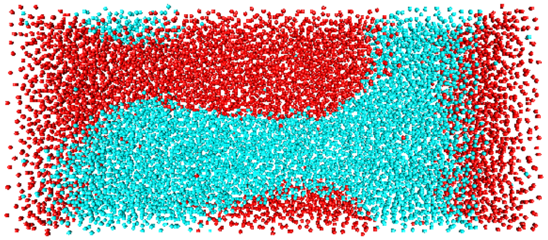
$t = 0.6$ ns



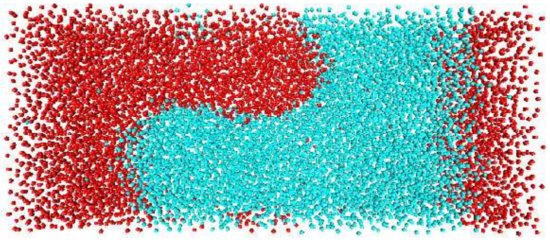
$t = 1.0$ ns



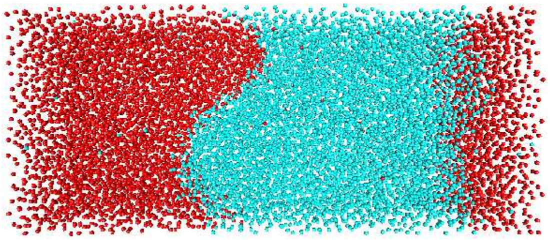
$t = 1.36$ ns



$t = 2.4$ ns

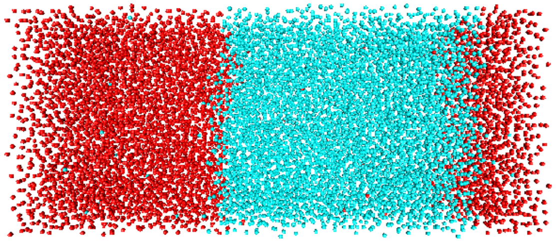


$t = 2.8$ ns



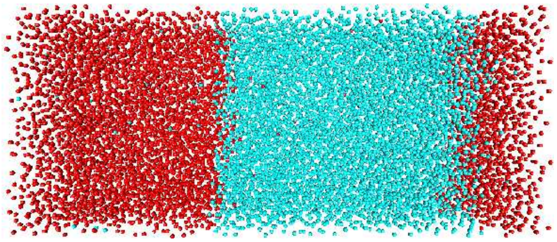
↑ interface ↑

$t = 3.0$ ns



↑ interface↑

$t = 5.0$ ns

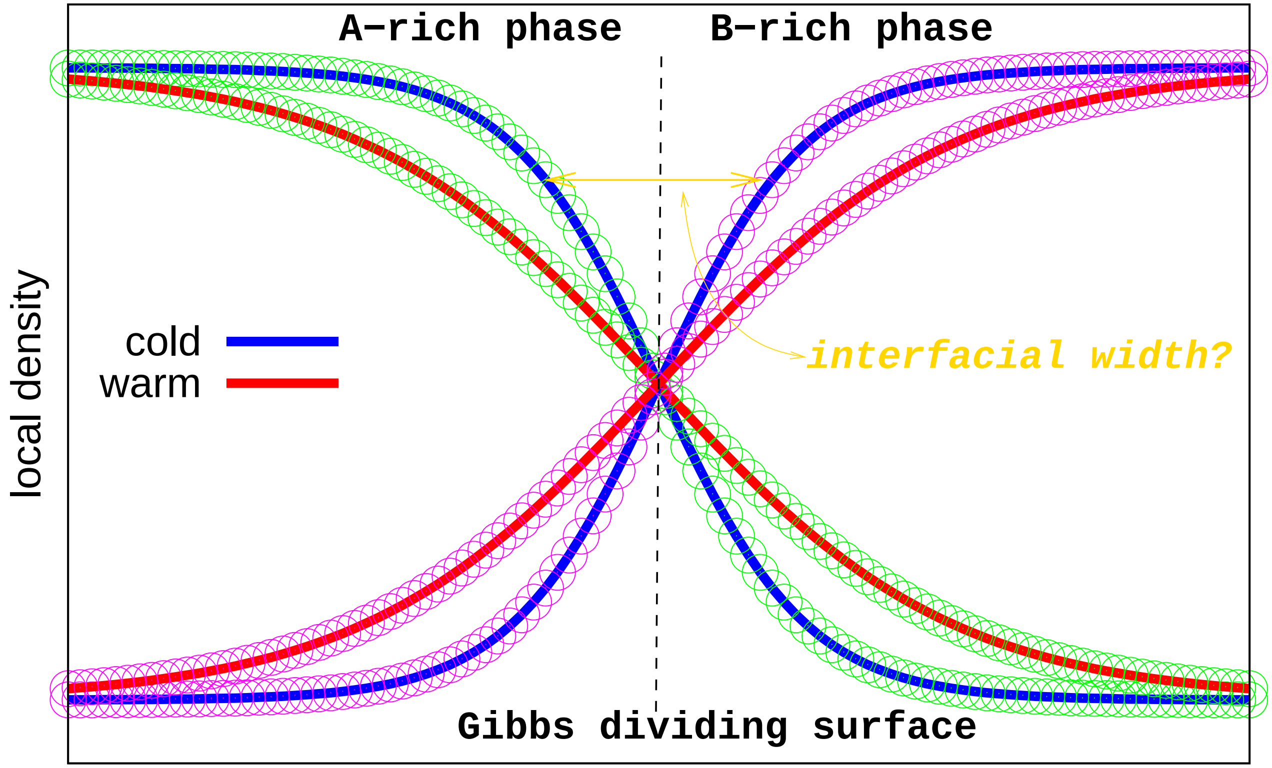


At the time (mid 2000) this took
1 - 2 months on a 'cluster'

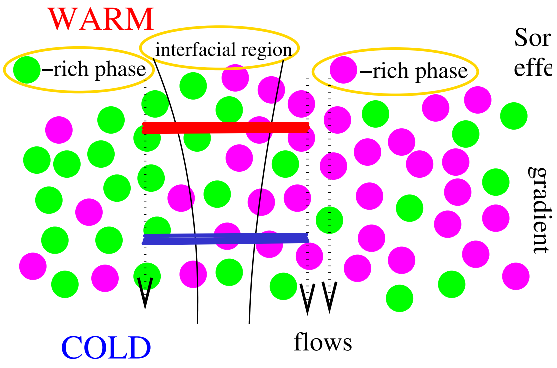
2012:
≈ 2 h on cluster **KALKYL** at SNIC-UPPMAX (Uppsala)
(Daniel Spångberg, own code)

Prof. Kalkyl

Schematic density profiles across liquid-liquid interface



compare to molecular dimension



Model liquid-liquid interfaces between partially miscible Lennard-Jones particles with Argon masses have been studied previously in MD simulations at equilibrium [1,2].

We focus here on such systems subject to a
temperature gradient parallel to the interfaces
and try to find (microscopic) Marangoni convection [3].
(A flow near an interface from the warm to the cold region)

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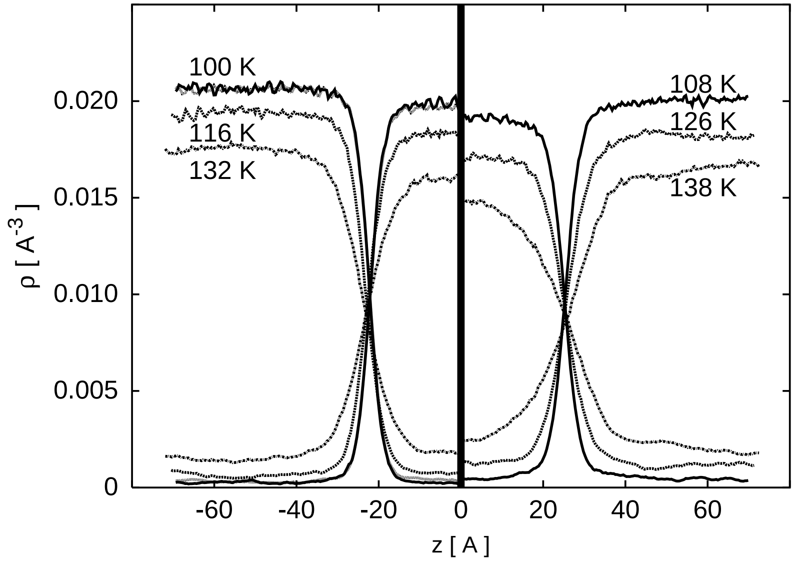
[1] A Molecular Dynamics Study of a Liquid-Liquid-Interface: Structure and Dynamics, J. B. Buhn, Ph. A. Bopp, and M. J. Hampe, Fluid Phase Equilibria, 224, 221 (2004)

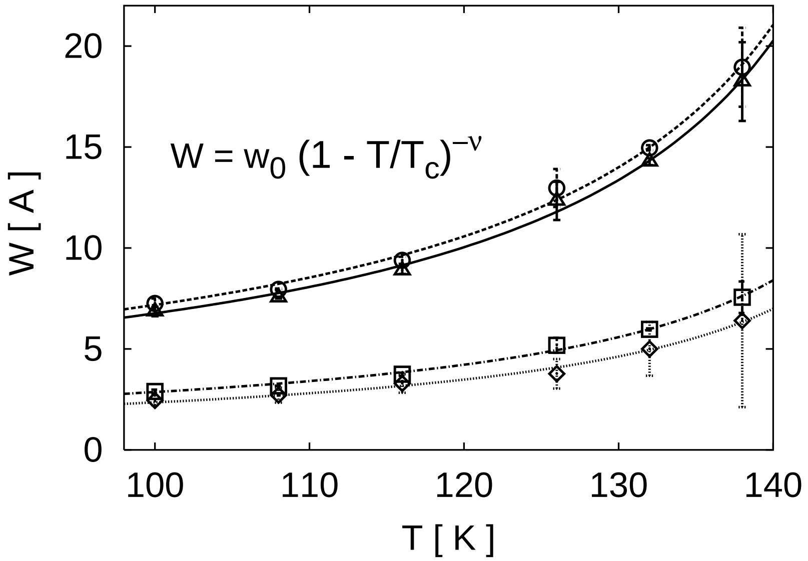
[2] Structural and dynamical properties of liquid-liquid interfaces: A systematic molecular dynamics study, J. B. Buhn, Ph. A. Bopp, and M. J. Hampe, J. Mol. Liq. 125, 187 (2006)

[3] Über die Ausbreitung eines Tropfens einer Flüssigkeit auf der Oberfläche einer anderen, C. Marangoni, Annalen der Physik und Chemie 143, (1871)

Previous: **Model liquid-liquid interface at constant temperature**



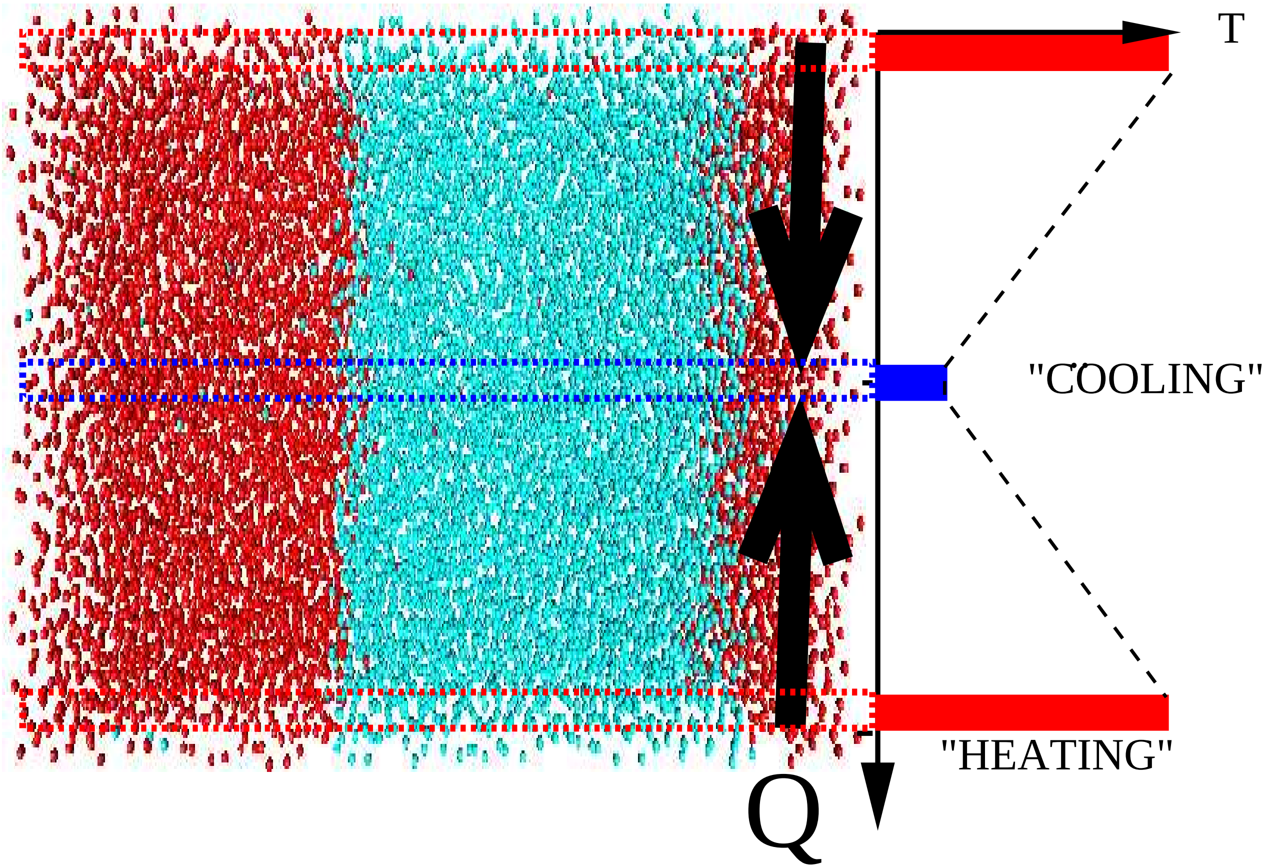
Density profiles
of A- and B-type particles
at 6 different temperatures
(only one half of the box
is depicted)



Analytical expression fitted to
W-values from two different types of fits
to the Figure above
Top: Particles of equal size
Bottom: Particle size ration 1.2

Schematically:

System with a temperature gradient parallel to the interfaces:



Simulations

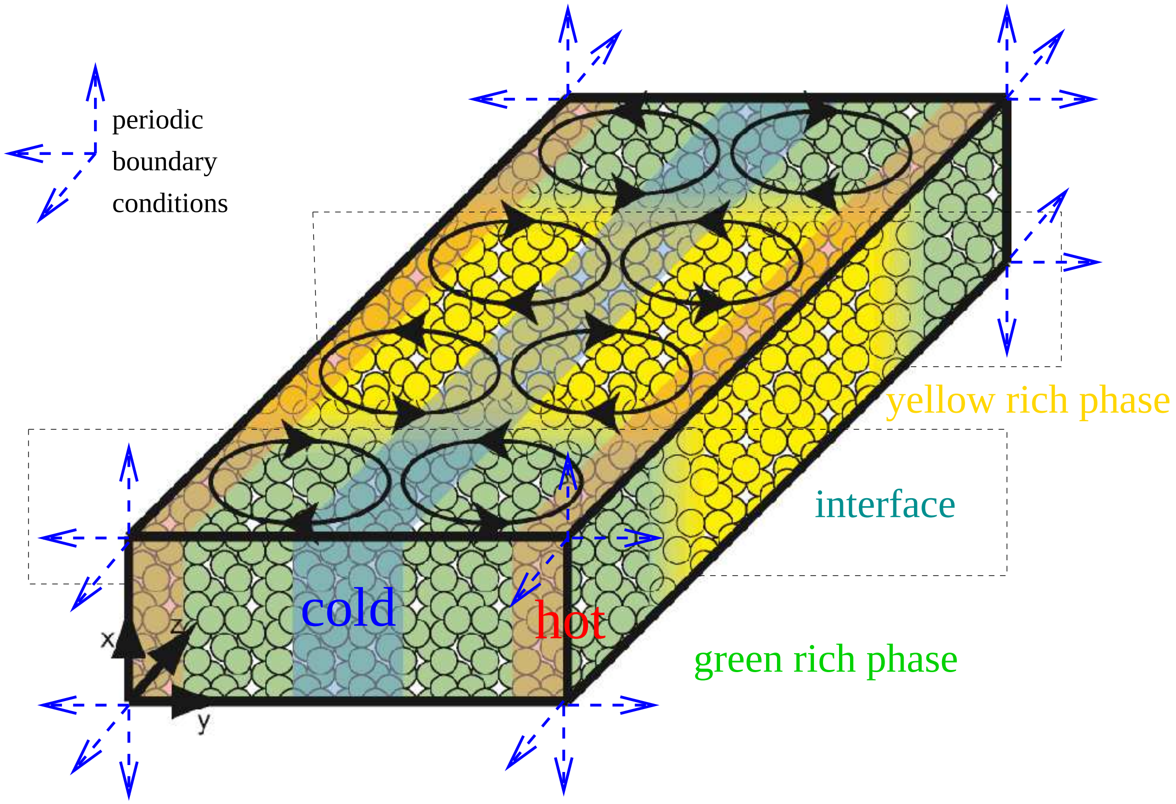
We perform **equilibrium** (NVE) or (NVT) (*for reference*)
and **stationary non-equilibrium** (NVT_1T_2)
Molecular Dynamics (MD) computer simulations
on systems like the one sketched
and on one-phase systems of similar compositions.

Systems are usually simulated for some 75 nanoseconds, which need**ed** about 70 CPU-hours per run for the smallest system and up to 1000 for the largest.

The (many!) analyses of the trajectories may also be quite CPU-time consuming (0.1 - 0.5 the time for the simulation)

Modified (thermostats etc.) (older) version of DL_POLY

Model system with 3-D Periodic Boundary Conditions



usually ≈ 5000 - 10000 particles (and up to 10 times more)

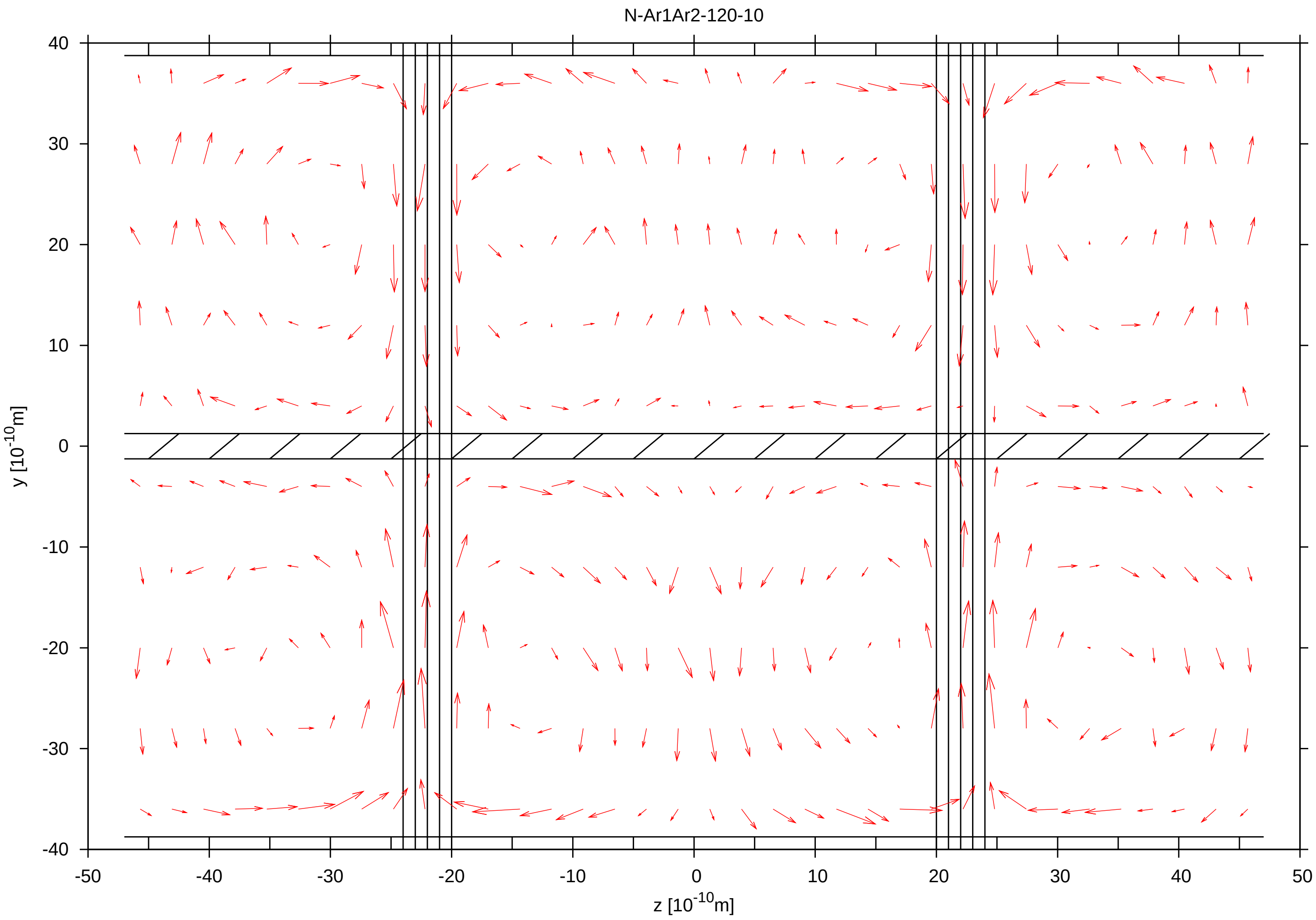
(NVT_1T_2)-ensemble with

$< T > \approx$ 0.8 - 0.9 T_c , $\Delta T = T_2 - T_1 = 10 - 40\ K$ $t_{\text{simulation}} \approx 75$ ns

red: Thermostat $< T > +0.5 \cdot \Delta T$ blue: Thermostat $< T > -0.5 \cdot \Delta T$

Particles here yellow/green instead of red/blue above.

Computing the average particle velocities in small volume elements results in a field* typically like this



warm

cold

warm

*Projections of locally averaged particle velocities onto the laboratory $y - z$ plane

The analysis is often difficult because of poor statistics
(even with very long simulation runs)

$$\begin{aligned} \text{locally averaged particle velocity} &= <v>_{x,y,z} \\ &= < \frac{1}{N_i(x,y,z)} \sum_{j=1}^{N_i(x,y,z)} \vec{v}_j(x,y,z) >_{t_i,t_i+\delta t} \\ &\quad (x,y,z) = \text{a small volume around } x,y,z \end{aligned}$$

$$\text{in general, however, } <v>_{x,y,z} \ngtr v_i(t) \text{ (for a particle } i\text{)}$$

Things that **can** be studied:

– Technical parameters:
Influence of the 'thermostats', the cut-off radii of interactions, simulation box size, ...

– Physical parameters:
Influence of the temperature gradient $(\Delta T/(L_y/2))$: Linear response?
Influence of the interactions (ϵ and σ parameters): Miscibility
Influence of the particle masses $(m_{\mathrm{A}}, m_{\mathrm{B}})$
Influence of the external conditions (e.g. pressure)
etc. etc. etc.

We discuss here only:

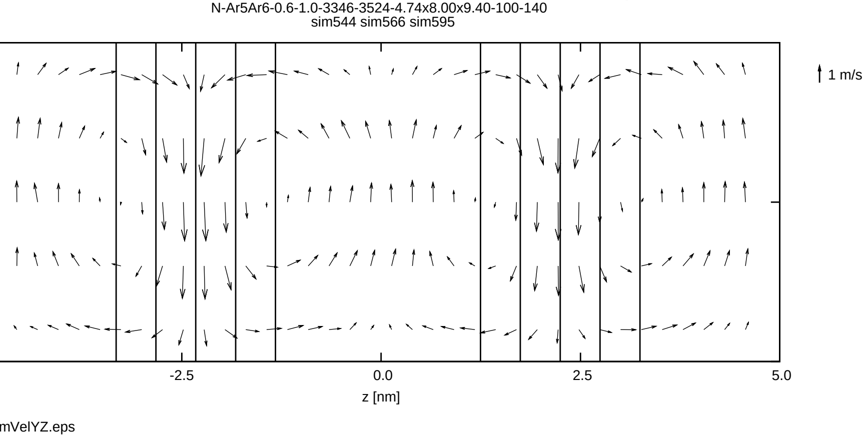
(i) Influence of the temperature gradient

(ii) Influence of the LJ cross parameters, i.e. (*cum grano salis*) miscibility

(iii) Influence of the box size

(i) Influence of the temperature gradient

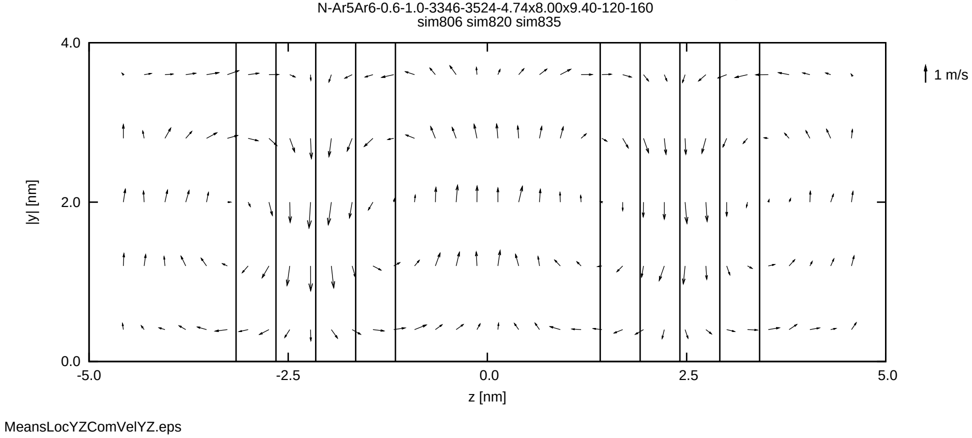
100 - 140 K (120 ± 20)



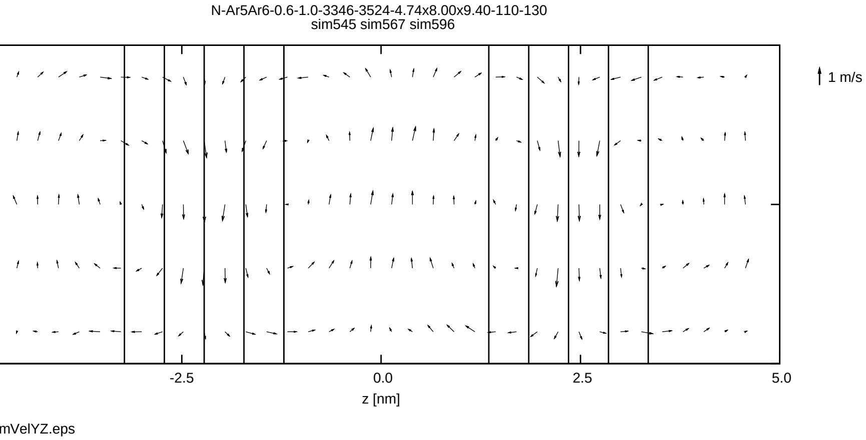
hot

cold

120 - 160 K (140 ± 20)



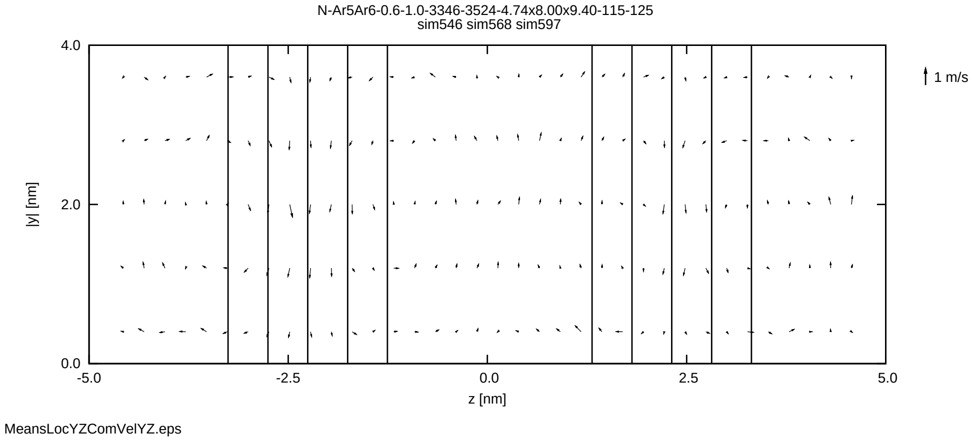
110 - 130 K (120 ± 10)



hot

cold

115 - 125 K (120 ± 5)



Compare with top half of previous Figure

Conclusions (i):

→ Direction of average velocities always hot to cold in
the vicinity of the interface

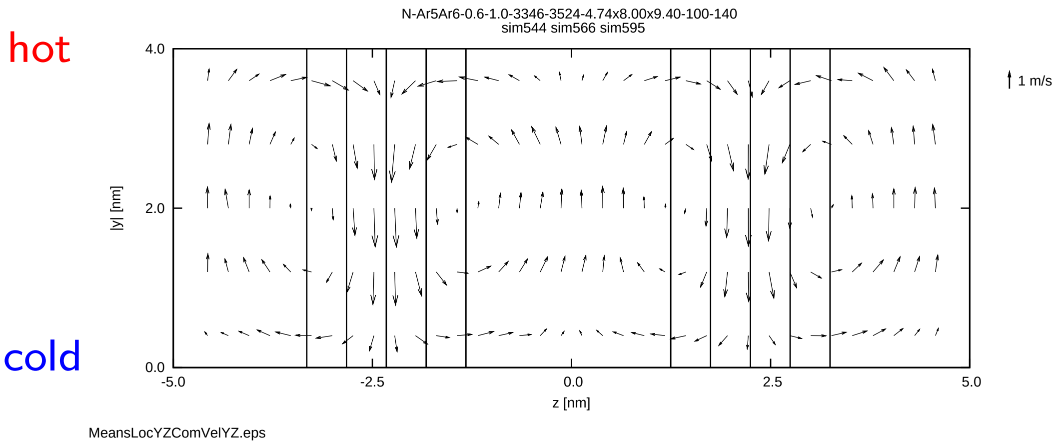
→ Velocities increase with increasing temperature gradient

→ Average velocities decrease with increasing average temperature
(i.e. decrease with decreasing distance from the critical lines
in our cases $T_c \approx 160 - 180$ K)

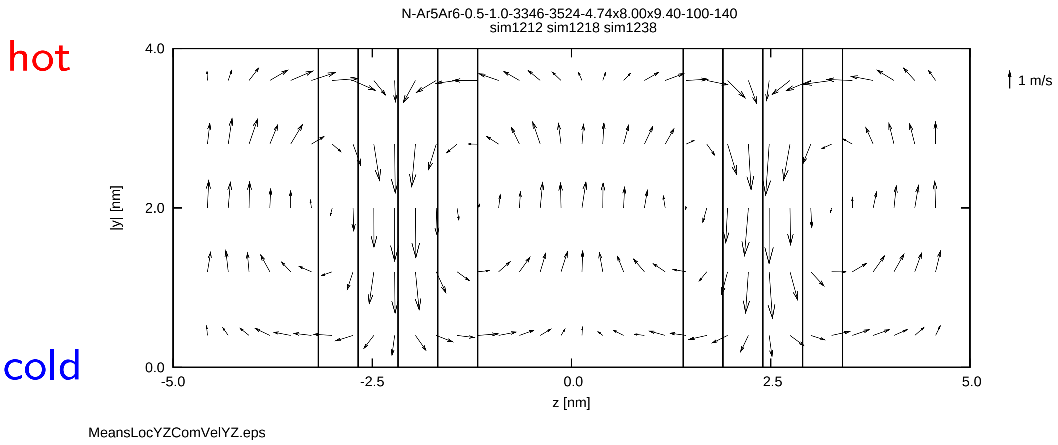
$\Longrightarrow$ This is as expected for a macroscopic Marangoni pattern
(under 'moderate' conditions)

(ii) Influence of the cross interaction (→ miscibility, interfacial width)

100 - 140 K (120 ± 20)



Same system as above



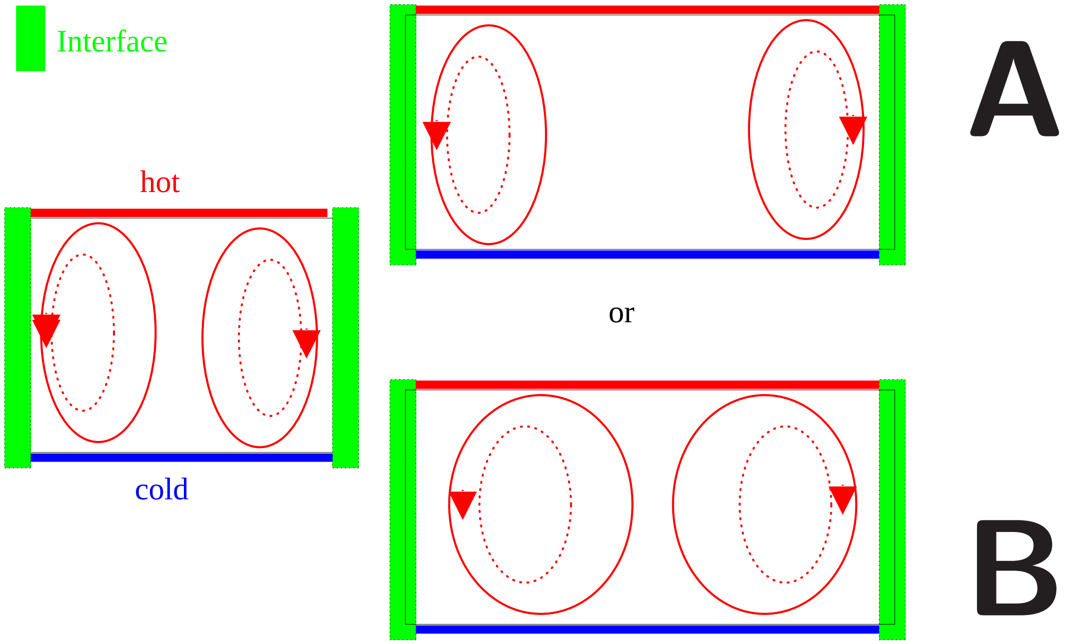
Less miscible: Thinner interfaces

Conclusions (ii):

→ At a given temperature thinner interfaces (less miscible liquids)
favor the convection vortices
(This was tested only in a few cases)

(iii) Influence of the box size

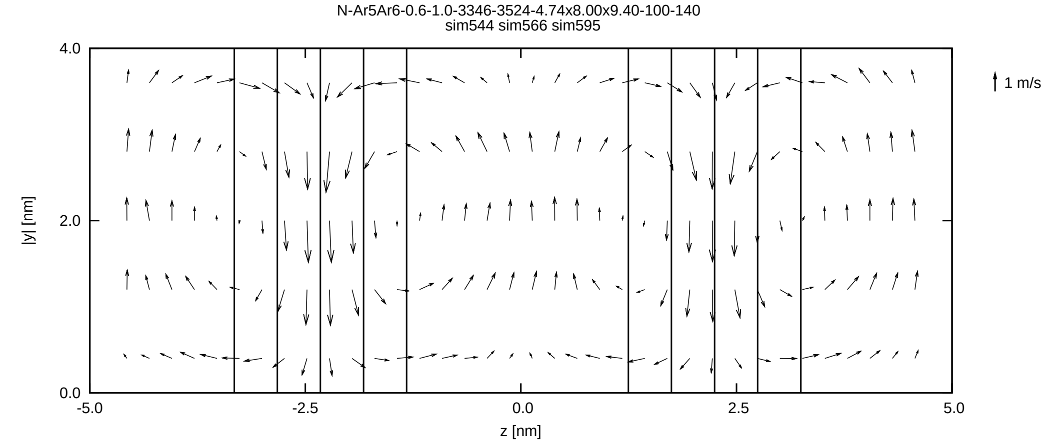
When the size of the simulation box is increased, are the vortices becoming localized near the interfaces (schematically **case A**)
or do they move out into the bulk (schematically **case B**)?



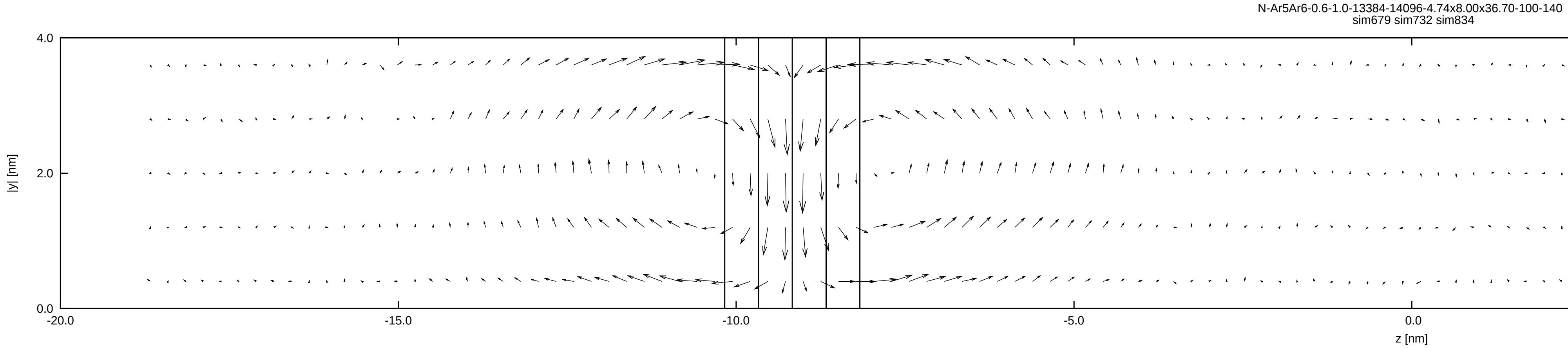
100 - 140 K (120 ± 20)

reference system

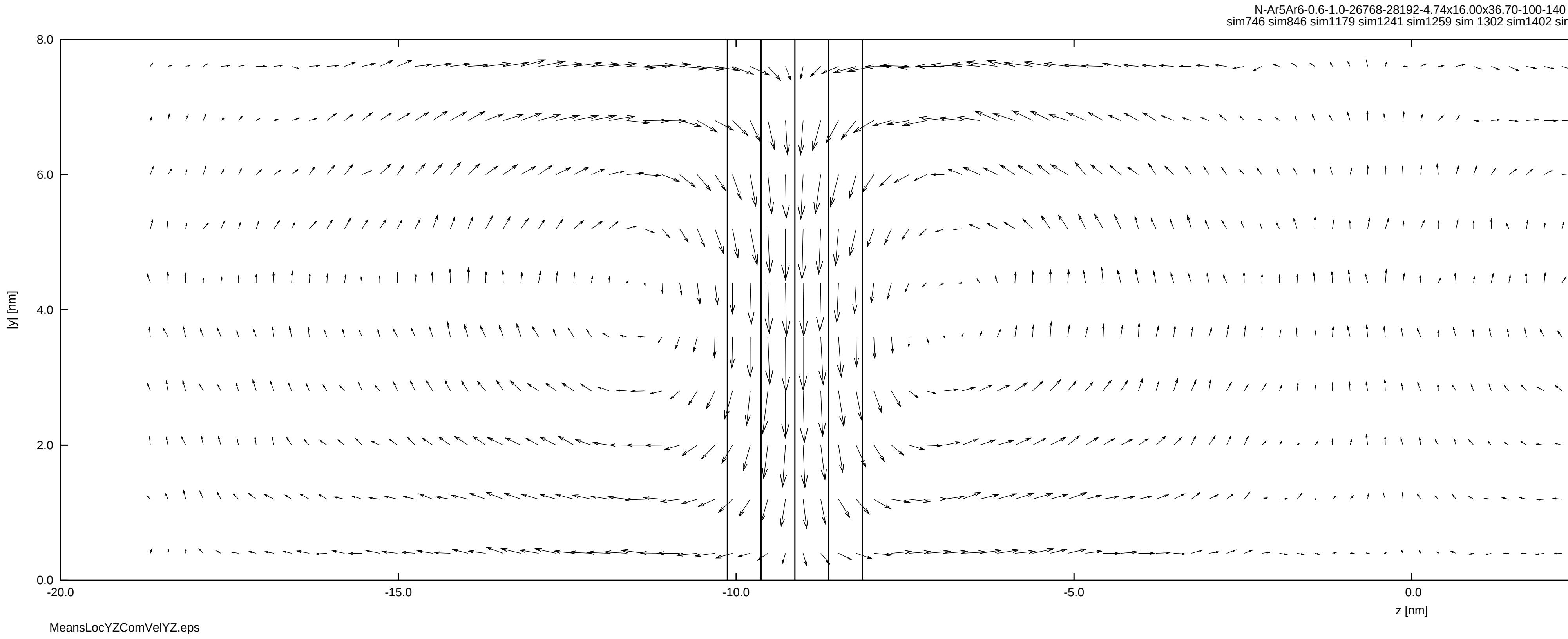
as above



MeansLocYZComVelYZ.eps



MeansLocYZComVelYZ.eps



Same scale as previous graphs

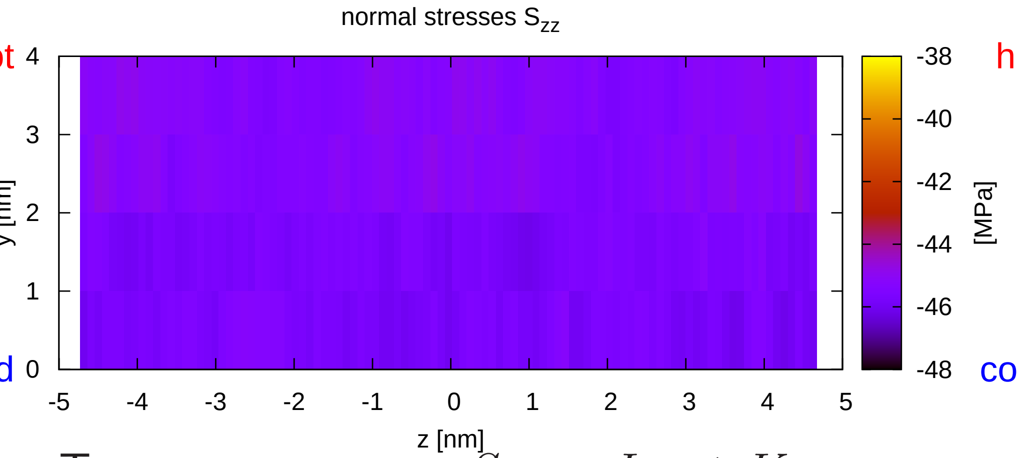
Biggest system simulated, 54960 particles

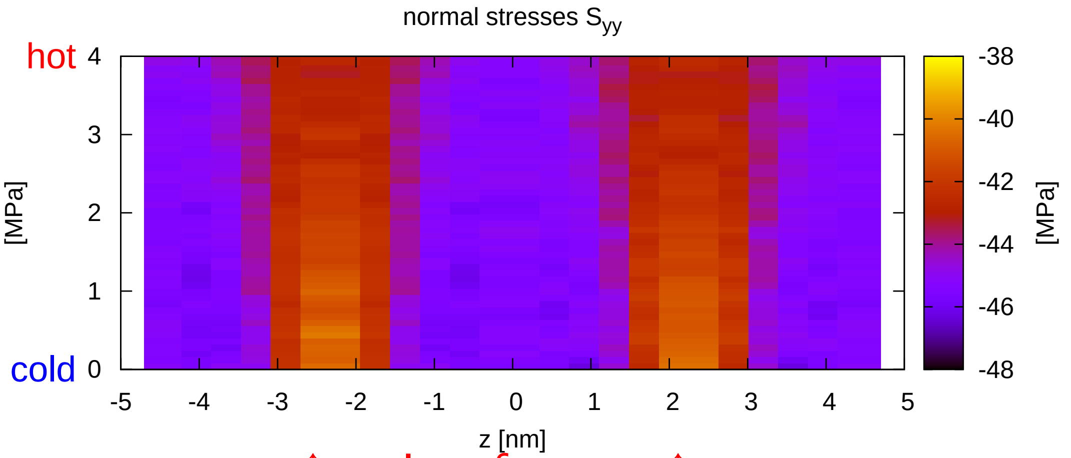
Conclusions (iii):

→ The centers of the vortices remain in the vicinity of the interfaces and do not move out into the bulk when the box size is increased (**case A**).
Since the vortices remain associated with the interfaces it is really an interfacial phenomenon, not a bulk phenomenon
(*which we also know from the fact that we never saw anything like that in one-phase simulations under similar conditions (Soret systems)*)

Further Analyses (I):

Stress-tensor $\mathbf{S}$ (according to H.Heinz, W.Paul, K.Binder, Phys.Rev. E72,066704, 2005)

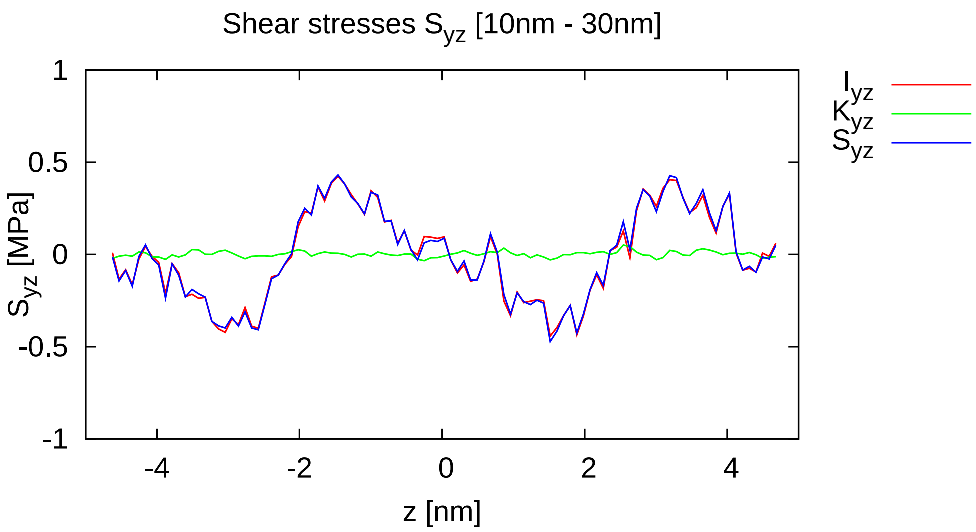




Tensor components $S_{\alpha\beta} = I_{\alpha\beta} + K_{\alpha\beta}$

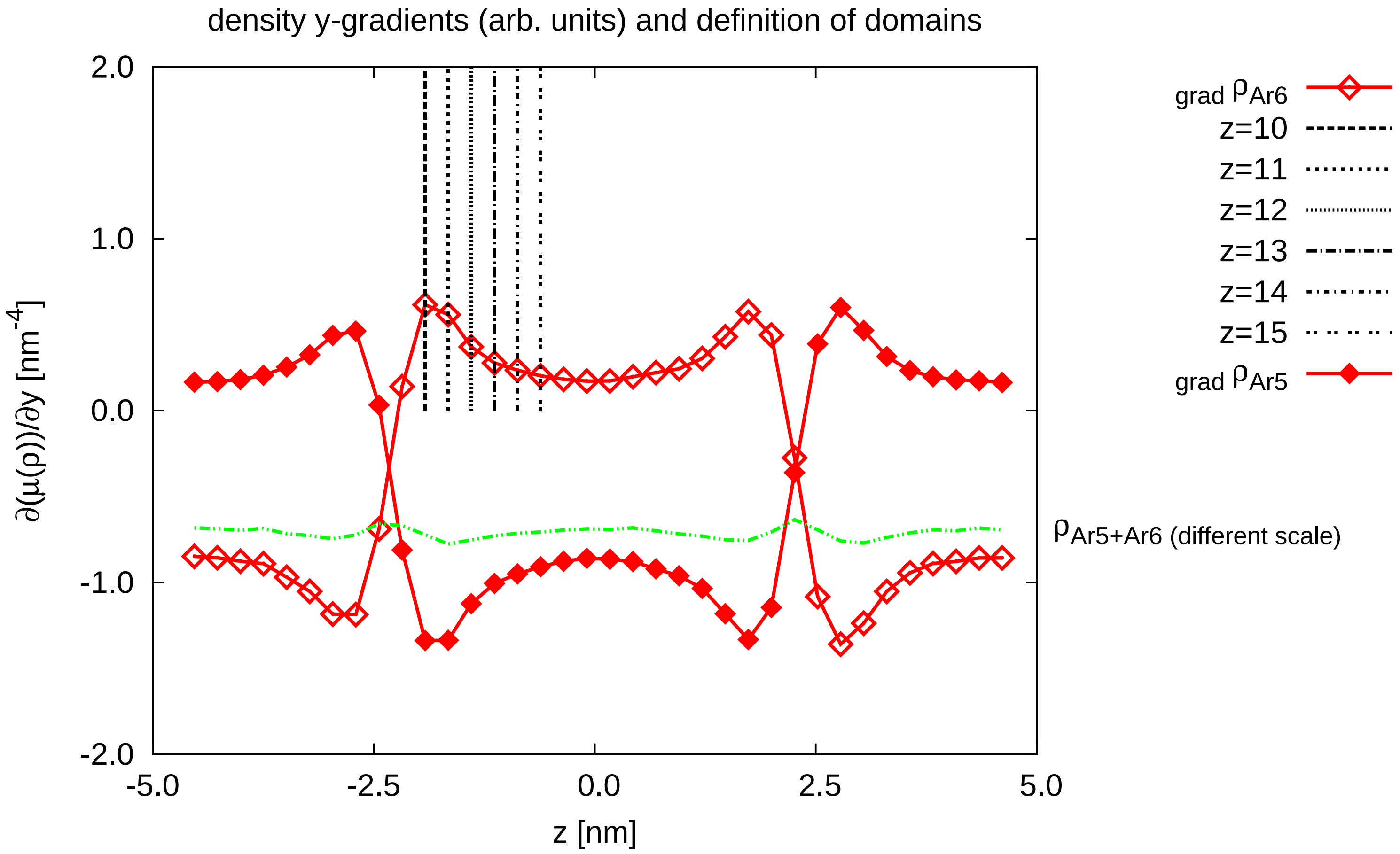
(K: kinetic, I: interactions)

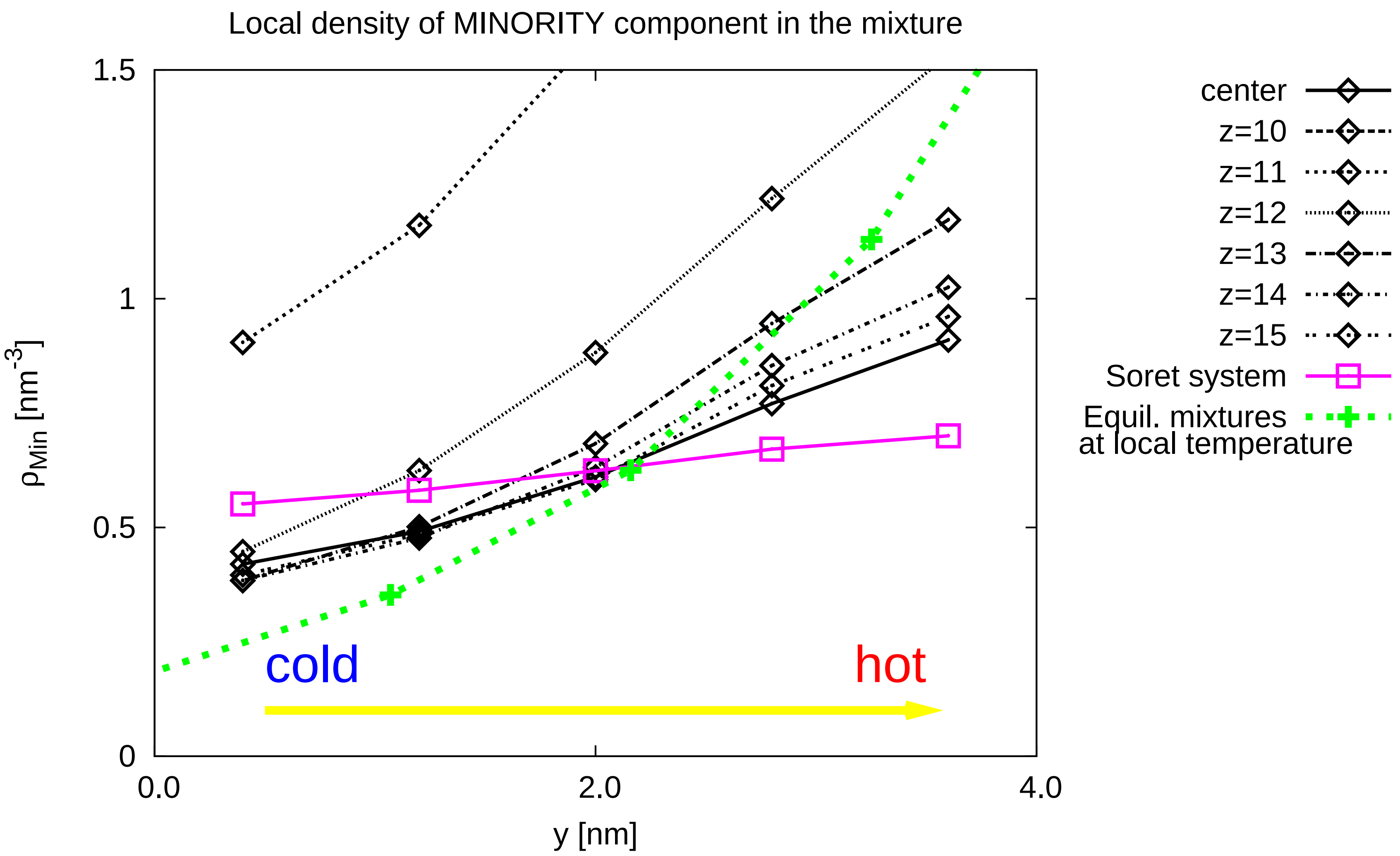
↑ interfaces ↑

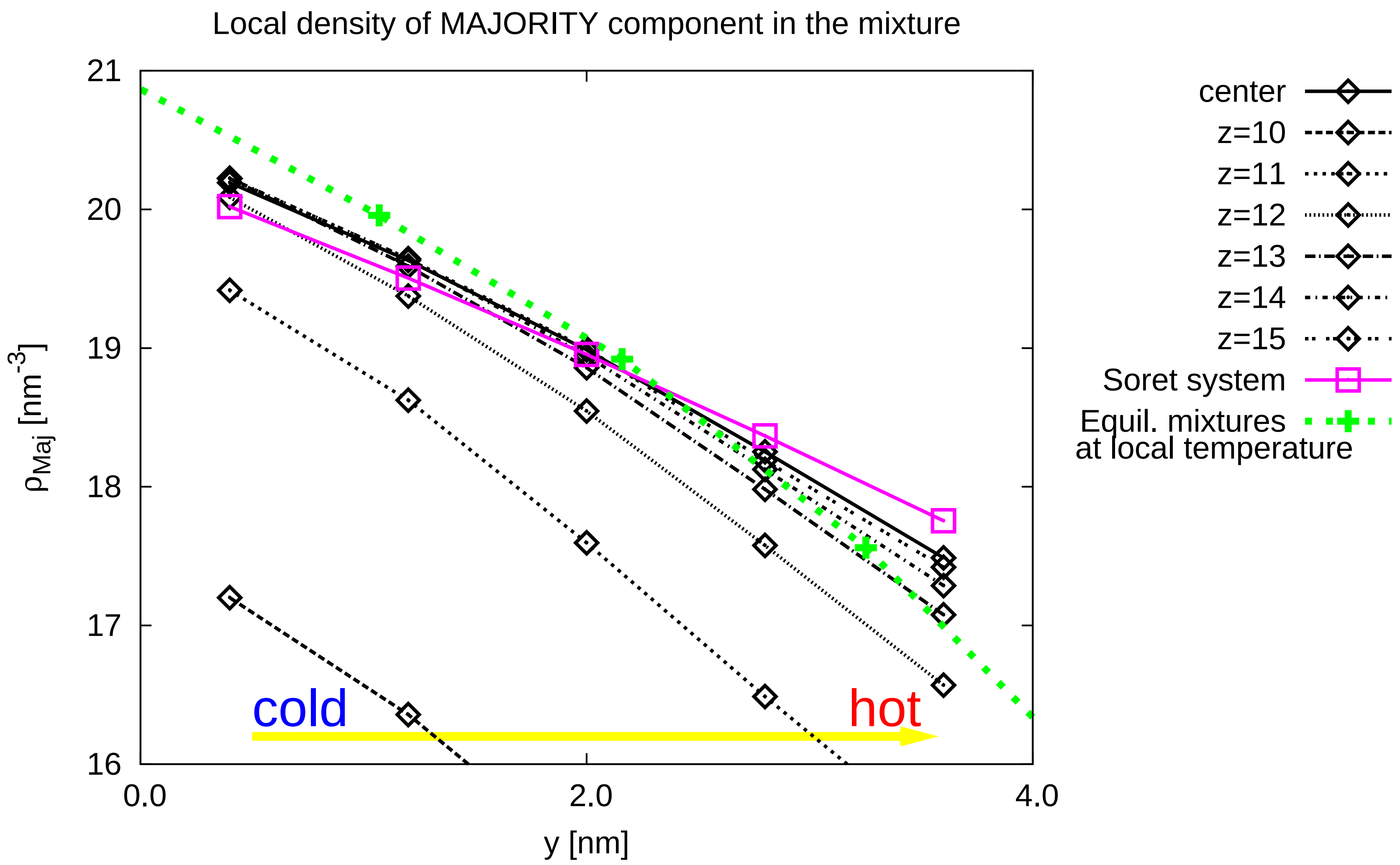


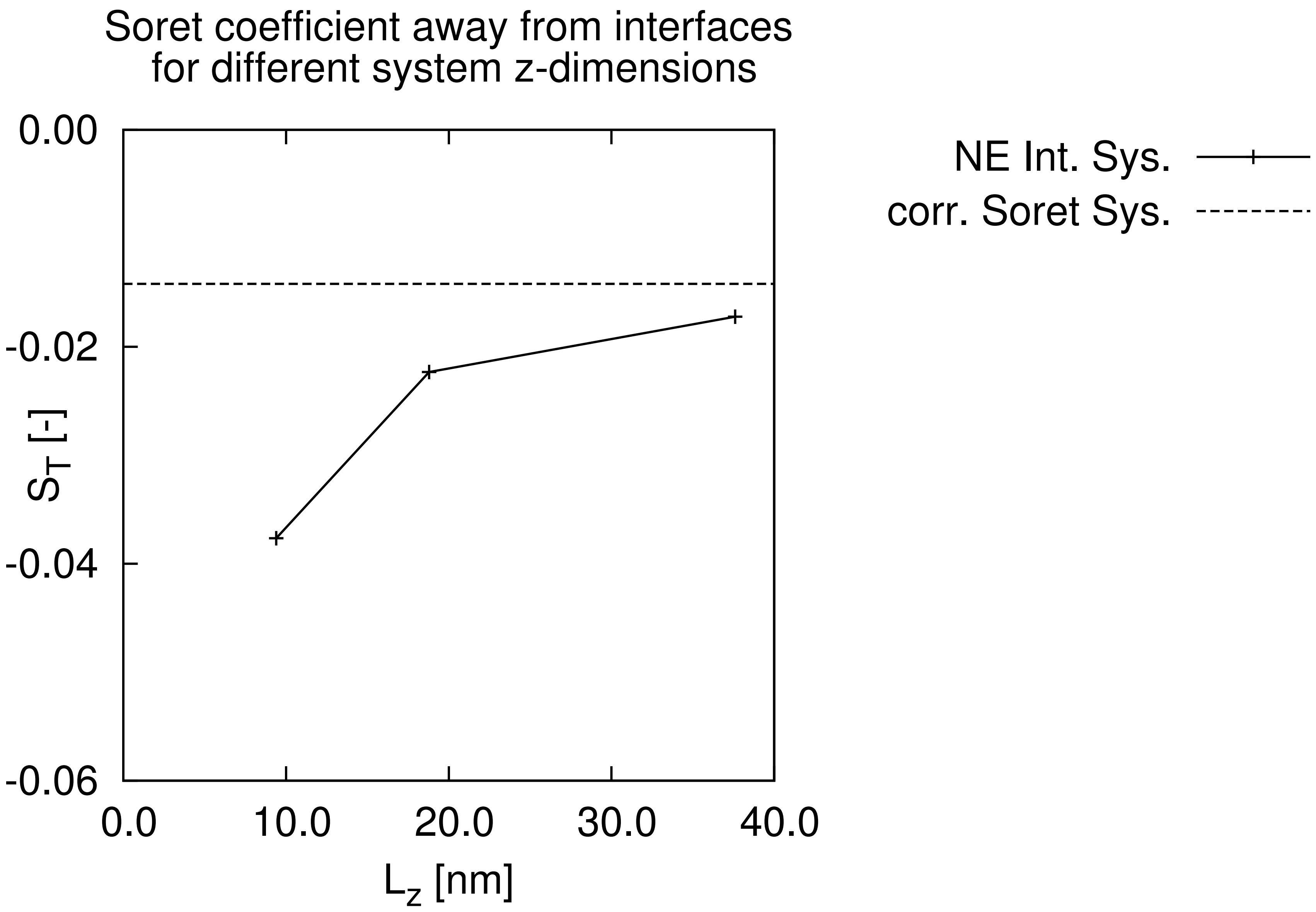
Further Analyses (II):

Relation to Soret system
(concentration gradient resulting from a temperature gradient in a mixture)




Local density of MINORITY component in the mixture
ρ_{Min} [nm^{-3}]
y [nm]
0
0.5
1
1.5
0.0
2.0
4.0
center
z=10
z=11
z=12
z=13
z=14
z=15
Soret system
Equil. mixtures at local temperature
cold
hot


Local density of MAJORITY component in the mixture
ρ_{Maj} [nm^{-3}]
21
20
19
18
17
16
0.0
2.0
4.0
y [nm]
cold
hot
center
z=10
z=11
z=12
z=13
z=14
z=15
Soret system
Equil. mixtures
at local temperature


Soret coefficient away from interfaces
for different system z-dimensions
0.00
-0.02
-0.04
-0.06
S_T [-]
0.0
10.0
20.0
30.0
40.0
L_z [nm]
NE Int. Sys.
corr. Soret Sys.

Take Home Message

- The convection is always directed from hot to cold in the vicinity of the interfaces
- The convective patterns are localized close to the interfaces
- Even with very high temperature gradients, the systems respond linearly
- Molecular transport mechanisms dominate convective ones in all non-equilibrium simulations
- Normal thermal diffusion (Soret effect) is observed away from the interfaces
- Local 'phase equilibria' are seen along the interfaces

$\Longrightarrow$ Thermocapillary effect demonstrated at the microscopic scale
Marangoni Convection at the molecular level

Acknowledgments

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He thanks Dr. Maxim Fedorov and Prof. Kersti Hermansson and their coworkers for their hospitality in Leipzig and Uppsala.

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– the Wenner Gren Foundations (Stockholm)
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