Hydrodynamics and phase transitions

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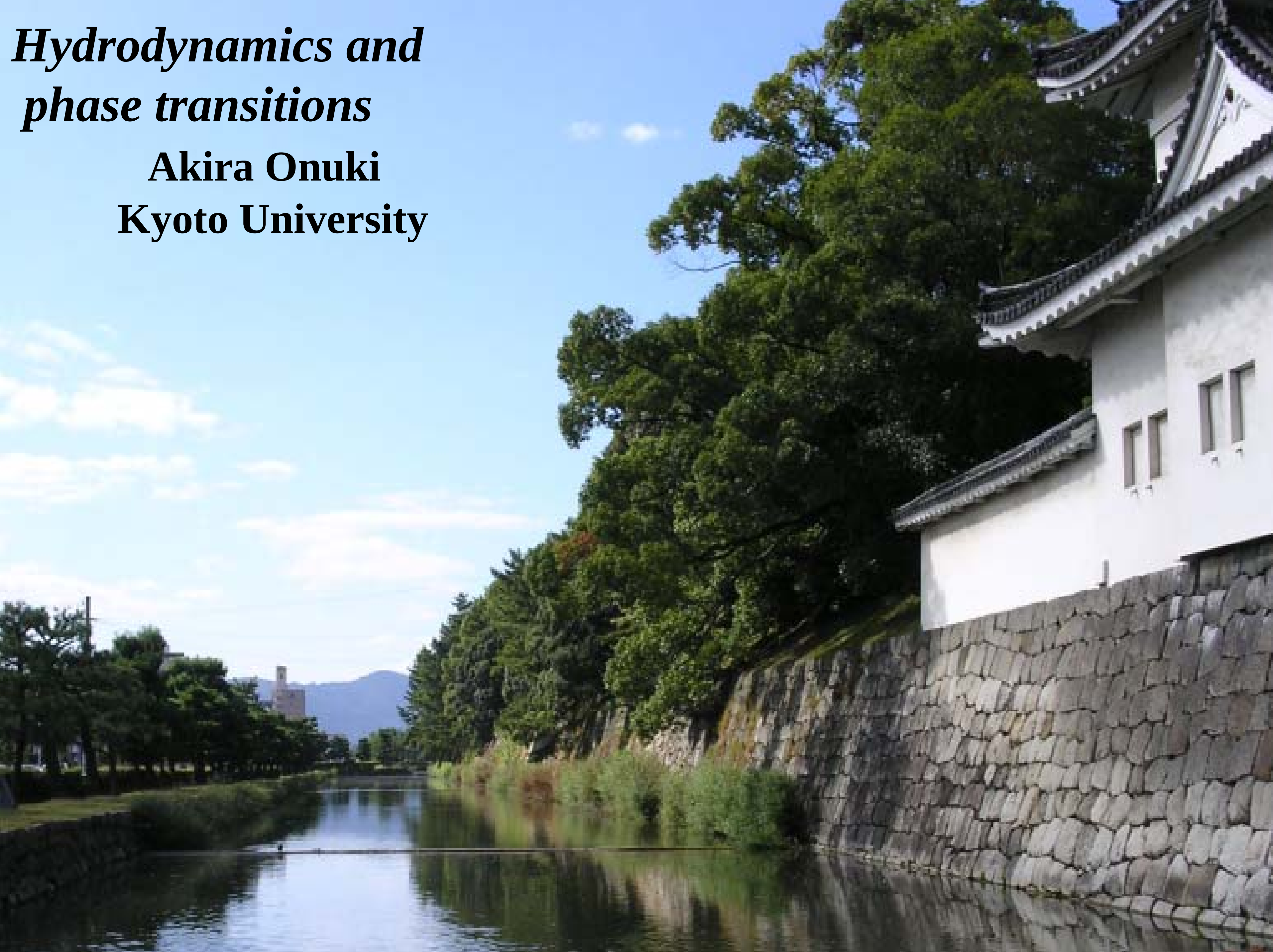


気体の状態方程式(Equation of State)

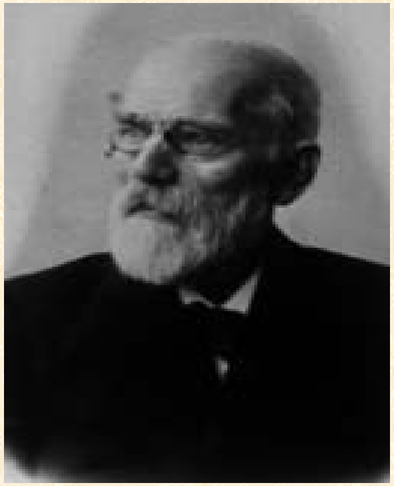
k: Boltzmann

理想気体(Ideal Gas)の状態方程式

p= nkT

$$pv = RT$$

R: 気体定数(Gas Constant)



Van der Waals 1837-1923

1873 thesis で

van der Waalsの状態方程式

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

a/v^2: 分子間ポテンシャルによる圧力減少
b: 気体分子体積総和による自由空間体積減少

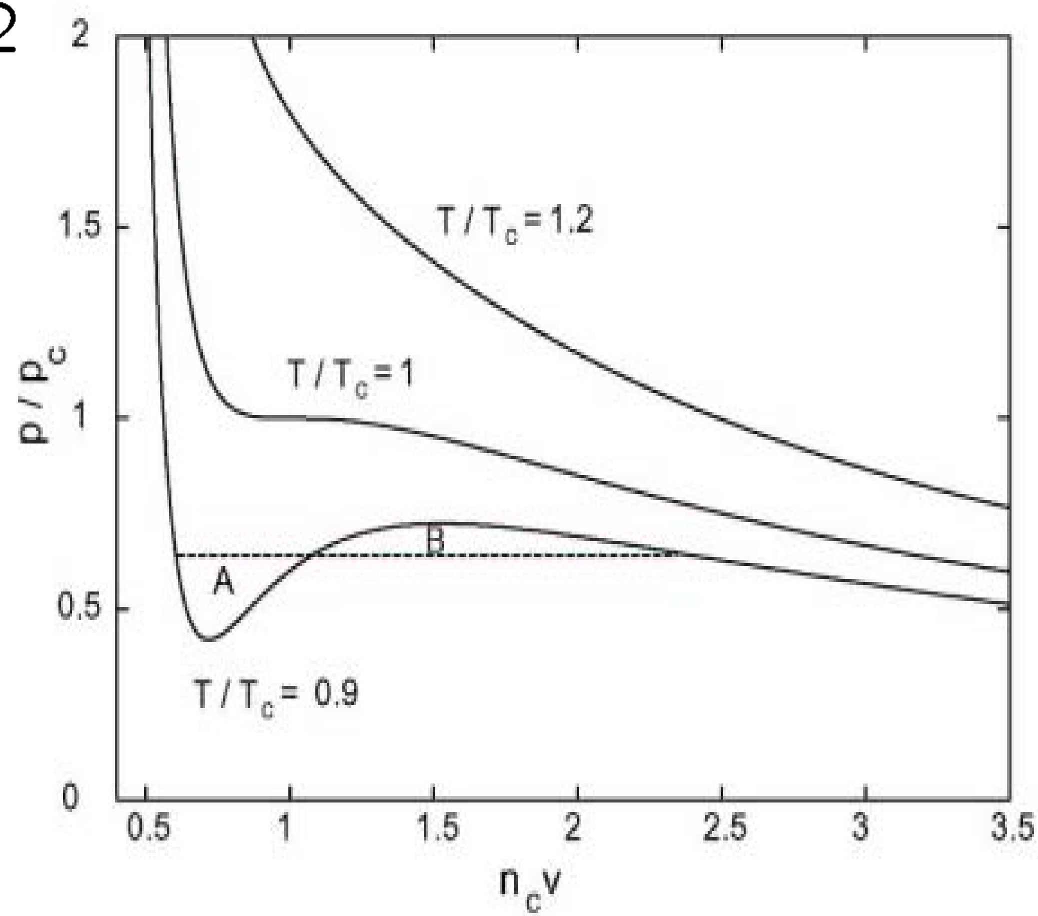
$$p = \frac{nk_BT}{1 - v_0 n} - \epsilon v_0 n^2$$

$$s/k_B = -\ln(n/T^{3/2}) + \ln(1 - v_0 n) + \mathrm{const}$$

$$e = 3nkT/2 - \epsilon v_0 n^2$$

- **液体･気体を記述**

Maxwell rule 1875
area A= area B



Dutch school

1908年にヘリウムの
液化に成功し1913年にノーベル賞を受けた
カメリング·オンネス(Kamerlingh Onnes)

But no fundamental understanding of

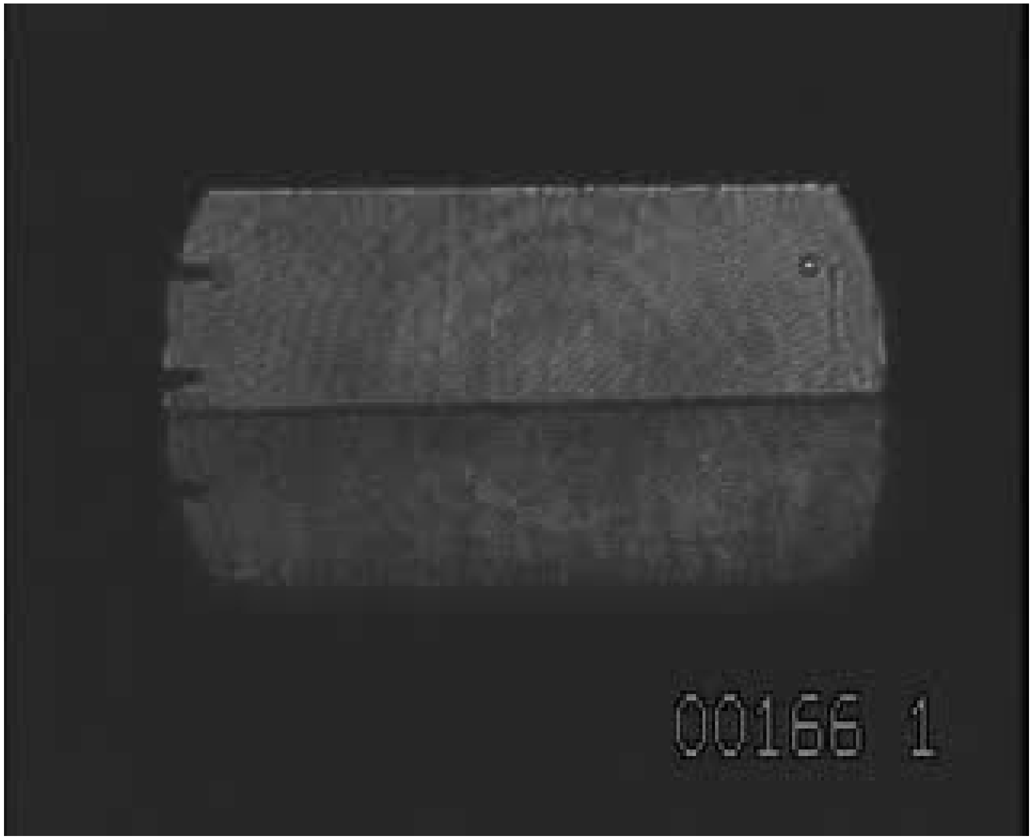
nonequilibrium phase transition: T(r,t)

液化、蒸発、沸騰、濡れ、

HEAT PIPE (aircon)

気象現象

Exp and theory of boiling in g in two phase T<Tc



Boiling occurs at extremely weak heating near criticality

熱膨張係

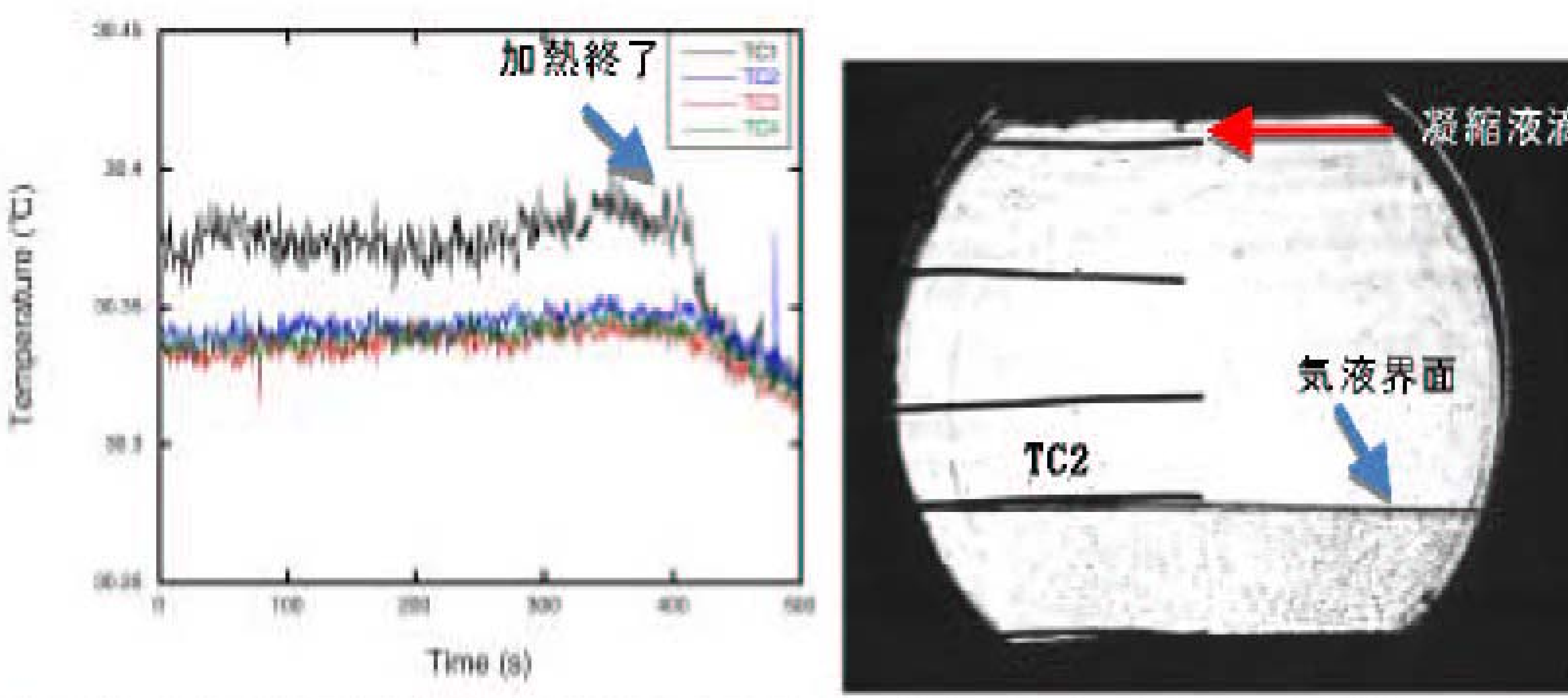
$$(\partial\rho/\partial T)_p \sim (T_c - T)^{-1}$$

CO_2: Tc-T =1 K, bottom heating 0.1 K under 1 g, Yoshihara et al (JAXA)

New experiment Kawanami et al (Japan)

Heating from below with liquid and gas

Gas temperature is homogeneous. T-Tc=0.1 K



1 2：セル内部温度の時間履歴とそのときの流体挙動（T-Tc=500mK, heat flux: 8kW/m^2)

Ginzburg-Landau scheme is not appropriate for inhomogeneous $T(\mathbf{r},t)$

Start with entropy functional of order parametrer ψ ***and energy density e (micro-canonical)***

$$\mathcal{S} = \int d\mathbf{r}[S(\psi,e) - C|\nabla\psi|^2/2]$$

gradient entropy

Definition of T: $\frac{1}{T} = \frac{\delta \mathcal{S}}{\delta e}$ at fixed ψ

One-component fluids:

n: number density, e: internal energy density

Entropy $\mathcal{S} = \int d\mathbf{r}[ns(n,e) - C|\nabla n|^2/2]$

regular (bulk) *gradient*

Internal energy $\mathcal{E} = \int d\mathbf{r}\hat{e}$

internal energy density $\hat{e} = e + K|\nabla n|^2/2$

regular (bulk) *gradient*

Definition of T: $1/T = \delta\mathcal{S}/\delta e$

at fixed n

Equilibrium:maximize S at fixed

$$\mathcal{N} = \int d\mathbf{r} n \text{ and } \mathcal{E}$$

Then T=const. and

$$-T\left(\frac{\delta S}{\delta n}\right)_{\hat{e}} = \mu - T\nabla \cdot \frac{M}{T}\nabla n = \text{const}$$

$$M = CT + K$$

$$\text{interface}: \mu(n,T) - M\nabla^2 n = \mu_{cx}$$

This was first derived by van der Waals.

van der Waals $(v_0, \epsilon = \text{const})$

$$s = k_B \ln[(e/n + \epsilon v_0 n)^{d/2}(1/v_0 n - 1)] + \textit{const.}$$

$$e = dnk_B T/2 - \epsilon v_0 n^2$$
$$p = nk_B T/(1 - v_0 n) - \epsilon v_0 n^2$$

Stress tensor for K=0

$$\Pi_{ij} = p\delta_{ij} - CT[n\nabla^2 n + (\nabla n)^2/2]\delta_{ij}$$
$$+CT\nabla_i n \nabla_j n - \sigma_{ij}$$

reversible stress + viscous stress (η,ζ)

$$\frac{\partial}{\partial t}\rho = -\nabla(\rho\mathbf{v}),\ \ (\rho = mn)$$

$$\rho(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla)\mathbf{v} = -\nabla\cdot\Pi - \rho g\mathbf{e}_z$$

$$\frac{\partial}{\partial t}e_T = -\nabla\cdot(e_T + \Pi\cdot)\mathbf{v}$$

$$+\nabla\lambda\nabla T - \rho g v_z,\ \ (e_T = \hat{e} + \rho v^2/2)$$

Stress Π ***contains gradient terms***

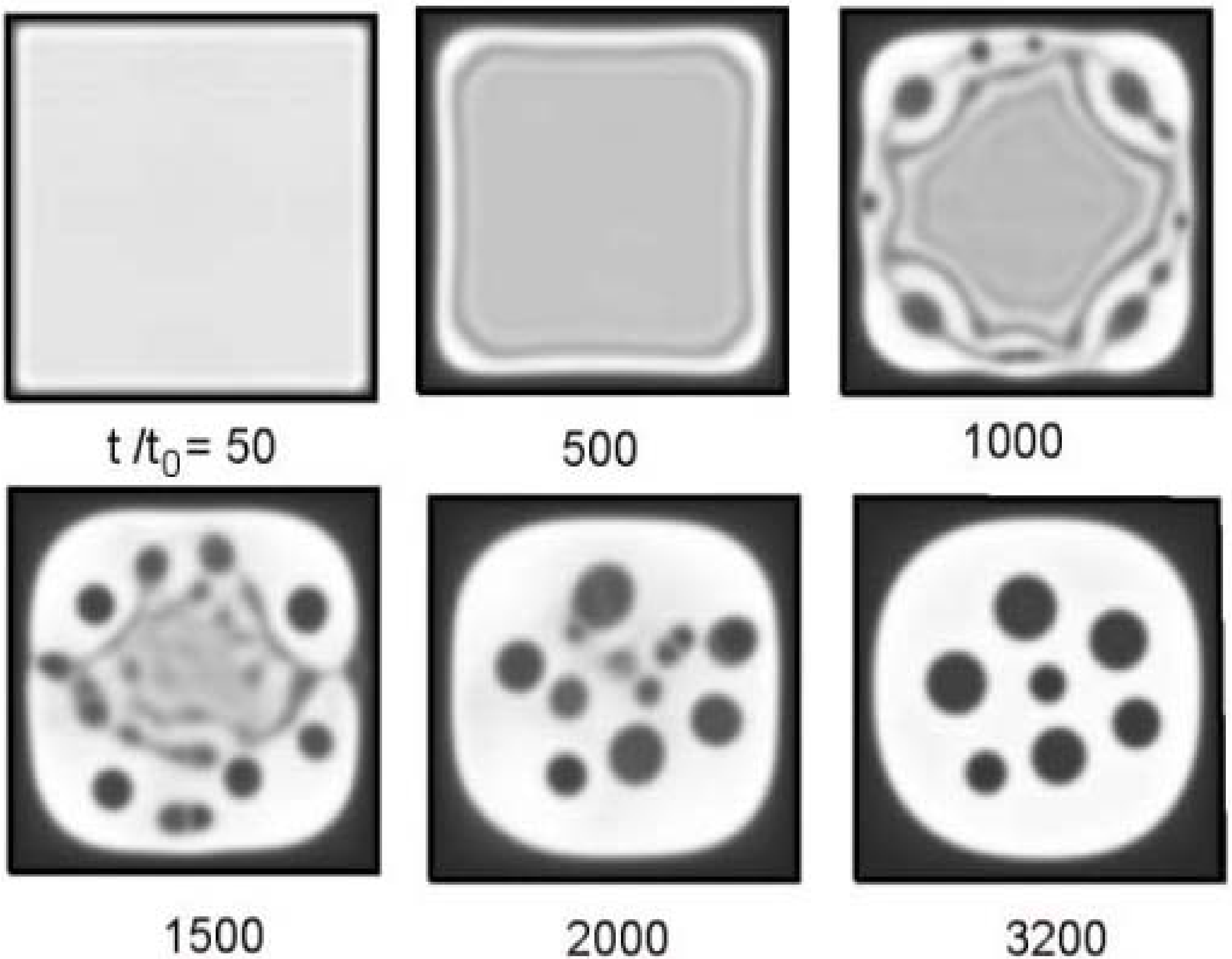
Entropy production >0 if no heat from outside

$$\frac{\partial}{\partial t}S = \int d\boldsymbol{r}\frac{1}{T}[\nabla \cdot \lambda \nabla T + \sum_{ij} \sigma_{ij}\nabla_i v_j]$$

Gradient terms are included

1-1

Adiabatic cooling from boundary
$T=1.1T_c$ to $T_{wall}=0.9T_c$ at $<n>=n_c$



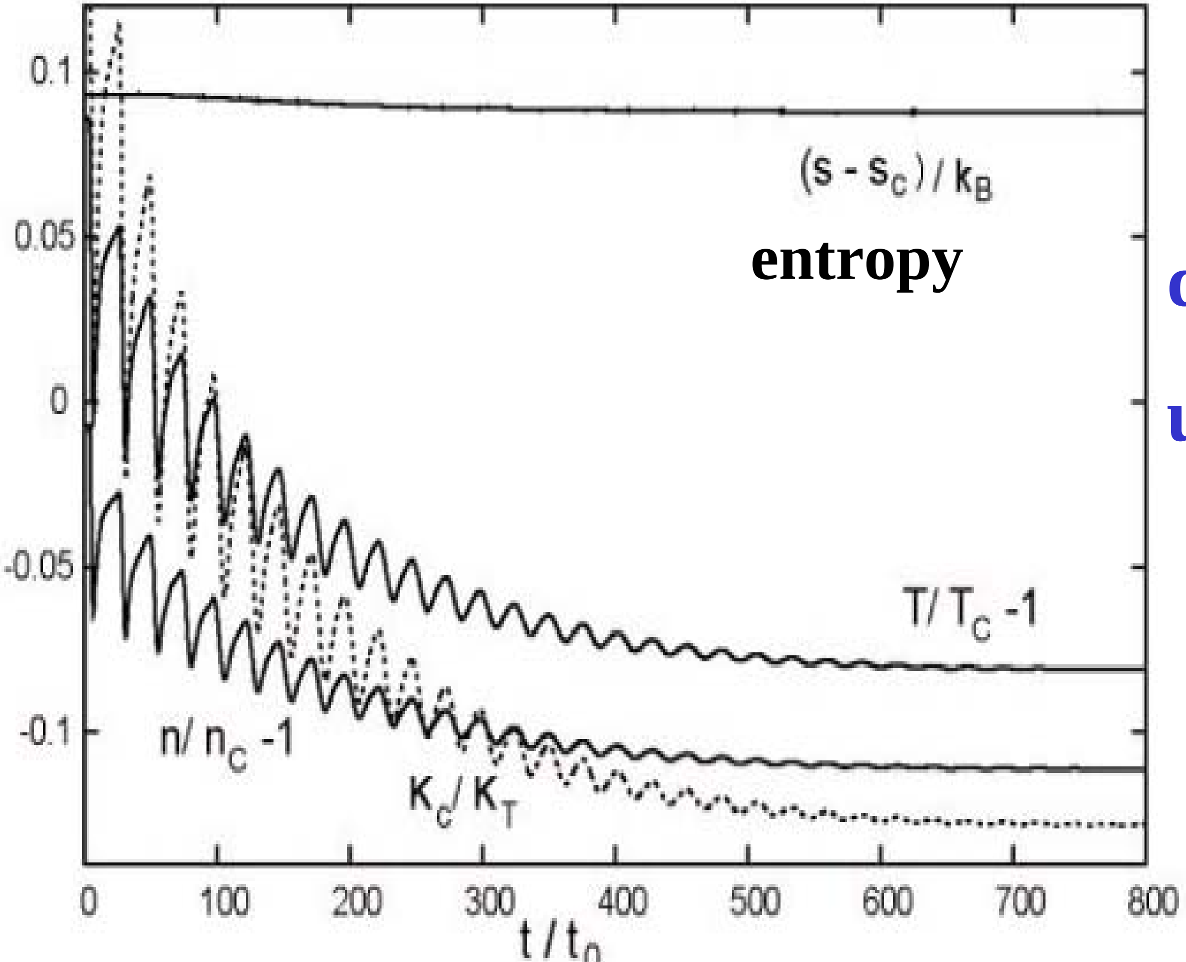
$t_0 = \ell^2/\nu_0$
ℓ = interface width

Liquid wetting layer is a piston expanding interior

1-2

Early stage adiabatic expansion by sounds

Changes at cell center. Still no domains in interior

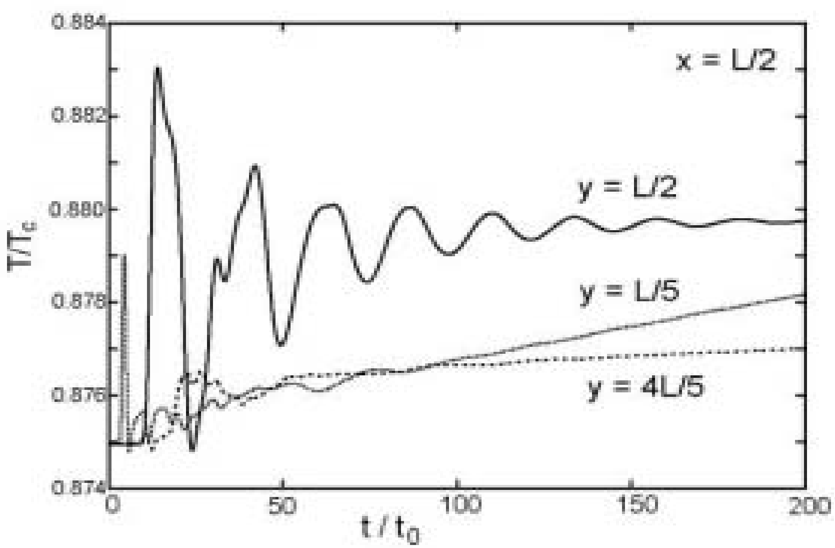


$$\frac{1}{K_T} = \rho\left(\frac{\partial p}{\partial \rho}\right)_T$$
$$\propto T - T_s(n)$$

spinodal

driven to

unstable state



2 *Sounds to a bubble*

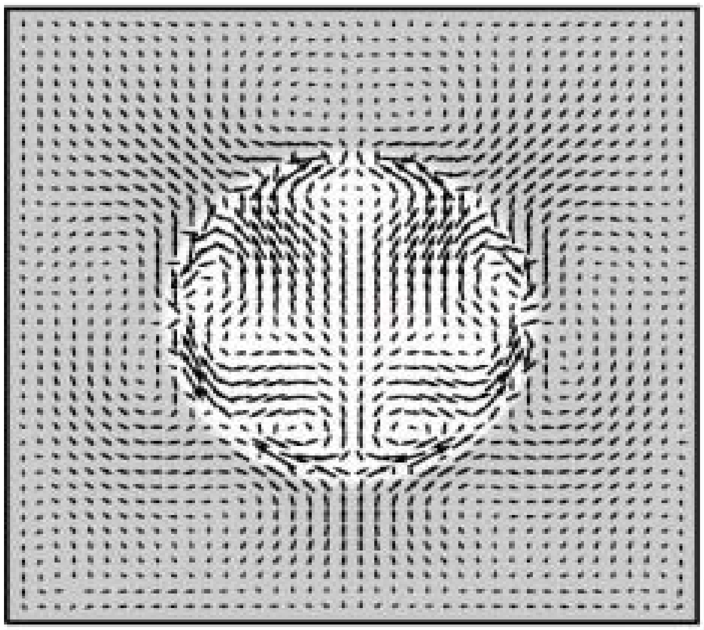
T_{bot}/T_c is changed from 0.875 to 0.895

$(\frac{\partial T}{\partial p})_s$ is 9 times larger in gas than in liquid

warmer in gas than in liquid

L

y



0 x $t=50t_0$ L

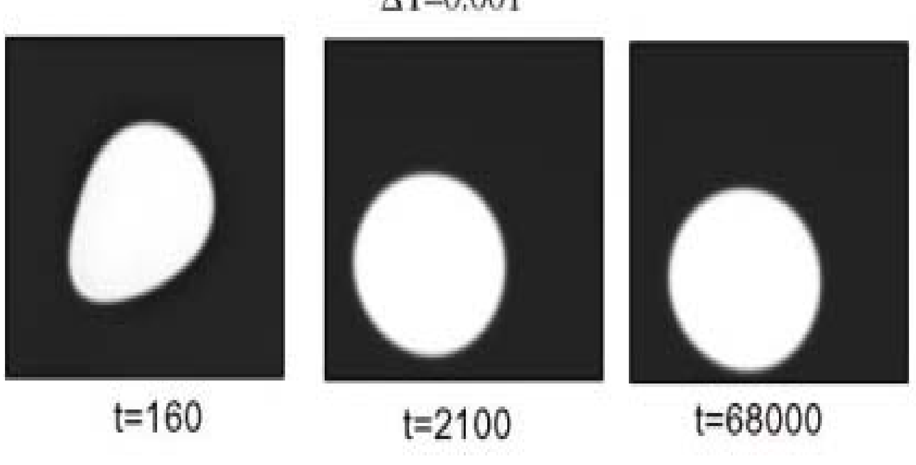
Bubble oscillates!

2-1. Bubble in heat flow

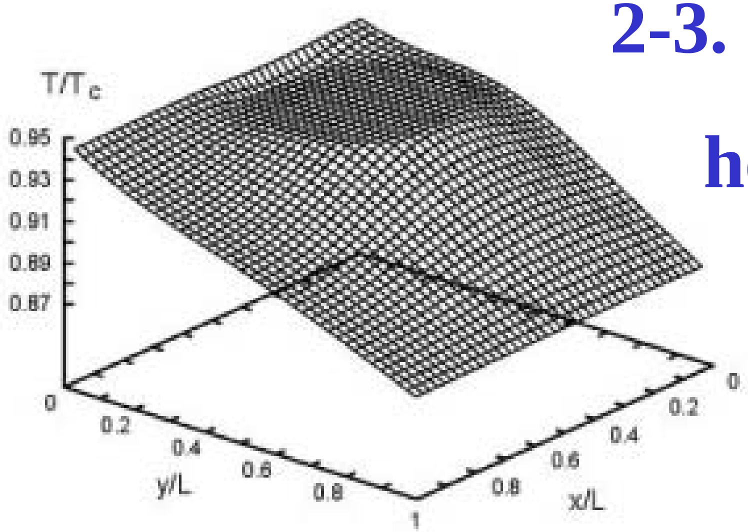
$t<0$: gas droplet at center, $T=0.875T_c$ in equilibrium

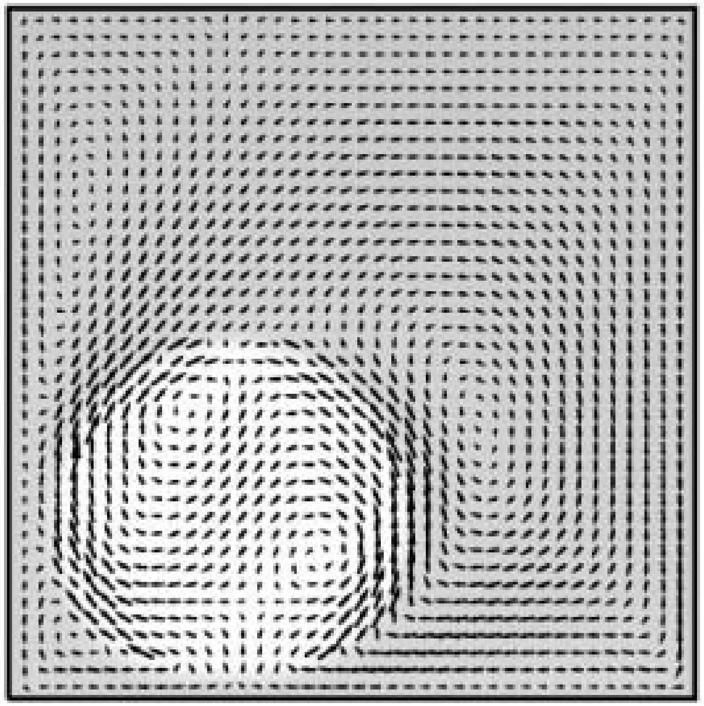
$t>0$: $T_{bot}= 0.875T_c+ \Delta T$ (heated), T_{top} is fixed

No gravity



2-3. Bubble is attracted to heated wall. Apparent partial wetting



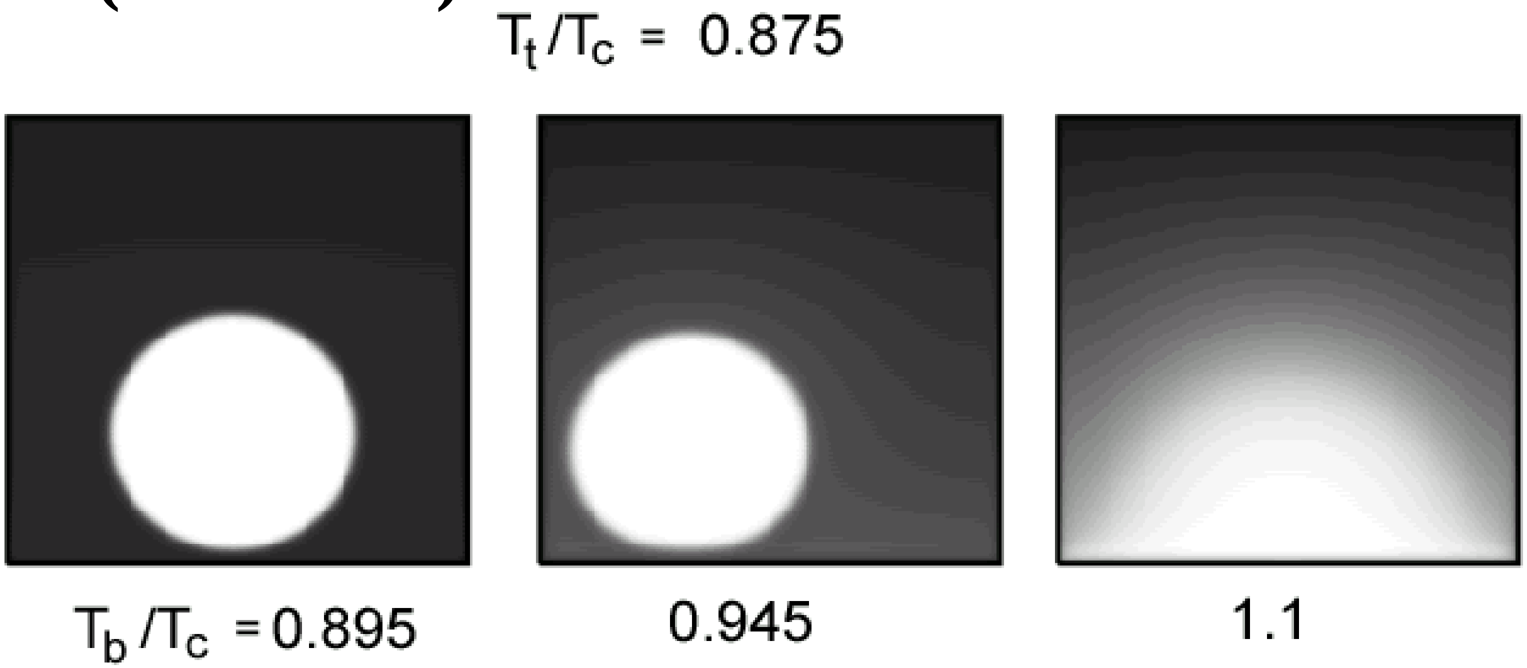


T_{bot}/T_c is changed from 0.875 to 0.945

$T_{\mathrm{top}}/T_c = 0.875$

T is flat within bubble = Tcx(p)

2-2. Apparent wetting in heat flow (continued)

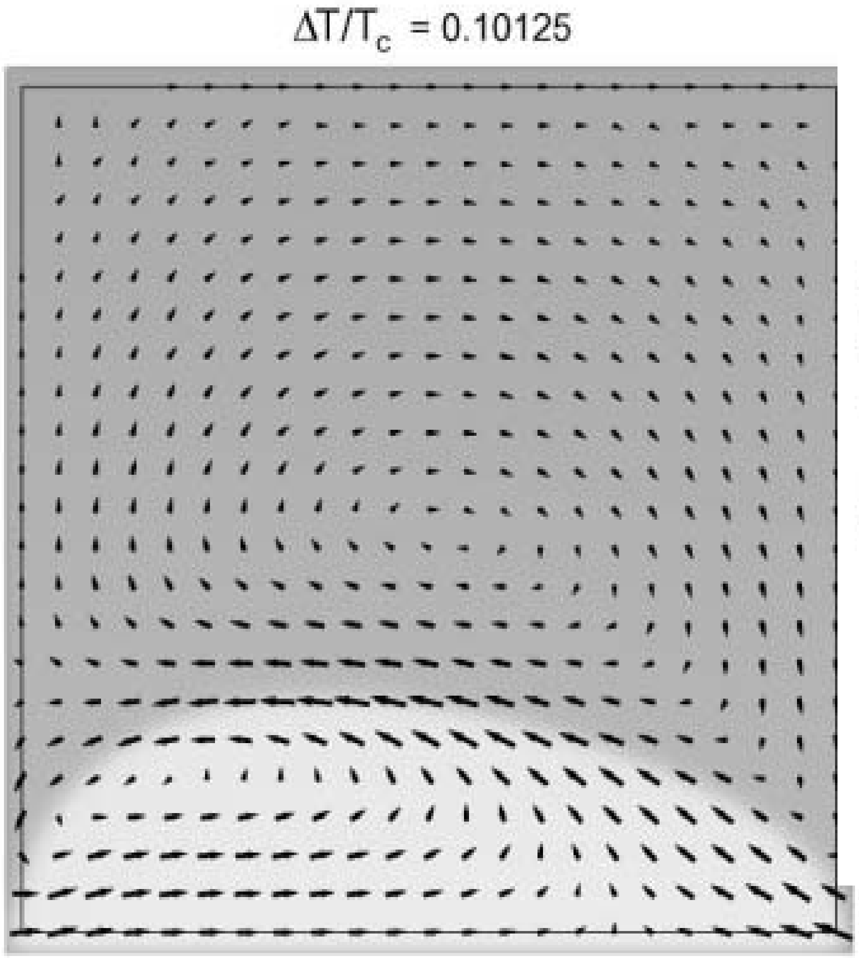


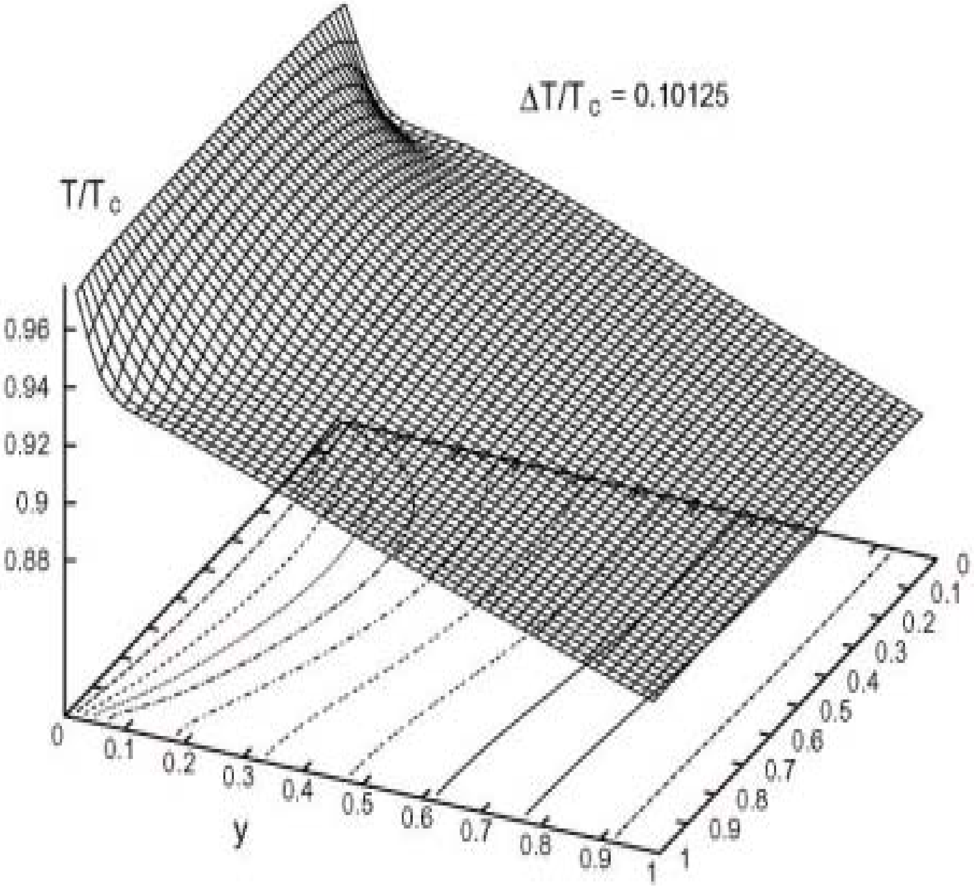
$\Delta T/Tc$=0.225

Steady convection with no gravity

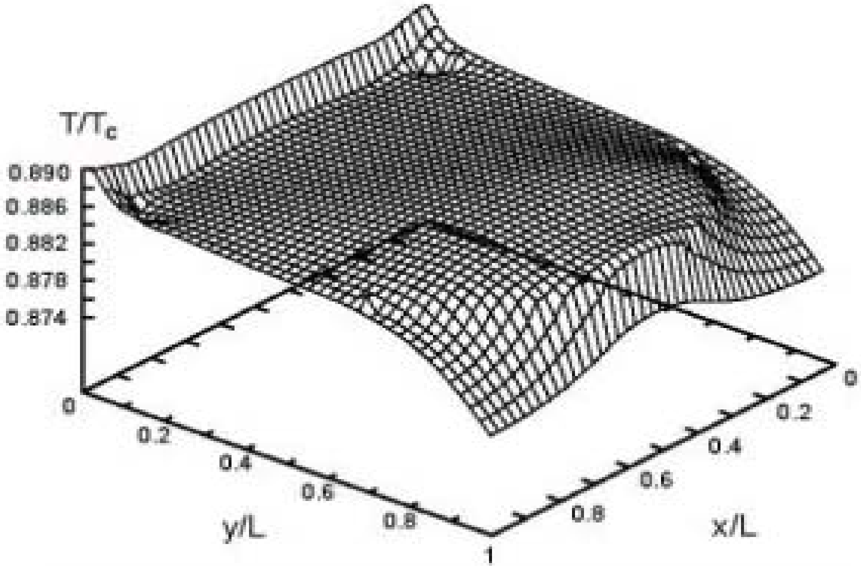
Diffuse profile

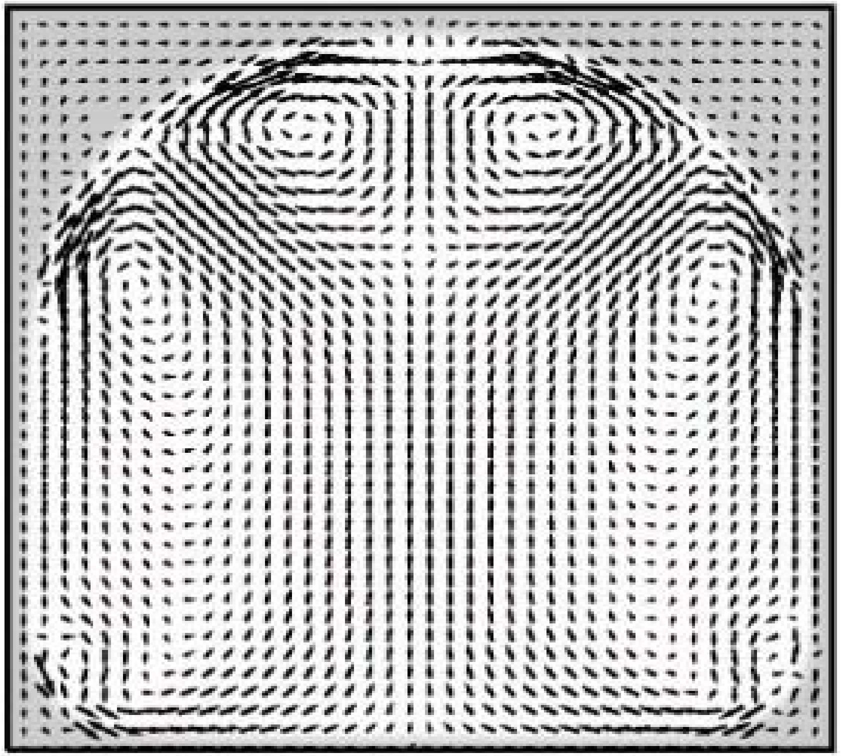
2-4. Latent heat transport is suppressed
Large gradient in gas film





$\lambda = An \quad (\lambda_{liq}/\lambda_{gas} = 5)$





2.5 Efficient heat transport by flow along wetting layer, no gravity

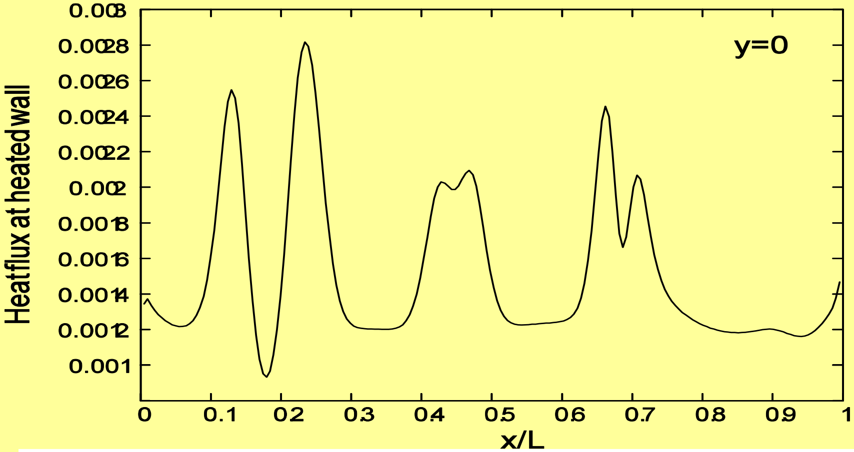
$$\lambda_{\text{liq}} = 5\lambda_{\text{gas}}$$

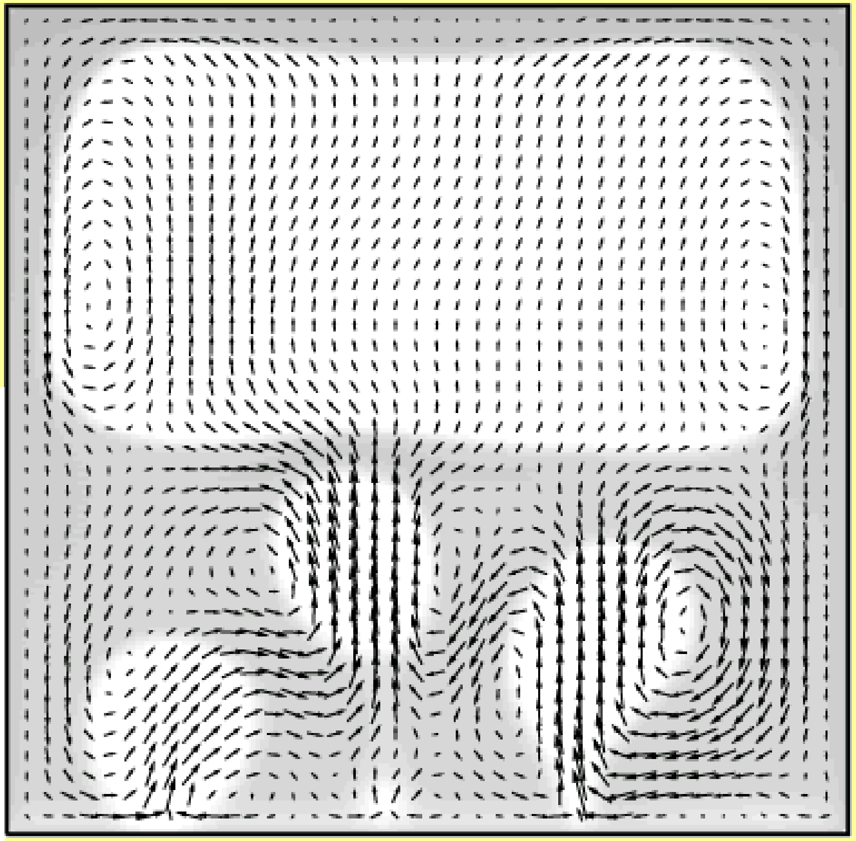
$$Nu = \frac{\lambda_{\text{eff}}}{\lambda_{\text{liq}}} = 5$$

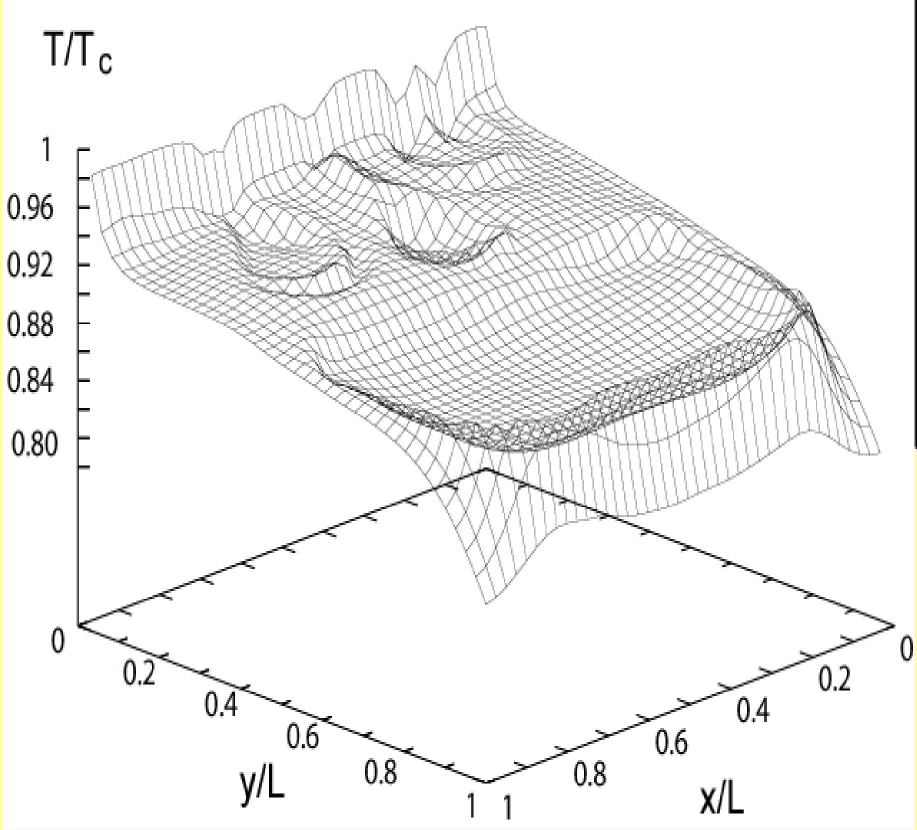
$$T_{\text{bot}}/T_c = 0.895$$

$$T_{\text{top}}/T_c = 0.875$$

Steady flow, but drying for larger Tbot





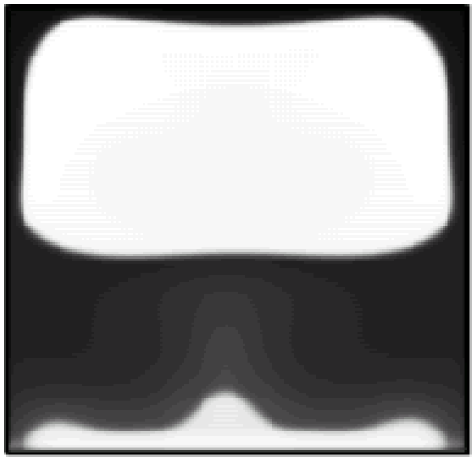


In boiling ∇T is small even in bulk liquid and is localized at boundary walls

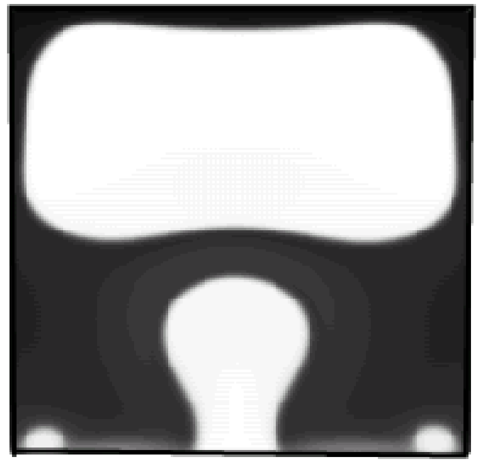
$Nu = 10$

Fully developed: t=70000

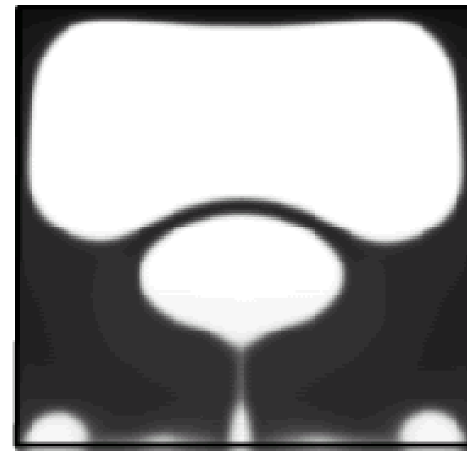
8-1. Boiling: g applied , Tt/Tc=0.77 , Tb/Tc is changed from 0.94 to 1 at t=34000



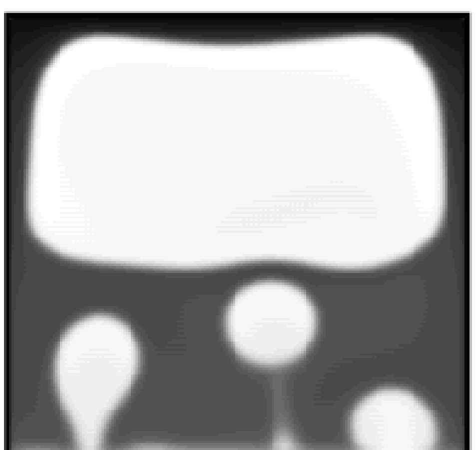
t=34600



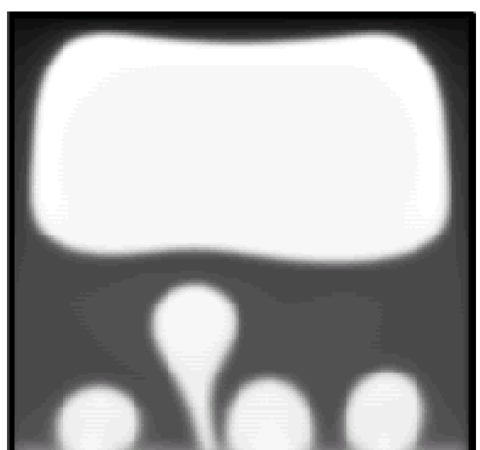
t=35100



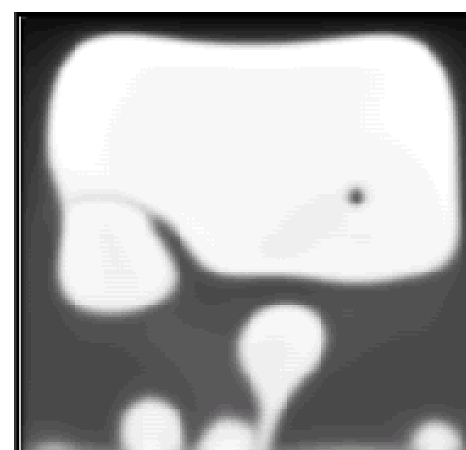
t=35230



t=66300



t=71000



t=74100

PART 3

Wetting dynamics:
evaporation, spreading,….

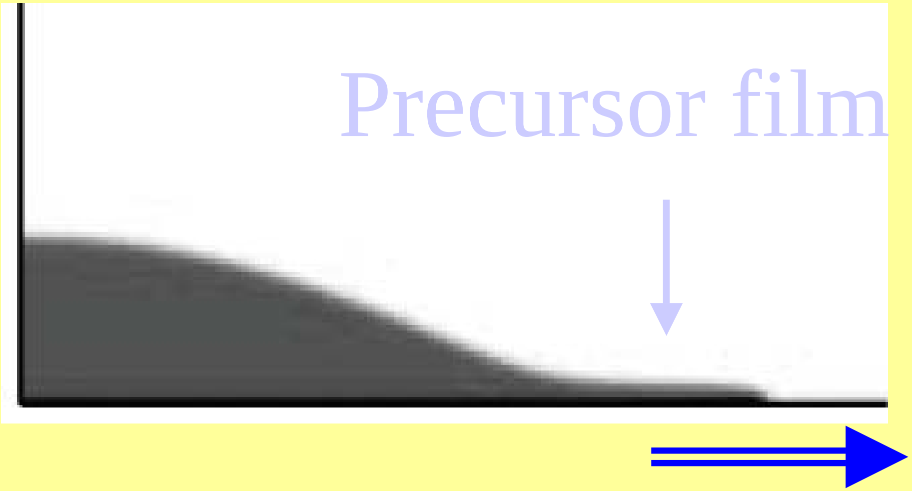
2D simulations but 3D axisymmetric droplets

M2勅使河原

3a) Precursor film formation in complete wetting

Plate temperature Tw was not higher than initial liquid temperature

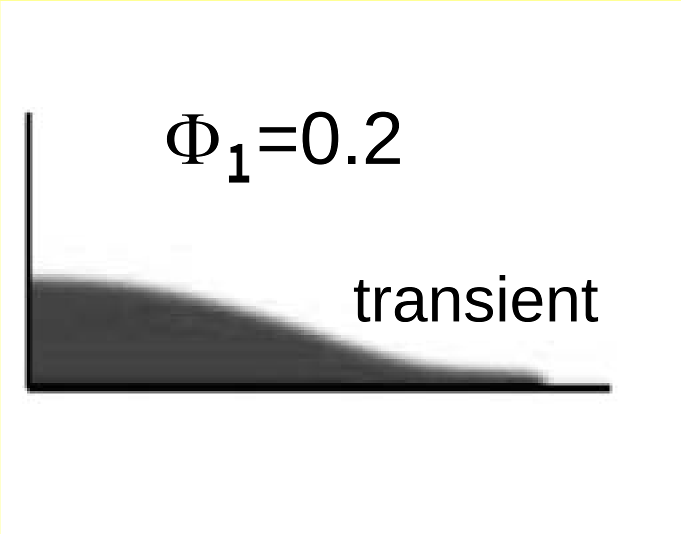
Complete wetting case



Fast growth of precurser
film due to evaporation and condensation

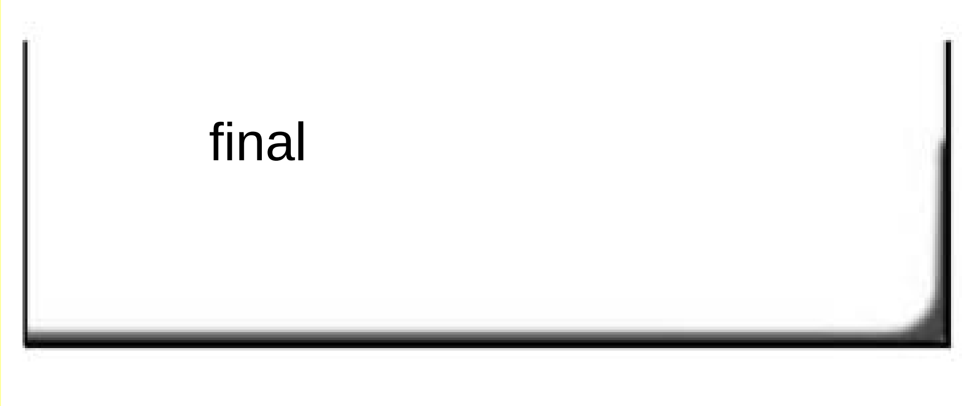
Large Φ_1 ⇒ Precursor film extension

Nonequilibrium spreading: complete wetting : $\Phi_1 > 0.14$



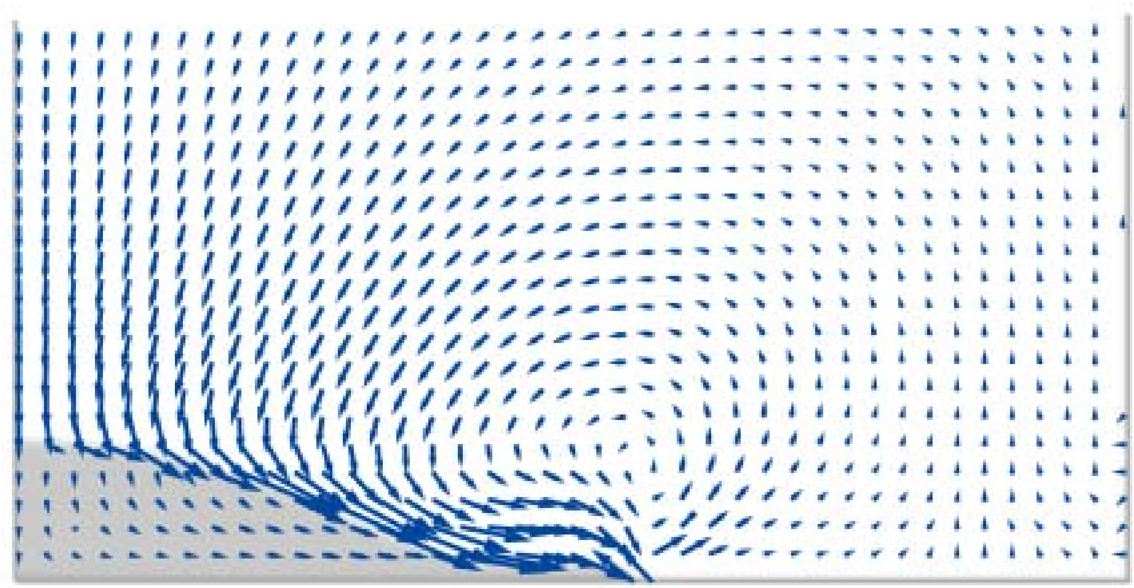
Spreading on dry wall surface.

Wall is cooler than in fluid.

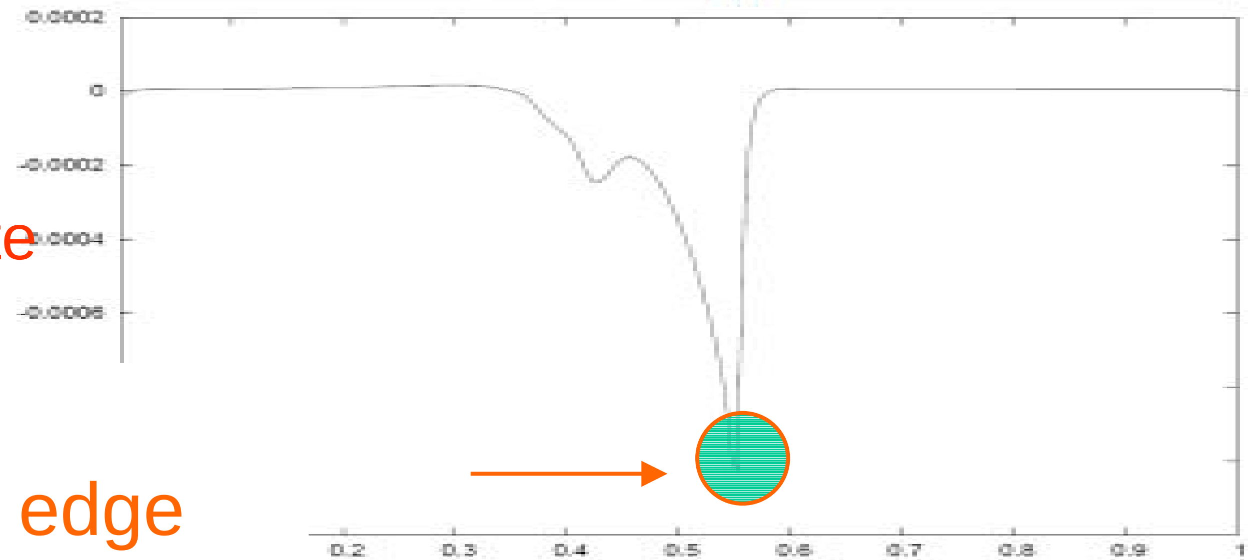


Precursor film formed ahead of droplet

Circulating velocity field



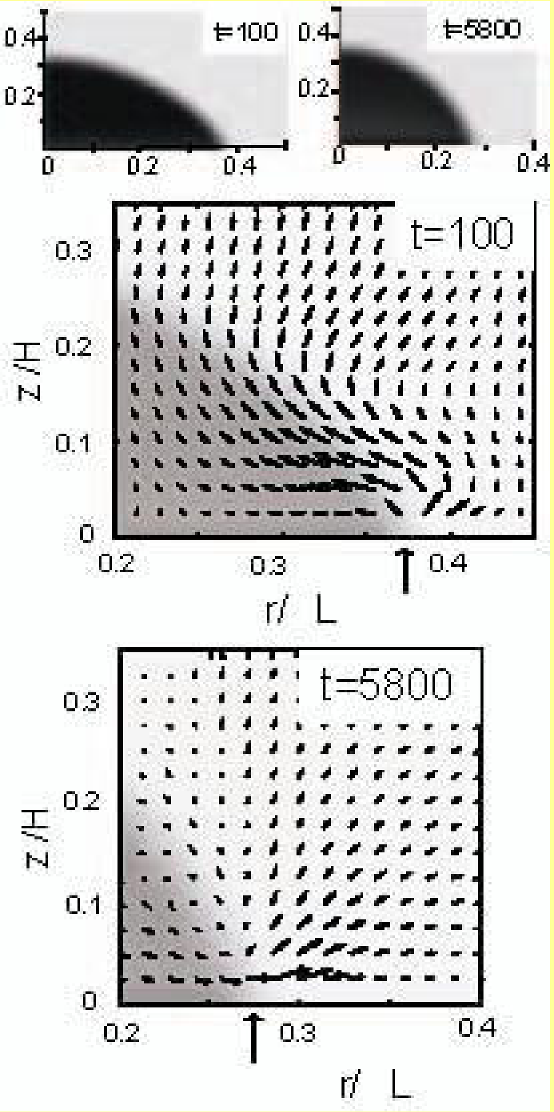
Heat flux from plate

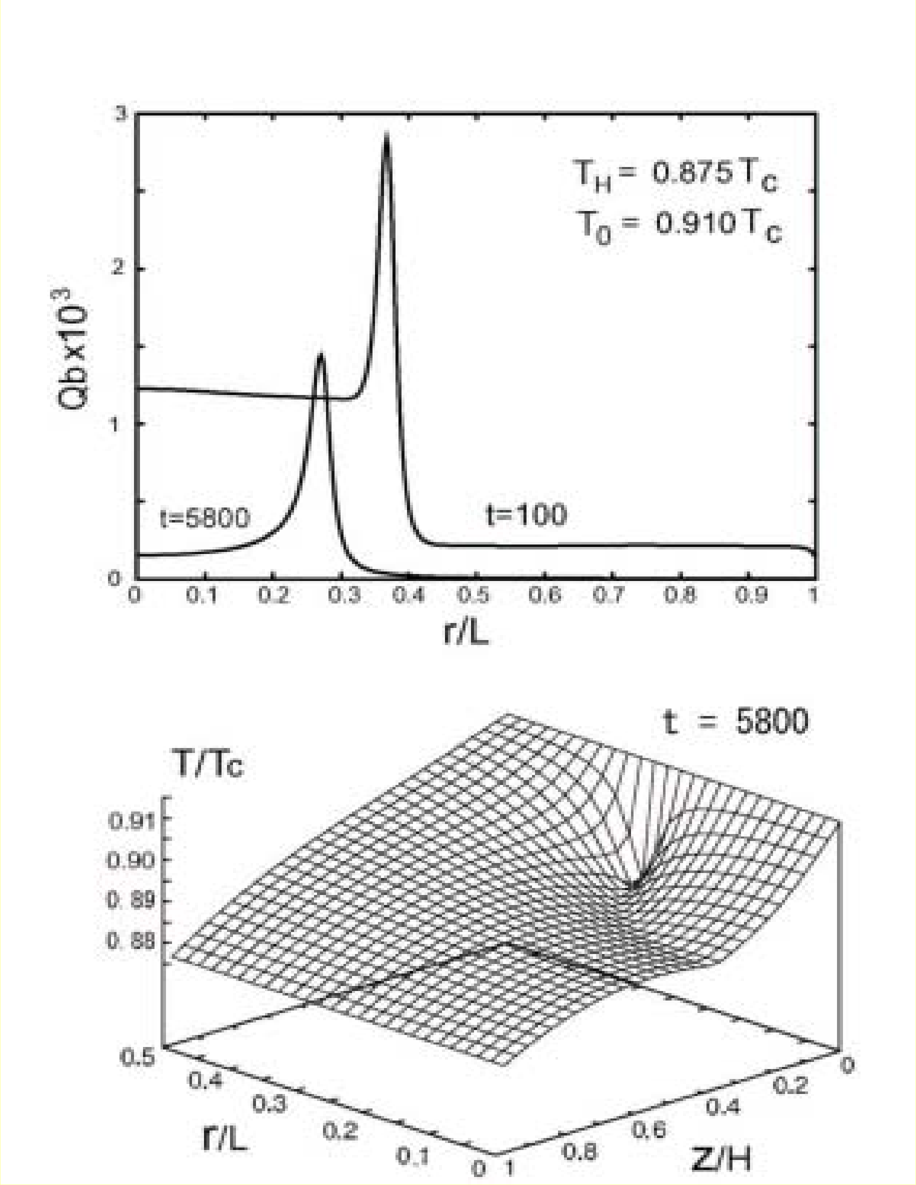


$$Q = -\lambda\, (\nabla T)_{plate}$$

Condensation and
heat absorption at edge

3b) Droplet evaporation in partial wetting



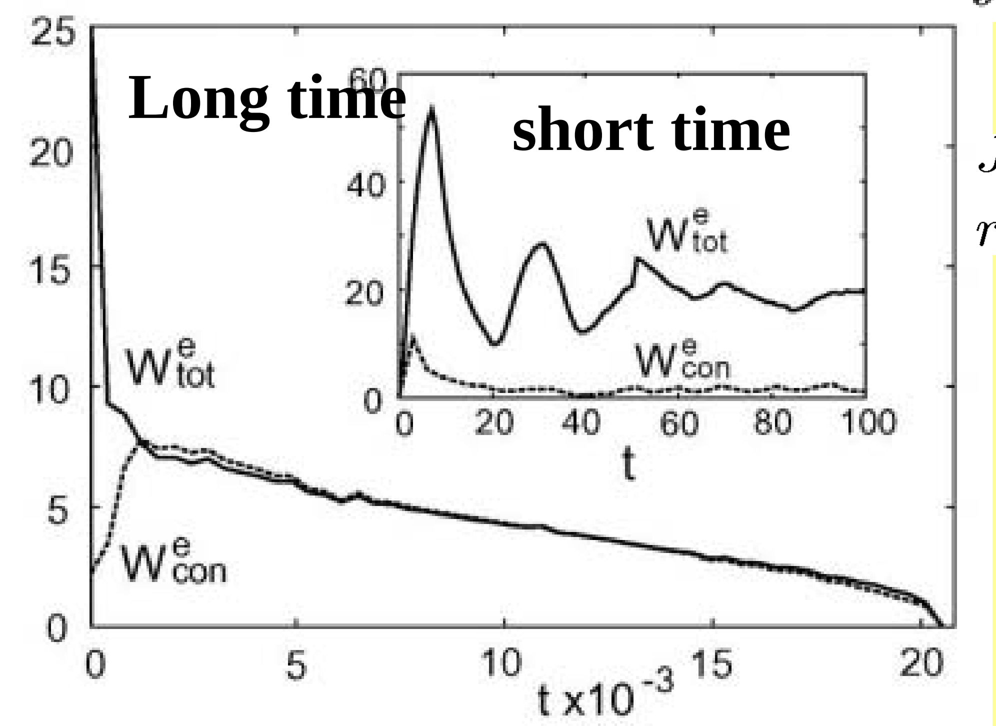


J: $$T\Delta s J - \boldsymbol{\nu}\cdot[(\lambda\nabla T)_{\mathrm{gas}} - (\lambda\nabla T)_{\mathrm{liq}}] = 0,$$

Evaporation rates

All surface $$W^e_{\mathrm{tot}} = 2\pi\int_0^{r_{\mathrm{c}}} dr\, r J/\sin\theta.$$

Near contact line
$$W^e_{\mathrm{con}} = 2\pi\int_{r_{\mathrm{c}}-r_w}^{r_{\mathrm{c}}} dr\, r J/\sin\theta.$$



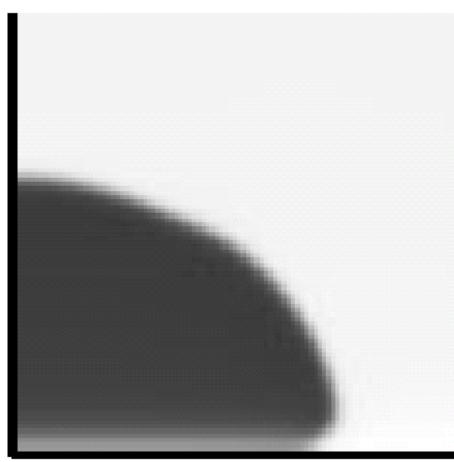
J:mass flux through interface
$r_w = 2\times$interface width

On long times evaporation occurs only at contact line

Droplet detachment by strong heating

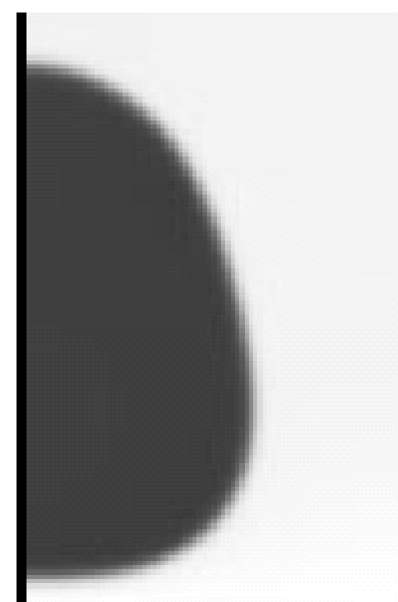
On wall T/Tc is changed from 0.875 to 0.975

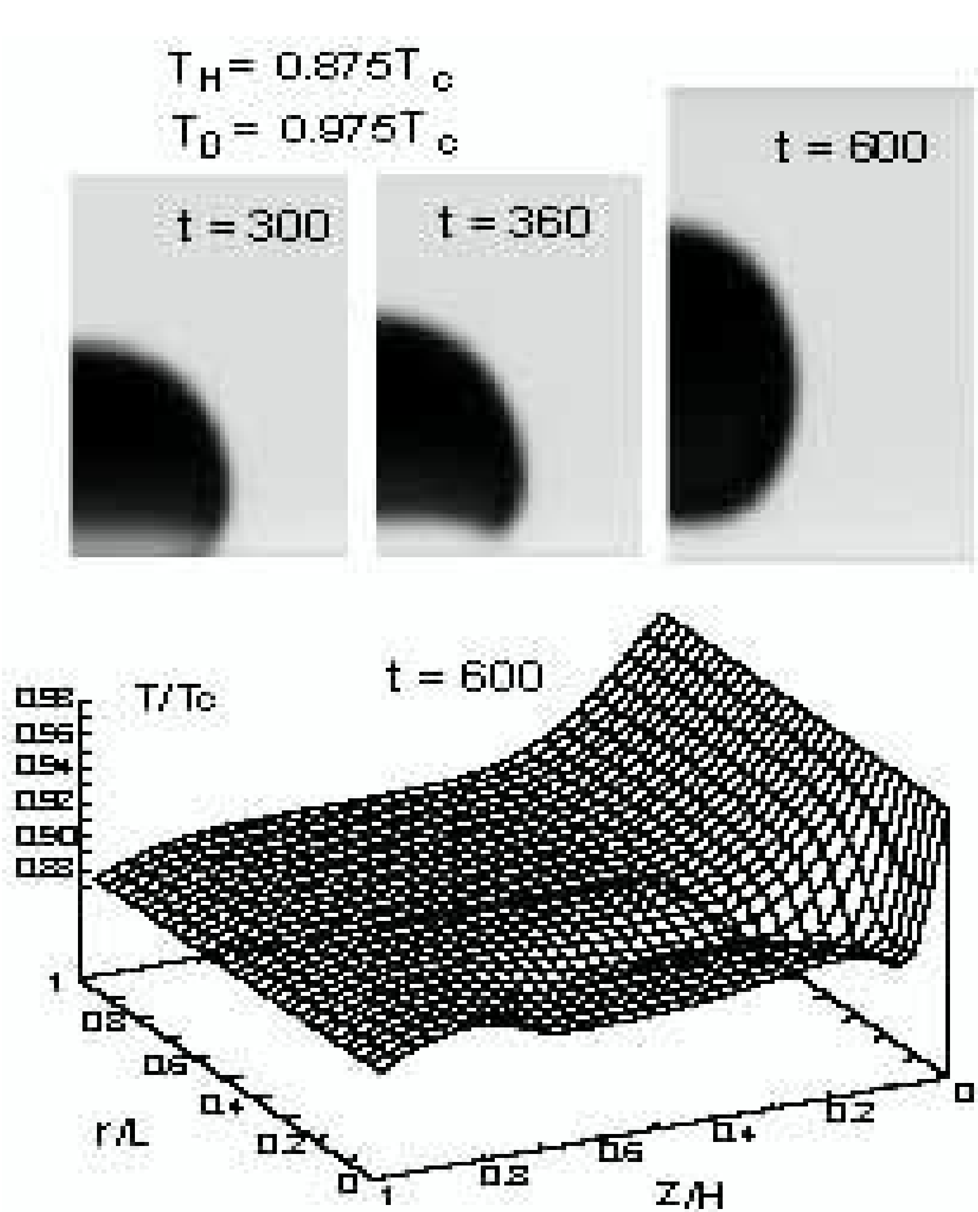
No gravity



Thin vapor layer formed

Gas pushes liquid droplet





$T_H = 0.875T_c$
$T_0 = 0.975T_c$
t = 300
t = 360
t = 600
t = 600
T/Tc
r/L
Z/H

PART 4

Marangoni effect in mixtures

surface tension change:

tangential component of shear stress

$$[\sigma \cdot \mathbf{n}]_{\text{jump}} = \nabla \gamma$$

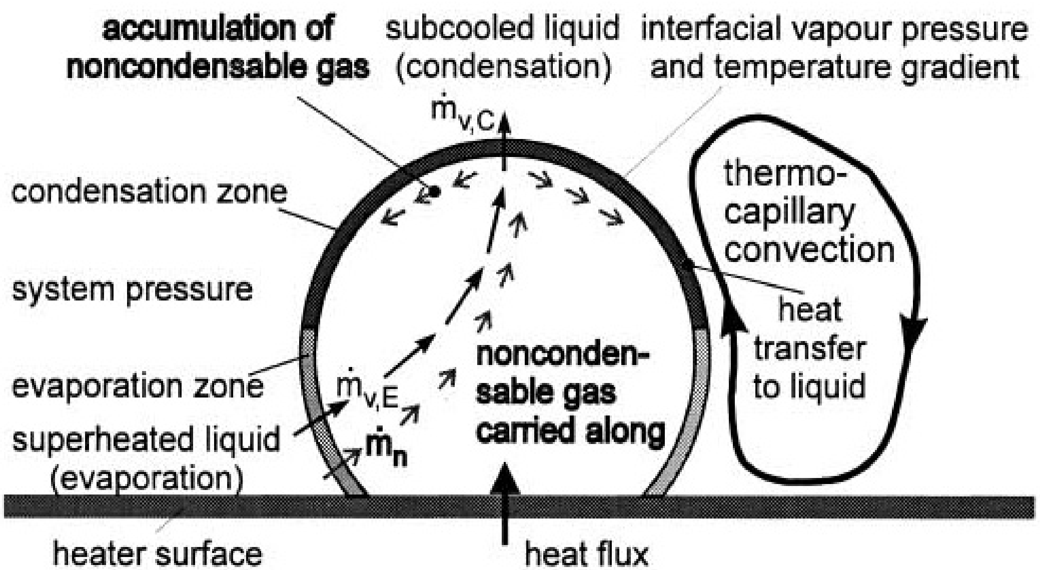


Fig. 13. Nondeformable isolated vapour bubble with steady-state mass flow.

沸騰バブル内対流は、混入ガスによる
Marangoni effect

PART 4

Marangoni effect in mixtures

surface tension change:

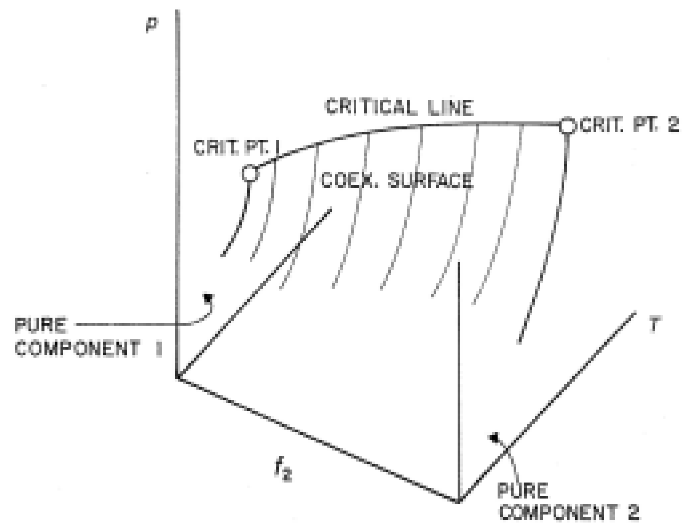
$$\delta\gamma = \left(\frac{\partial\gamma}{\partial T}\right)_\zeta \delta T + \left(\frac{\partial\gamma}{\partial\zeta}\right)_T \delta\zeta$$

Solute fugacity: $\zeta = e^{\mu_2/kT}$

Surface tension is defined on the coexistence surface P=Pcx(T,ζ). At constant P,

$$\delta T = (\partial T/\partial\zeta)_{\mathrm{cx},p}\delta\zeta$$

$$\gamma = \gamma_0 - k_B T\Gamma \text{ (Gibbs)}$$



No Marangoni for pure fluids P=Pcx(T) or T=Tcx(P)

solvent (C02 or H20)+solute

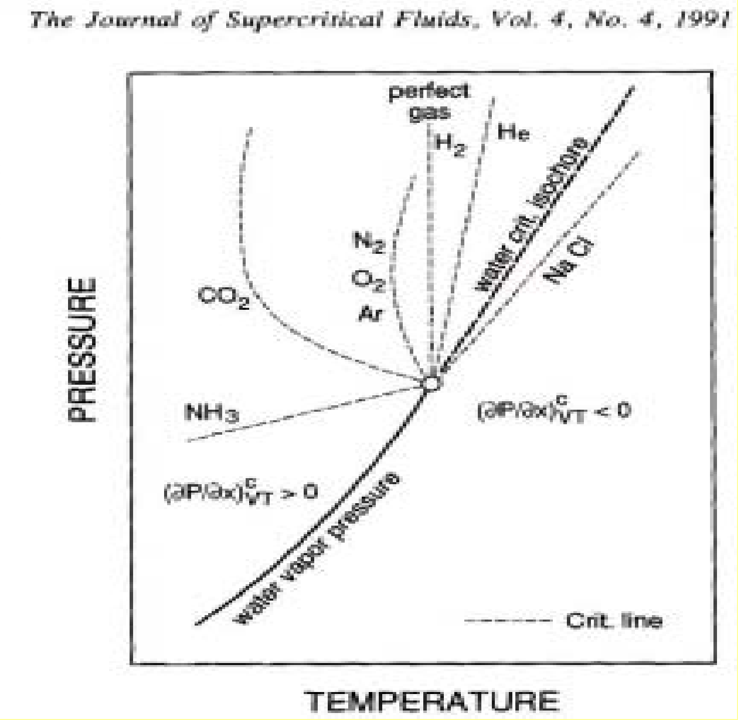
$$\gamma' = \left(\frac{\partial \gamma}{\partial T}\right)_{\mathrm{cx},p} = \frac{d\gamma_0}{dT} \times \frac{dp_c}{dX} / K_{\mathrm{cr}}$$

positive for ethanol…..
negative for argon….

TABLE I: T_c'/T_{c0}, $p_c'/n_{c0}T_{c0}$, $K_{\mathrm{Kr}}/n_{c0}T_{c0}$, and p_c'/K_{Kr} for CO_2+ solute and for H_2O + solute near the solvent critical point, where $T_c' = dT_c/dX$ and $p_c' = dp_c/dX$. The last quantity is related to the temperature-derivative of the surface tension in Eq.(2.66). Data are taken from Refs.[25–27].

Solvent	Solute	T_c'/T_{c0}	$p_c'/n_{c0}T_{c0}$	$K_{\mathrm{Kr}}/n_{c0}T_{c0}$	p_c'/K_{Kr}
CO_2	Neon	−0.0517	0.919	1.02	0.900
CO_2	Argon	−0.192	0.553	0.936	0.591
CO_2	Ethanol	0.539	0.694	−0.380	−1.81
CO_2	Pentanol	2.20	1.96	−2.42	−0.809
CO_2	Ethane	−0.182	−0.187	0.175	−1.07
H_2O	Toluene	−1.32	−0.948	1.434	−0.661
H_2O	D_2O	−0.0050	−0.0041	0.0050	−1.21

(Onuki 2008)



(Sengers)

Bubble velocity in mixture $v_g + v_M + v_c$

gravity

$$v_g \sim \frac{\rho - \rho'}{\eta} R^2 g$$

Marangoni

$$v_{\mathsf{M}} \sim \frac{c\gamma'}{\eta\lambda} RQ$$

(c:mass fraction)

Evaporation-condensation

$$v_c \sim \frac{Q}{\rho' T \Delta s}$$

$$v_c / v_M \sim \rho a / \rho' c R \; (a : \text{micro length})$$

Q:heat flux,ρ':gas density,Δs:entropy difference

η:**liquid viscosity, λ:liquid thermal conductivity**

$$v_M = \frac{2}{2\eta + 3\eta'} \frac{\gamma'}{3} R\mathcal{T}'$$

$$\mathcal{T}' \cong \frac{c}{\lambda_{\mathsf{eff}}}\left(\mathcal{Q} - T\frac{[s]}{[c]}\mathcal{I}\right).$$

$\mathcal{T}'$: temperature gradient within bubble

$\mathcal{Q}$: heat flux far from bubble

$\mathcal{I}$: diffusion flux far from bubble

γ' depends on solute species evenn at low densities

Summary

2. Two-phase dynamics with evaporation

and condensation

3 Wetting dynamics: evaporation, spreading,….

4 Marangoni effect in mixtures