On the (im-) possibility of cold to warm distillation

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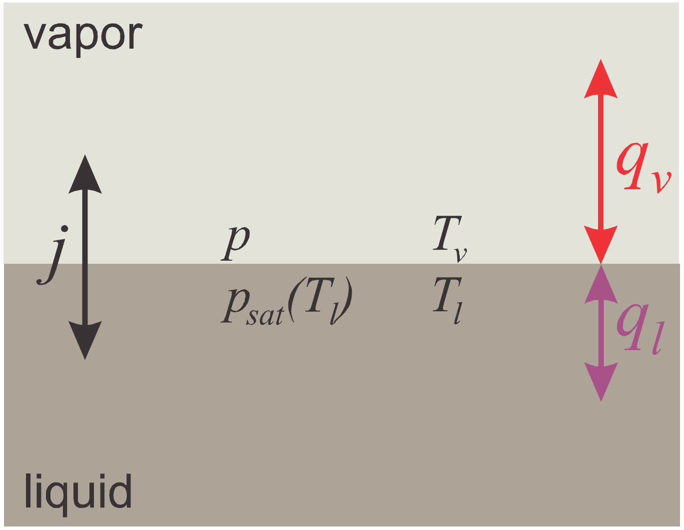
Non-eq. condensation/evaporation [e.g., Kjelstrup & Bedeaux 2010]



mass flux j, Fourier heat flux $q = -\kappa \frac{\partial T}{\partial x}$

Interface conditions (linearized): dimensionless resistivities $\hat{r}_{\alpha\beta}$

$$\begin{bmatrix} \frac{p_{sat}(T_l)-p}{\sqrt{2\pi R T_l}} \\ \\ -\frac{p_{sat}(T_l)}{\sqrt{2\pi R T_l}} \frac{T_v - T_l}{T_l} \end{bmatrix} = \begin{bmatrix} \hat{r}_{11} & \hat{r}_{12} \\ \\ \hat{r}_{21} & \hat{r}_{22} \end{bmatrix} \begin{bmatrix} j \\ \\ \frac{q_v}{R T_l} \end{bmatrix}$$

Onsager symmetry: $\hat{r}_{21} = \hat{r}_{12}$

positive entropy generation: $\hat{r}_{11} \geq 0 \,, \quad \hat{r}_{22} \geq 0 \,, \quad \hat{r}_{11}\hat{r}_{22} - \hat{r}_{12}\hat{r}_{21} \geq 0$

Questions: **a) values of $\hat{r}_{\alpha\beta}$?**

b) when must non-eq. interface be considered?

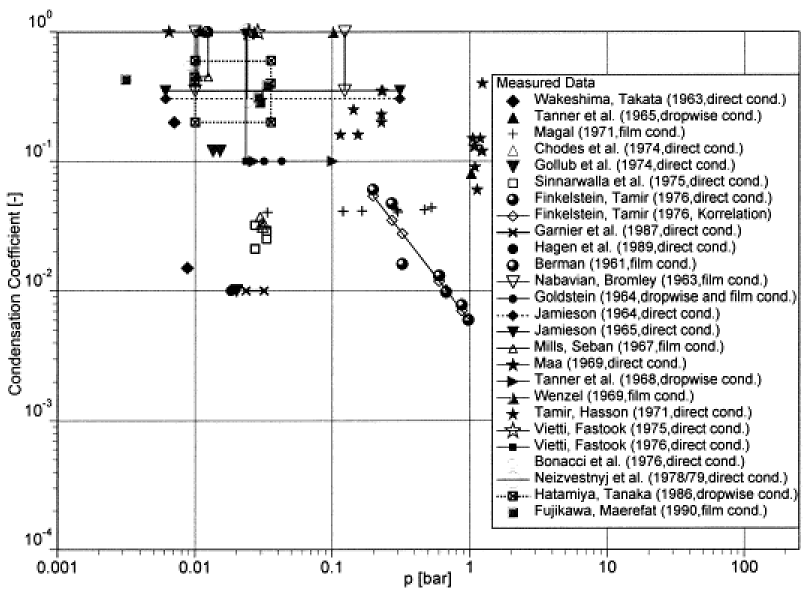
Interface resitivities

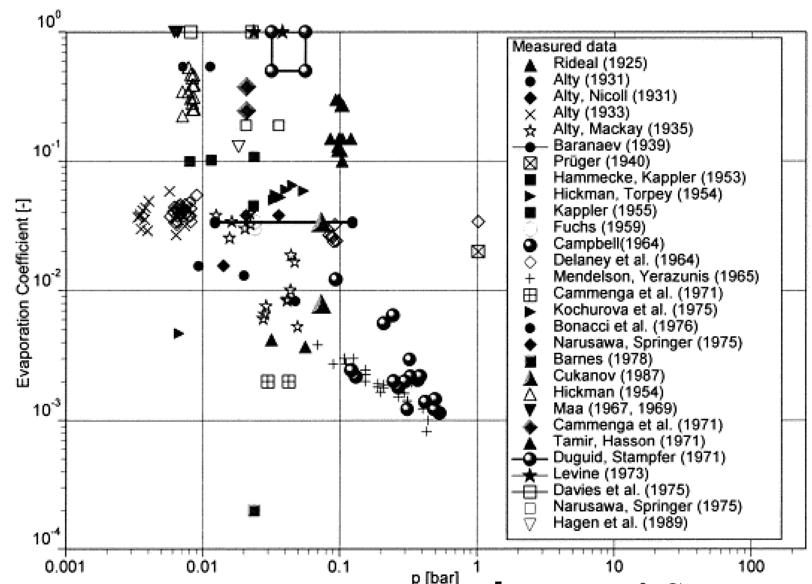
Kinetic theory prediction condensation coefficient $\psi \leq 1$

$$\hat{r}_{kin.\ theory} = \begin{bmatrix} \frac{1}{\psi} - 0.40044 & 0.126 \\ 0.126 & 0.294 \end{bmatrix}$$

Compare to Hertz–Knudsen–Schrage equation

$$j = \frac{2\mathcal{K}_{C/E}}{2 - \mathcal{K}_{C/E}} \left(\frac{p_{sat}(T_l)}{\sqrt{2\pi R T_l}} - \frac{p_v}{\sqrt{2\pi R T_v}} \right)$$



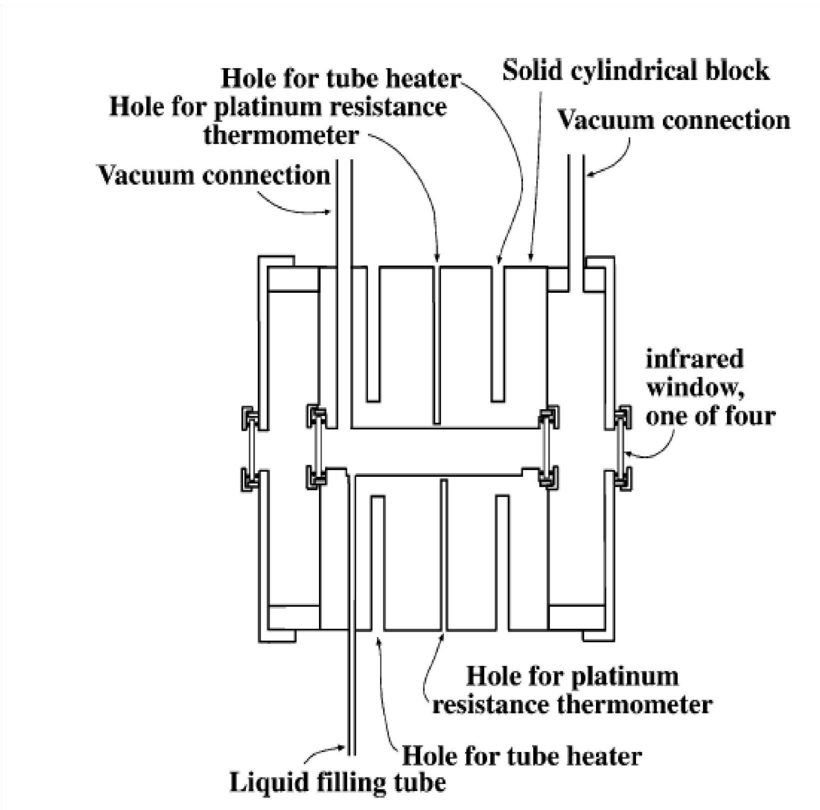


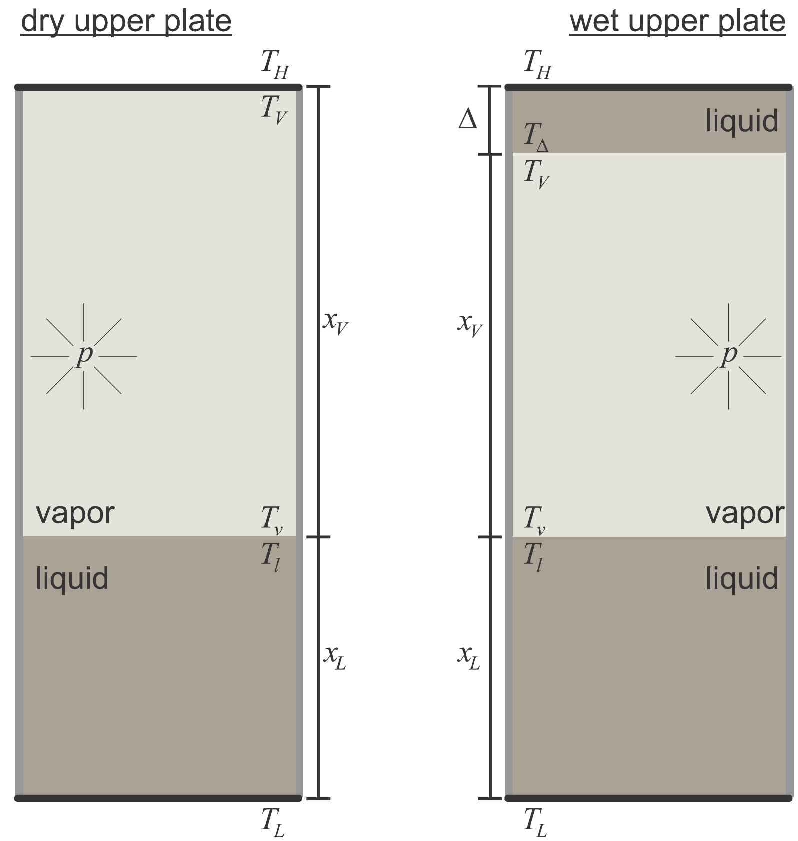
[Marek&Straub, 2001]

$\mathcal{K}_{C/E}$ — condensation/evaporation coefficients

$$\hat{r}_{11} \simeq \frac{2-\mathcal{K}_{C/E}}{2\mathcal{K}_{C/E}} : \ \mathcal{K}_{C/E} \in \left(10^{-3}, 1\right) \implies \hat{r}_{11} \in \left(\tfrac{1}{2}, 10^3\right)$$

Phillips-Onsager cell [Phillips et al., since 2002]





control: T_L , T_H **measure:** $p\,(T_H)$

compute: **Phillips' heat of transfer**

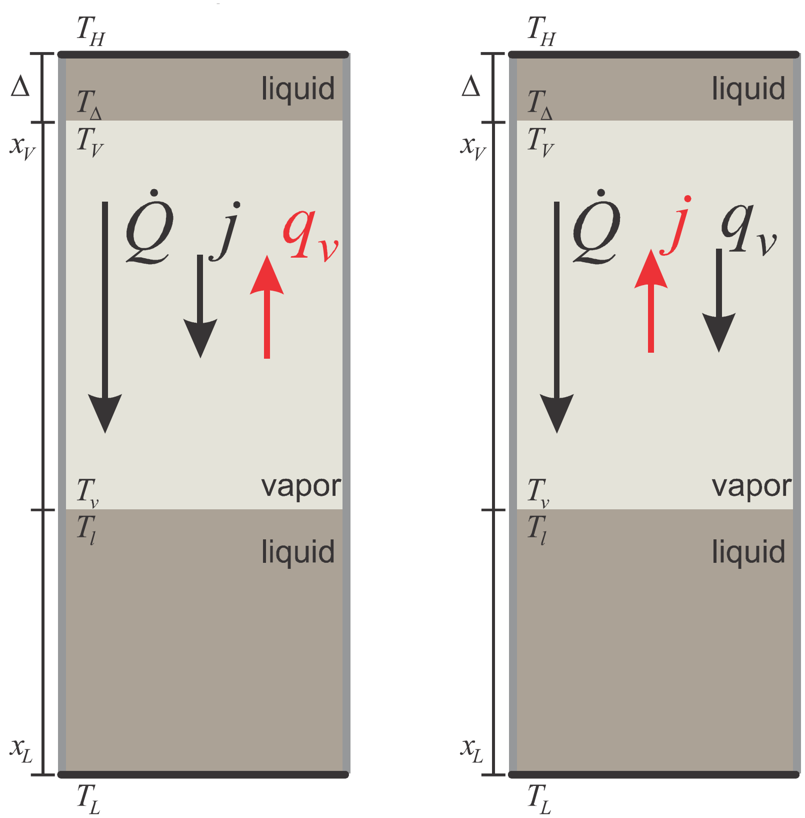
$$Q^* = -\frac{T_L}{p_{sat}\,(T_L)}\frac{dp\,(T_H)}{dT_H}$$

T - **difference is the sole driving force!!**

non-obvious transport modes (wet upper plate)

total heat flux in vapor: $\dot{Q} = jh_{fg} + q_v$

inverted T-profile	**cold to warm distillation**
heat $\dot{Q}$ and mass j go from warm to cold	heat $\dot{Q}$ goes from warm to cold
but Fourier flux q_v points from cold to warm	but mass j goes from cold to warm



predicted by non-eq. TD **measured by Phillips et al.??**

T - **difference is the sole driving force!!**

1-D model of Phillips-Onsager cell

Interface conditions (linearized): dimensionless resistivities $\hat{r}_{\alpha\beta}$

$$\begin{bmatrix} \frac{p_{sat}(T_l)-p}{\sqrt{2\pi R T_l}} \\ \\ -\frac{p_{sat}(T_l)}{\sqrt{2\pi R T_l}}\frac{T_v-T_l}{T_l} \end{bmatrix} = \begin{bmatrix} \hat{r}_{11} & \hat{r}_{12} \\ \\ \hat{r}_{21} & \hat{r}_{22} \end{bmatrix} \begin{bmatrix} j \\ \\ \frac{q_v}{RT_l} \end{bmatrix}$$

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positive entropy generation: $\hat{r}_{11} \geq 0\ ,\quad \hat{r}_{22} \geq 0\ ,\quad \hat{r}_{11}\hat{r}_{22} - \hat{r}_{12}\hat{r}_{21} \geq 0$

Mass and energy balances (1-D): $\alpha = l, v$ (liquid, vapor)

$$\frac{dj}{dx} = 0\ ,\quad \frac{d\dot{Q}}{dx} = \frac{d}{dx}\left[j h_\alpha + q_\alpha\right] = 0$$

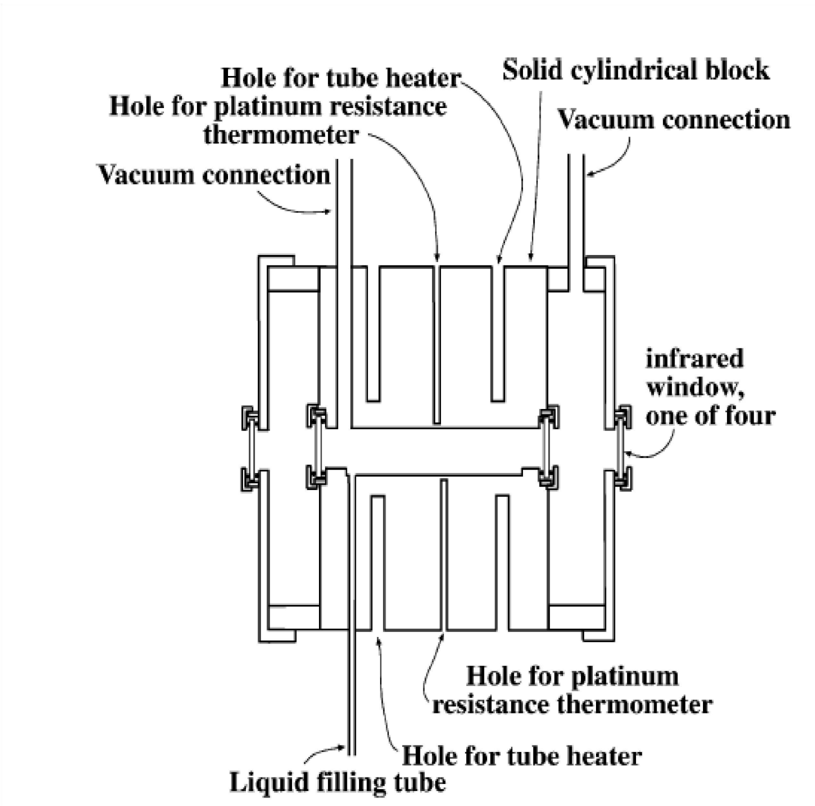
mass flux: j

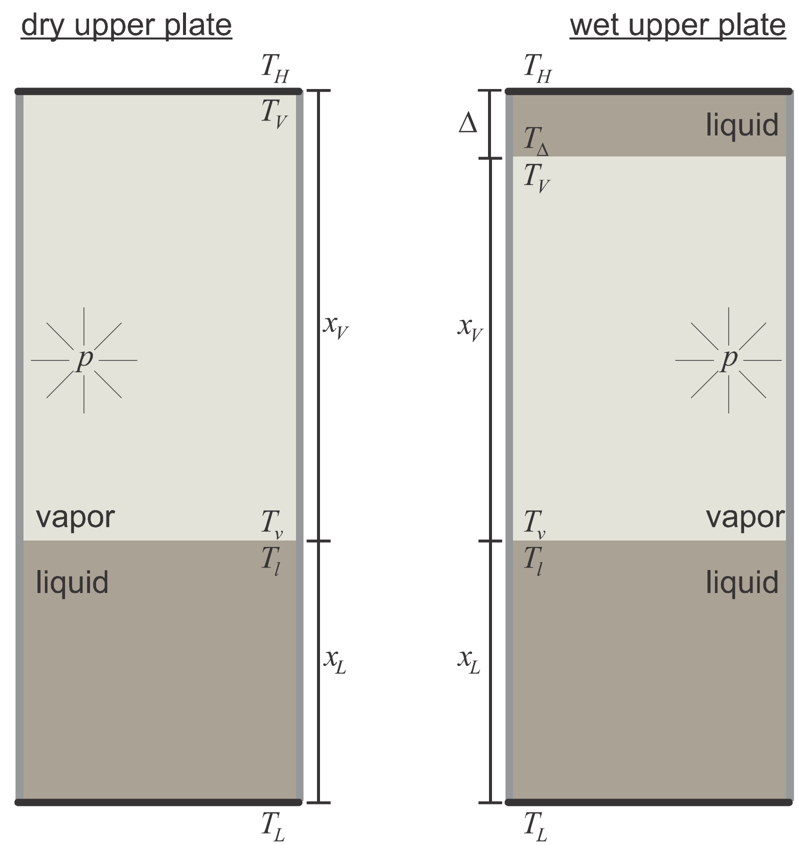
total energy flux: $\dot{Q}$

Fourier heat flux: $q_\alpha = -\kappa_\alpha \frac{\partial T}{\partial x}$

enthalpy: h_α

Phillips-Onsager cell [Phillips et al., since 2002]





control: $T_L\ ,\ T_H$ **measure:** $p\,(T_H)$

compute: **Phillips' heat of transfer**

$$Q^* = -\frac{T_L}{p_{sat}\,(T_L)}\frac{dp\,(T_H)}{dT_H}$$

observation of cold to warm distillation

Dry upper plate (linearized) [HS&SK&DB 2012]

no convection: $j = 0$, **conductive heat flux:** $\dot{Q} = q_v = q_l = const$

$$\dot{Q} = -\frac{p_{sat}\left(T_L\right) R}{\sqrt{2\pi R T_L}} \mathcal{Q}_d \left(T_H - T_L\right)$$

cell conduction coefficient (dim.less)

$$\frac{1}{\mathcal{Q}_d} = \frac{\kappa_V}{\kappa_L}\frac{x_L}{\lambda_0} + \frac{x_V}{\lambda_0} + \hat{r}_{22} + \frac{2-\chi}{4\chi}$$

microscopic reference length

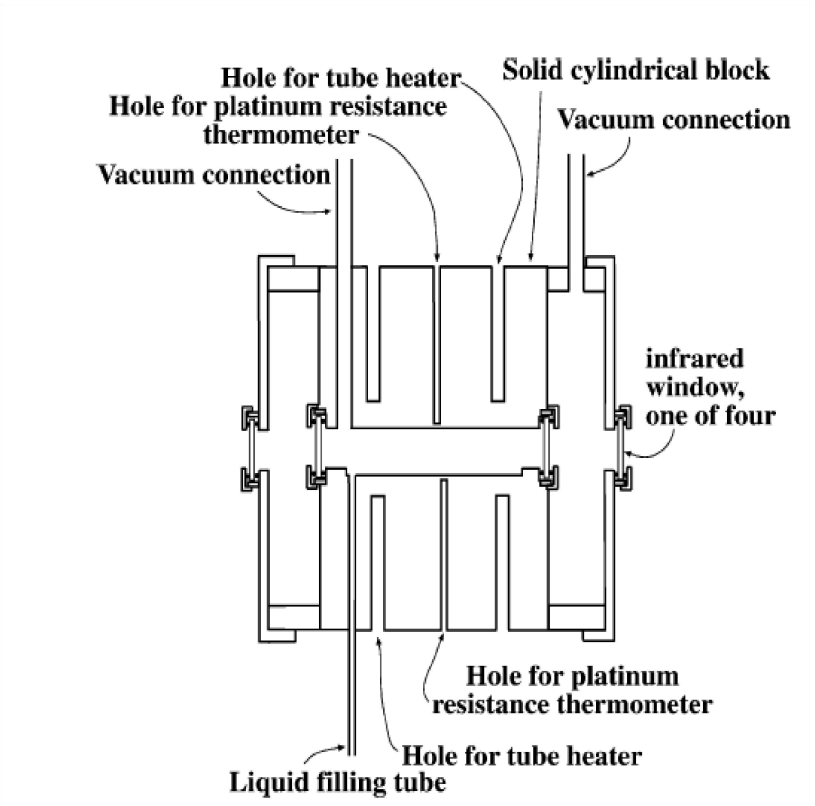
$$\lambda_0 = \frac{\kappa_V \sqrt{2\pi R T_L}}{p_{sat}\left(T_L\right) R} \lesssim 0.05\,\mathrm{mm}$$

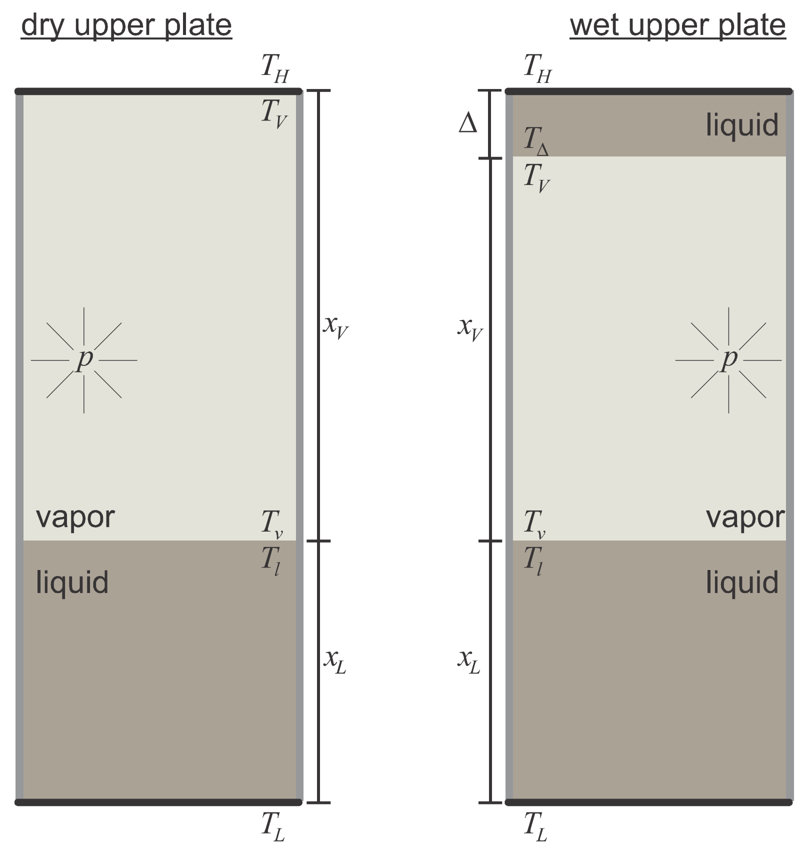
Phillips' heat of transfer $Q^*_{\mathrm{dry}} = -\frac{T_L}{p_{sat}(T_L)}\frac{dp(T_H)}{dT_H}$

$$Q^*_{\mathrm{dry}} = -\frac{\frac{h^L_{fg}}{RT_L}\frac{\kappa_V}{\kappa_L}\frac{x_L}{\lambda_0} + \hat{r}_{12}}{\frac{\kappa_V}{\kappa_L}\frac{x_L}{\lambda_0} + \frac{x_V}{\lambda_0} + \hat{r}_{22} + \frac{2-\chi}{4\chi}}$$

only small cells $\frac{x_V}{\lambda_0} \lesssim \left\{\hat{r}_{12}, \hat{r}_{22}, \frac{2-\chi}{4\chi}\right\}$ **affected by resist.** $\hat{r}_{\alpha\beta}$, **acc. coeff.** χ

Phillips-Onsager cell [Phillips et al., since 2002]





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compute: **Phillips' heat of transfer**

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observation of cold to warm distillation

Wet upper plate (linearized) [HS&SK&DB 2012]

convective and conductive transport

$$j = \frac{A}{2\left[C+D\right]+EB}\left[-\frac{p_{sat}\left(T_L\right)}{T_L\sqrt{2\pi R T_L}}\left(T_H - T_L\right)\right]$$

$$\dot{Q} = \frac{B}{2\left[C+D\right]+EB}\left[-\frac{p_{sat}\left(T_L\right)R}{\sqrt{2\pi R T_L}}\left(T_H - T_L\right)\right]$$

Phillips' heat of transfer $Q^*_{\text{wet}} = -\frac{T_L}{p_{sat}(T_L)}\frac{dp(T_H)}{dT_H}$

$$Q^*_{\text{wet}} = \frac{h^L_{fg}}{RT_L}\frac{1}{1+\frac{B+\frac{x_L+\Delta}{\Delta}\left[\frac{C+D}{E}\right]}{\frac{x_L}{\Delta}B+\frac{x_L+\Delta}{\Delta}\left[\frac{C+D}{E}\right]}}$$

where

$$A = \hat{Z}\frac{h^L_{fg}}{RT_L}\left(\frac{1}{2}\frac{x_V}{\lambda_0}+\hat{r}_{22}\right)-\hat{r}_{12}\ ,$$

$$B = \hat{Z}\frac{h^L_{fg}}{RT_L}\frac{h^L_{fg}}{RT_L}\left(\frac{1}{2}\frac{x_V}{\lambda_0}+\hat{r}_{22}\right)-\left(\hat{Z}+1\right)\frac{h^L_{fg}}{RT_L}\hat{r}_{12}+\hat{r}_{11}$$

$$C = \hat{r}_{11}\frac{1}{2}\frac{x_V}{\lambda_0}\geq 0\ ,\quad D = \hat{r}_{11}\hat{r}_{22}-\hat{r}_{12}^2\geq 0\ ,\quad E = \frac{\kappa_V}{\kappa_L}\frac{x_L+\Delta}{\lambda_0}\geq 0$$

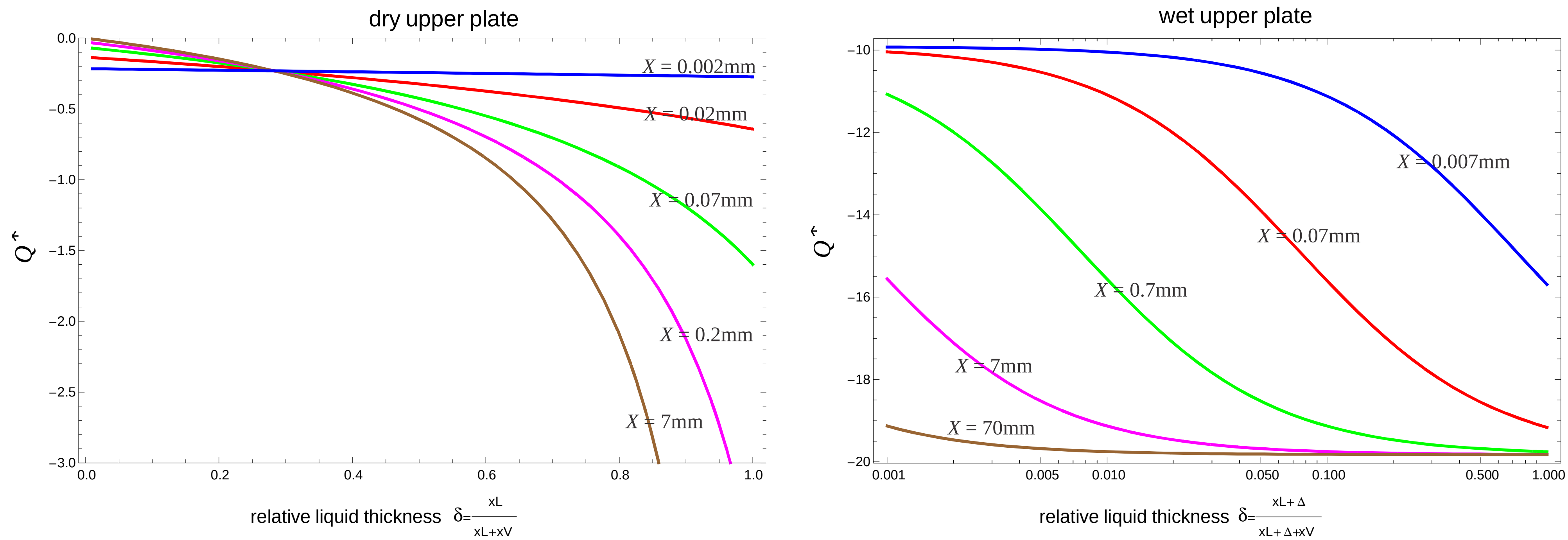
$$\frac{d\ln p_{sat}}{d\ln T} = \hat{Z}\frac{h^L_{fg}}{RT_L}$$

only small cells $\frac{x_V}{\lambda_0}\lesssim\{\hat{r}_{12},\hat{r}_{22}\}$ affected by resistivities $\hat{r}_{\alpha\beta}$

Heat of transfer [HS&SK&DB 2012]

$Q^* = -\frac{T_L}{p_{sat}(T_L)} \frac{dp(T_H)}{dT_H}$ **is system property**

$Q^*_{\text{dry}}, Q^*_{\text{wet}}$ depend strongly on thickness of bulk layers



X – cell thickness

experiment: $X \simeq 7\,\text{mm}$, $\delta \simeq 0.5$

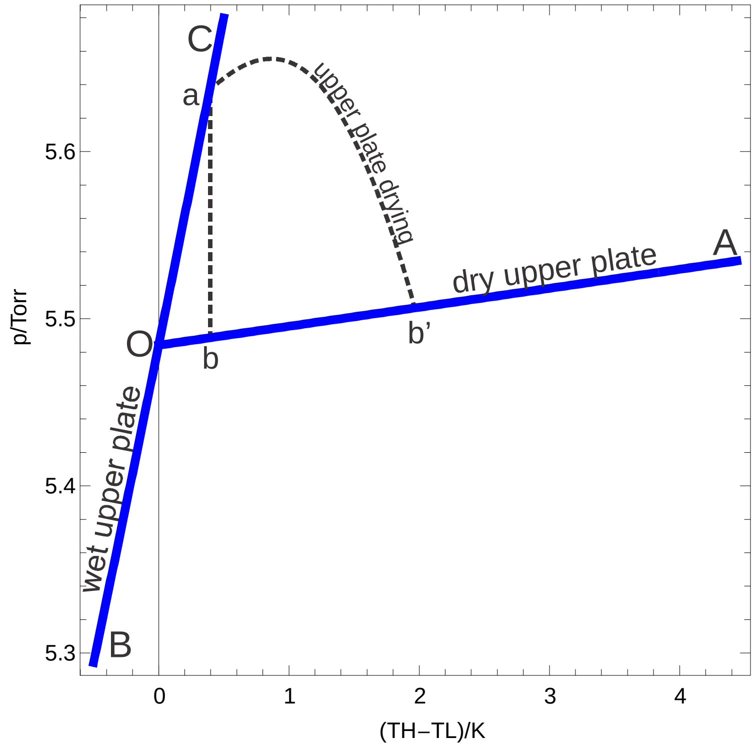
narrow cells (small X): **dominated by interfacial processes, small** $Q^*_{\text{dry}}, Q^*_{\text{wet}}$

wide cells (large X): **dominated by bulk processes, large** $Q^*_{\text{dry}}, Q^*_{\text{wet}}$

present measurements not sufficiently exact to determine resistivities $\hat{r}_{\alpha\beta}$ **!**

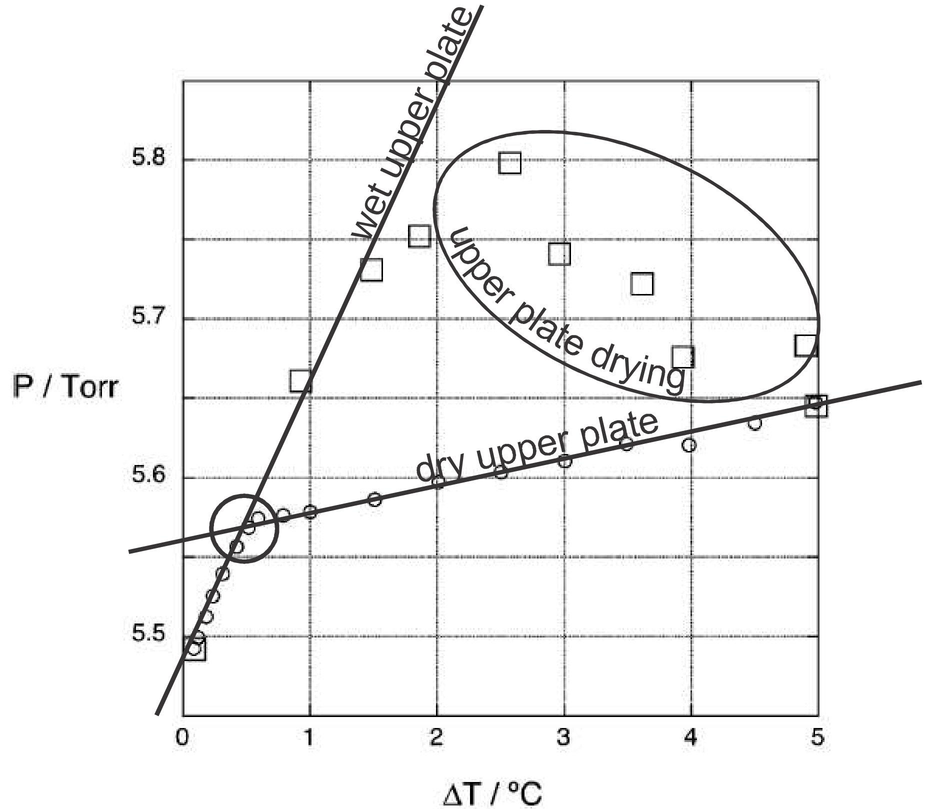
Pressure and heat of transfer [HS&SK&DB 2012]

model (kinetic theory coefficients): **experiment:**



$Q^*_{\rm dry} \simeq 0.42 \qquad Q^*_{\rm wet} = 18.4$

kink at $T_H = T_L$



$Q^*_{\rm dry} \simeq 0.9 \qquad Q^*_{\rm wet} = 10$

kink at $T_H = T_L + 0.5\,\mathrm{K}$

qualitative agreement . . . BUT

quantitative disagreement due to:

- **uncertainties in T-measurement ??**
- **different p_{sat} at upper plate (conditioning, wetting surface, . . .) ??**
- **values of $\hat{r}_{\alpha\beta}$??**

Wet upper plate: Inverted temperature profile [Pao 1971]

vapor conductive heat flow opposite total energy flow:

$$j < 0 \,, \quad \dot{Q} < 0 \quad , \quad q_v = \dot{Q} - j h_{fg}^L > 0$$

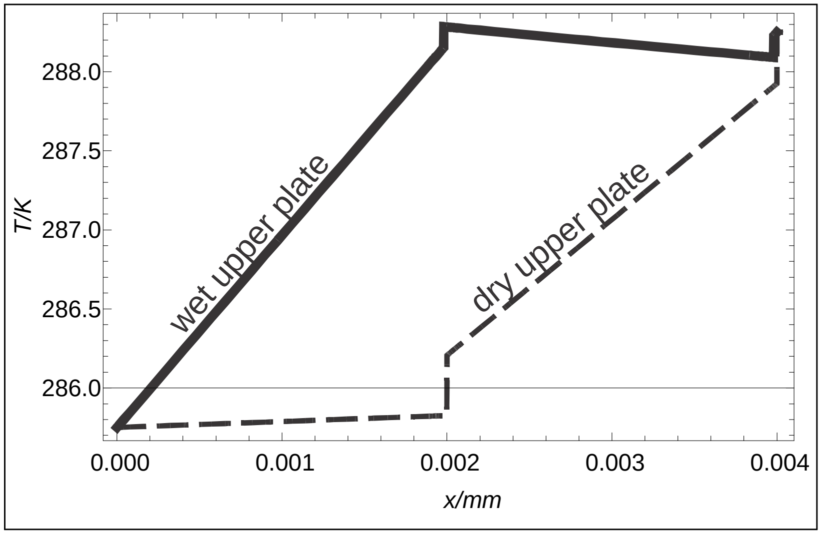
equivalent to

$$\hat{Z} \frac{h_{fg}^L}{RT_L} > \frac{\hat{r}_{11}}{\hat{r}_{12}}$$

water: $7 < \hat{Z} \frac{h_{fg}^L}{RT_L} = \frac{d \ln p_{sat}}{d \ln T} < 20$ between critical and triple points

reported values $\frac{\hat{r}_{11}}{\hat{r}_{12}} \simeq 8 - 10$

inverted temperature profile expected in Phillips-Onsager cell



. . . but look at the scale . . .

Wet upper plate: Cold to warm mass transfer [HS&SK&DB 2012]

convective vapor mass flow opposite total energy flow:

$$j > 0 \,, \quad \dot{Q} < 0 \quad , \quad q_v = \dot{Q} - j h_{fg}^L < 0$$

equivalent to:

$$0 < x_V < \frac{2\lambda_0 \hat{r}_{22}}{\hat{Z}\frac{h_{fg}^L}{RT_L}} \left[\frac{\hat{r}_{12}}{\hat{r}_{22}} - \hat{Z}\frac{h_{fg}^L}{RT_L} \right]$$

kinetic theory predicts:

$$\frac{\hat{r}_{12}}{\hat{r}_{22}} = 0.43$$

triple point:

$$\hat{Z}\frac{h_{fg}^L}{RT_L} \simeq 20$$

$\Longrightarrow$

$$x_V < 0$$

cold to warm distillation impossible with kinetic theory data!!

Wet upper plate: Cold to warm mass transfer [HS&SK&DB 2012]

if observation true, what does it mean for coefficients $r_{\alpha\beta}$?

rewrite previous criterion, entropy condition $\hat{r}_{11}\hat{r}_{22} - \hat{r}_{12}\hat{r}_{12} \geq 0$:

$$\hat{r}_{12} > \hat{Z}\frac{h^L_{fg}}{RT_L}\left(\frac{x_V}{2\lambda_0} + \hat{r}_{22}\right) \quad , \quad \hat{r}_{11} \geq \frac{\hat{r}^2_{12}}{\hat{r}_{22}}$$

combine for necessary criterion for evaporation resitivitiy

$$\hat{r}_{11} \geq \left(\hat{Z}\frac{h^L_{fg}}{RT_L}\right)^2 \left(\frac{1}{4\hat{r}_{22}}\left(\frac{x_V}{\lambda_0}\right)^2 + \frac{x_V}{\lambda_0} + \hat{r}_{22}\right)$$

rhs has minimum at $\hat{r}_{22|\min} = \frac{1}{2}\frac{x_V}{\lambda_0}$

minimum required evaporation resitivitiy

$$\hat{r}_{11} > 2\left(\hat{Z}\frac{h^L_{fg}}{RT_L}\right)^2 \frac{x_V}{\lambda_0} = \frac{x_V}{5.7 \times 10^{-8}\,\mathrm{m}} \simeq 6.1 \times 10^4$$

recall: $\hat{r}_{11} \simeq \frac{2-\mathcal{K}_{C/E}}{2\mathcal{K}_{C/E}} \in \left(\frac{1}{2}, 10^3\right)$

$\Longrightarrow$ **impossible for Phillips' data $x_V = 3.5\,\mathrm{mm}$!!**

Conclusions

- **interface resistivities $\hat{r}_{\alpha\beta}$ relevant mainly for microscopic flows**
- **experimental determination of resistivities $\hat{r}_{\alpha\beta}$ requires:**
  - **carefully instrumented microscopic devices**
  - **complete numerical simulation of device**
- **refined description of bulk phases might be necessary**
  $\Longrightarrow$ **kinetic theory, extended hydrodynamics etc**
- **molecular dynamics gives insight into resistivities** [SK&DB]
- **Phillips-Onsager cell measures (macroscopic) system property Q^***
  $\Longrightarrow$ **only mildly affected by resistivities $\hat{r}_{\alpha\beta}$**
- **cold to warm distillation appears to be impossible!!**
  $\Longrightarrow$ **requires extreme values of $\hat{r}_{\alpha\beta}$**

Effect of upper plate saturation pressure [HS&SK&DB 2012]

saturation pressure at the upper plate

$$p_{sat}^{\mathrm{up}}(T_\Delta) = p_{sat}^{\mathrm{up}}(T_L)\left[1 + \frac{h_{fg}^{L,\mathrm{up}}}{RT_L}\frac{T_\Delta - T_L}{T_L}\right] = P_{\mathrm{up}} p_{sat}(T_L)\left[1 + H_{\mathrm{up}}\frac{h_{fg}^{L}}{RT_L}\frac{T_\Delta - T_L}{T_L}\right]. \quad (1)$$

where P_{up} and H_{up} are the ratios of saturation pressure and enthalpy between the wetted upper plate and pure water, at T_L.