2.43 ADVANCED THERMODYNAMICS

Spring Term 2024

LECTURE 15

Room 3-442
Tuesday, April 2, 2:30pm - 4:30pm

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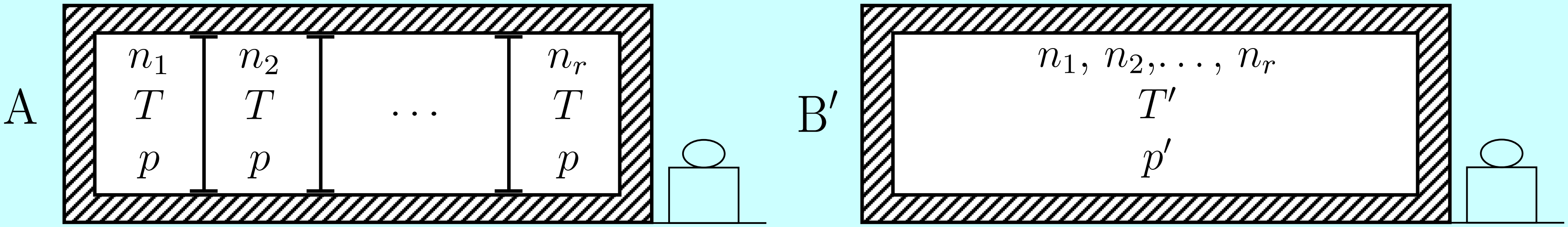
Room 3-351d

Stable-equilibrium properties of MIXTURES (within the simple-system model)

Mixing and separation

Stratification

Entropy of spontaneous mixing



Remove partitions allowing spontaneous mixing. Using energy, volume, and entropy additivity for A, and ideal G-D-mixture model for B′,

$$U_{\rm A} = \sum_i n_i u_{ii}(T) \qquad V_{\rm A} = \sum_i n_i v_{ii}(T,p) = \frac{nRT}{p} \qquad S_{\rm A} = \sum_i n_i s_{ii}(T,p)$$

$$U_{\rm B'} = \sum_i n_i u_{ii}(T') \qquad V_{\rm B'} = \sum_i n_i v_{ii}(T',p') = \frac{nRT'}{p'} \qquad S_{\rm B'} = \sum_i n_i s_{ii}(T',p'_{ii})$$

Energy balance for the isolated system, $U_{\rm B'} - U_{\rm A} = 0$, recalling $du_{ii} = c_{v,ii}(T)\,dT$,

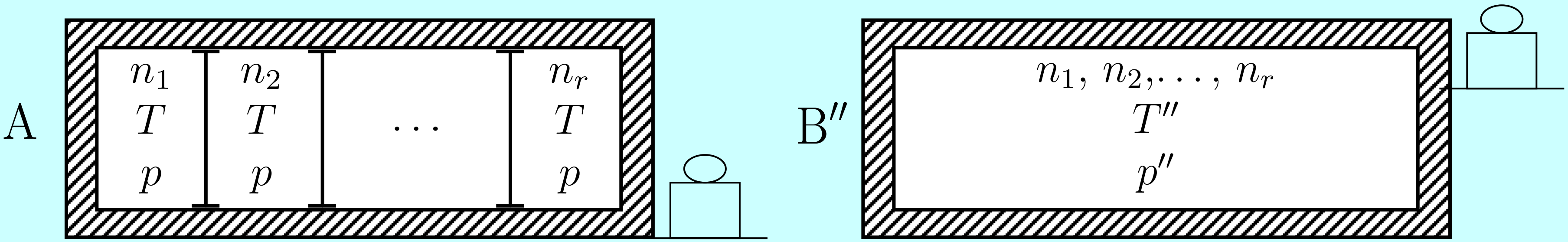
$$U_{\rm B'} - U_{\rm A} = \sum_i n_i [u_{ii}(T') - u_{ii}(T)] = \sum_i n_i \int_T^{T'} c_{v,ii}(\theta)\,d\theta = 0$$

Since $c_{v,ii}(T) > 0$ for any T, the integral can only be zero if $T' = T$. Therefore, the volume balance $V_{\rm B'} = U_{\rm A}$ yields $p' = p$.

Entropy balance for the isolated system, $S_{\rm B'} - S_{\rm A} = s_{\rm irr}$, recalling $ds_{ii} = c_{p,ii}(T)\,dT/T - R\,dp/p$, so that $s_{ii}(T',p'_{ii}) = s_{ii}(T',p') - R\ln y_i$, yields (for $T' = T$ and $p' = p$)

$$S_{\rm irr} = S_{\rm B'} - S_{\rm A} = \sum_i n_i [s_{ii}(T',p'_{ii}) - s_{ii}(T,p)] = \sum_i n_i \Delta s_i^{\rm mix} = \sum_i n_i[-R\ln y_i] = -nR\sum_i y_i \ln y_i \geq 0$$

Extracting the adiabatic availability of mixing



Do the mixing with a reversible weight process. Using energy, volume, and entropy additivity for A, and ideal G-D-mixture model for B'',

$$U_{\rm A} = \sum_i n_i u_{ii}(T) \qquad V_{\rm A} = \sum_i n_i v_{ii}(T,p) = \frac{nRT}{p} \qquad S_{\rm A} = \sum_i n_i s_{ii}(T,p)$$

$$U_{\rm B''} = \sum_i n_i u_{ii}(T'') \qquad V_{\rm B''} = \sum_i n_i v_{ii}(T'',p'') = \frac{nRT''}{p''} \qquad S_{\rm B''} = \sum_i n_i s_{ii}(T'',p''_{ii})$$

The volume balance $V_{\rm B''} = V_{\rm A}$ imposes $p''/T'' = p/T$. Thus, recalling $p''_{ii} = y_i\, p''$, assuming constant specific heats, defining $c_{v,mix} = \sum_i y_i\, c_{v,ii}$, and using

$$s_{ii}\Big(T'', p''_{ii} = y_i \frac{T''}{T} p\Big) - s_{ii}(T,p) = c_{p,ii} \ln\frac{T''}{T} - R\ln\Big(y_i\frac{T''}{T}\Big) = c_{v,ii}\ln\frac{T''}{T} - R\ln y_i$$

the entropy balance for the reversible weight process, $S_{\rm B''} - S_{\rm A} = 0$, becomes

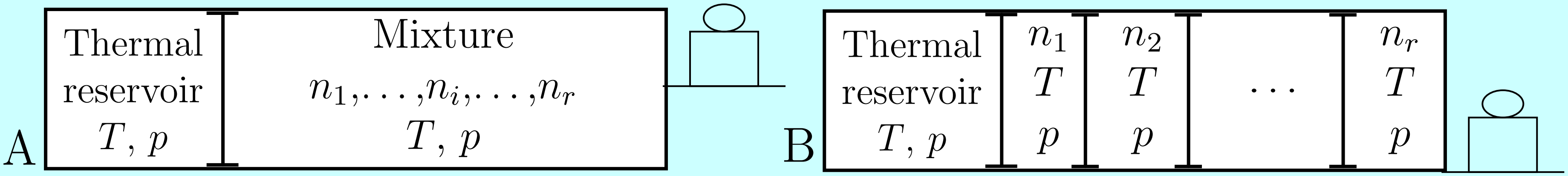
$$0 = S_{\rm B''} - S_{\rm A} = \sum_i n_i[s_{ii}(T'',p''_{ii}) - s_{ii}(T,p)] = \sum_i n_i[c_{v,ii}\ln\frac{T''}{T} - R\ln y_i] = n[c_{v,mix}\ln\frac{T''}{T} - R\sum_i y_i \ln y_i]$$

and yields $T'' = T\,\exp\Big(\frac{R}{c_{v,mix}}\sum_i y_i \ln y_i\Big)$ (clearly $T'' < T$). Therefore, the energy balance for the weight process, $U_{\rm B''} - U_{\rm A} = -W^{\rightarrow}_{\rm rev}$, yields

$$W^{\rightarrow}_{\rm rev} = U_{\rm A} - U_{\rm B''} = \sum_i n_i[u_{ii}(T'') - u_{ii}(T)] = n\,c_{v,mix}(T - T'') = \boxed{n\,c_{v,mix}T\Big[1 - \exp\Big(\frac{R}{c_{v,mix}}\sum_i y_i \ln y_i\Big)\Big]}$$

Isothermobaric demixing of ideal gas mixtures or ideal solutions:

Minimum work of complete separation



Volume balance: $(V_B - V_A) + (V_B^R - V_A^R) = 0$

Energy balance: $(E_B - E_A) + (E_B^R - E_A^R) = W_{\rm sep}^{\leftarrow}$

Entropy balance: $(S_B - S_A) + (S_B^R - S_A^R) = S_{\rm gen}$

Fund.rel. for R: $E_B^R - E_A^R = T_R\,(S_B^R - S_A^R) - p_R\,(V_B^R - V_A^R)$

Eliminate $(V_B^R - V_A^R)$, $(E_B^R - E_A^R)$, and $(S_B^R - S_A^R)$, and use $T_A = T_B = T_R$ to yield:

$$W_{\rm sep}^{\leftarrow} = E_B - E_A - T\,(S_B - S_A) + p\,(V_B - V_A) + T\,S_{\rm gen} = W_{\rm sep,rev}^{\leftarrow} + T\,S_{\rm gen}$$

$$W_{\rm sep,rev}^{\leftarrow} = G_B - G_A = \sum_i n_i\mu_{ii}(T,p) - \sum_i n_i\mu_i(T,p,\boldsymbol{y}) \overset{\text{ideal solution}}{\underset{\text{or GDgasmix}}{=}} -nRT\sum_i y_i \ln y_i$$

Assume dry air is just 1=N2, 2=O2, 3=Ar, 4=CO2, with $\{M_i\} = \{28.02, 32, 39.95, 44.01\}$

If we take $\boldsymbol{y}[\%] = \{78.08, 20.95, 0.93, 0.04\}$, $M = \sum_i y_i M_i = 28.97$ we obtain (at $T = 298\,\mathrm{K}$)

$W_{\rm sep,rev}^{\leftarrow}/nM = -(RT/M)\sum_i y_i \ln y_i = 48.5\,\mathrm{kJ/kg}$

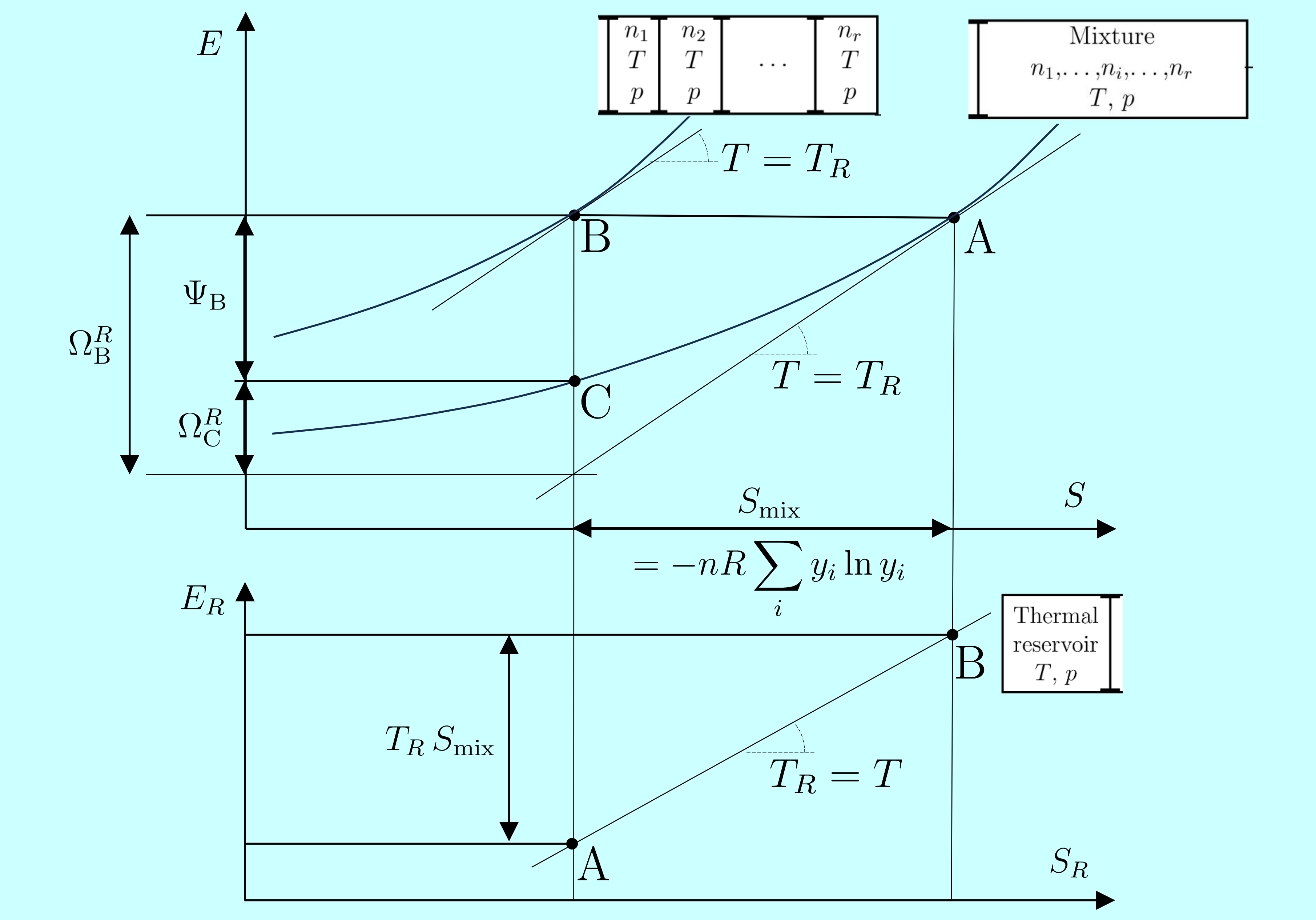
But note that for $\boldsymbol{y}[\%] = \{78.84, 21.16, 0, 0\}$, $M = 28.86$ we have $W_{\rm sep,rev}^{\leftarrow}/nM = 44.3\,\mathrm{kJ/kg}$

Consider ideal liquid solutions of 1=H2O and 2=CH3CH2OH, with $\{M_i\} = \{18.015, 46.07\}$ and $\{\rho_{ii}[\mathrm{g/cm^3}]\} = \{1, 0.789\}$: For example, wine with volume fraction $\phi_2 = 14\%$ $(y_2 = 4.7\%)$

$W_{\rm sep,rev}^{\leftarrow}/nM = -(RT/M)\sum_i y_i \ln y_i = 24.2\,\mathrm{kJ/kg}$

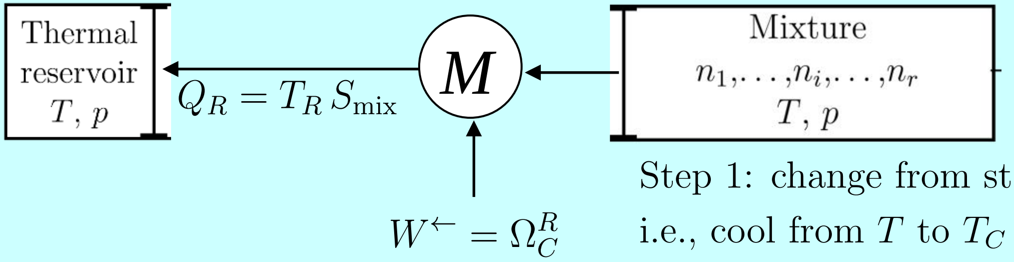
Isothermobaric demixing of an ideal mixture of ideal gases:

Minimum work of complete separation



Isothermobaric demixing of an ideal mixture of ideal gases:

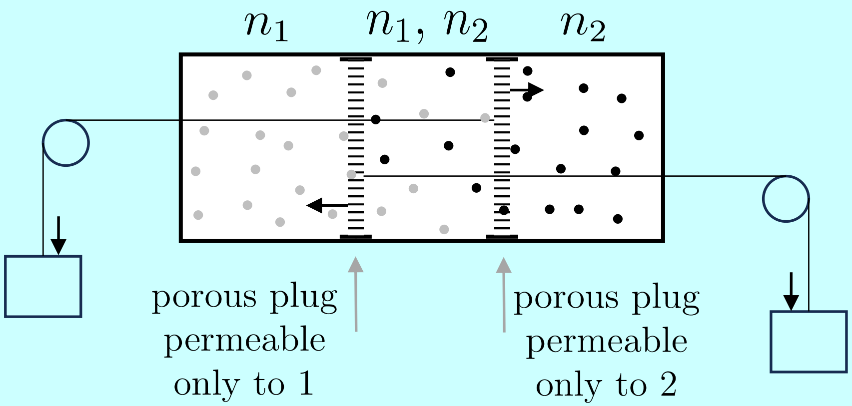
Minimum work of complete separation



Step 1: change from state A to state C
i.e., cool from T to T_C $(< T)$

Step 2: use semipermable membranes to partially compress the components from state C (mixed) into their separate compartments (state B)

$$W^{\leftarrow} = \Psi_B$$

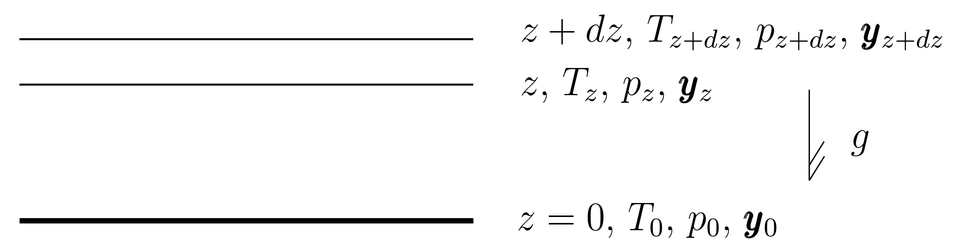


Stratification of ideal gas and liquid mixtures in a uniform gravitational field

$$E_z = U(S_z, V_z, \boldsymbol{n}_z) + m_z g z \qquad m_z = \textstyle\sum_i n_{iz} M_i$$

$$\mu_{i,z}^{\rm tot} = \left(\frac{\partial E_z}{\partial n_{iz}}\right)_{S_z, V_z, \boldsymbol{n}'_{iz}} = \mu_i(T_z, p_z, \boldsymbol{y}_z) + M_i g z$$

$=$ total potential of constituent i



Assume (locally only) $T_{z+dz} \approx T_z$ and impose, for every constituent i, the equality of total potentials, $\mu_{i,z+dz}^{\rm tot} = \mu_{i,z}^{\rm tot}$, between adjacent layers

$$\mu_{i,z+dz}^{\rm tot} \approx \mu_i(T_z, p_{z+dz}, \boldsymbol{y}_{z+dz}) + M_i g(z+dz) = \mu_{ii}(T_z, p_{z+dz}) + RT_z \ln y_{i,z+dz} + M_i g(z+dz)$$

$\mu_{i,z}^{\rm tot} = \mu_i(T_z, p_z, \boldsymbol{y}_z) + M_i g z = \mu_{ii}(T_z, p_z) + RT_z \ln y_{i,z} + M_i g z$ (we assumed ideal mixture behavior).

Therefore, $\mu_{i,z+dz}^{\rm tot} = \mu_{i,z}^{\rm tot}$ implies $\mu_{ii}(T_z, p_{z+dz}) + RT_z \ln(y_{i,z} + dy_{i,z}) + M_i g\, dz = \mu_{ii}(T_z, p_z) + RT_z \ln y_{i,z}$

Finally, $v_{ii}(T_z, p_z)\, dp_z + RT_z\, dy_{i,z}/y_{i,z} + M_i g\, dz = 0$ where we used $\ln(1 + dy_{i,z}/y_{i,z}) = dy_{i,z}/y_{i,z}$

For a pure substance this is $v(T,p)\, dp = -M g\, dz$ and integration yields the barometric formula and the Stevin static equation

$$\Rightarrow \begin{cases} \text{ideal gas } p_z = p_0 \exp\left(-\dfrac{Mg}{R}\displaystyle\int_0^z \frac{dz}{T_z}\right) \\ \text{incompr.liquid } p_z = p_0 - \rho g z \qquad \rho = M/v \end{cases}$$

For a mixture of ideal gases, instead, recalling that under ideal behavior $y_{i,z} p_z = p_{ii,z}$, it becomes

$$RT_z\, dp_z/p_z + RT_z\, dy_{i,z}/y_{i,z} = RT_z\, dp_{ii,z}/p_{ii,z} = -M_i g\, dz \quad \Rightarrow \quad p_{ii,z} = p_{ii,0} \exp\left(-\frac{M_i g}{R}\int_0^z \frac{dz}{T_z}\right)$$

so that, once we have the $p_{ii,z}$'s, we find $p_z = \sum_i p_{ii,z}$ and $y_{i,z} = p_{ii,z}/p_z$.

For a binary mixture of incompressible liquids, setting $y_z = y_{11,z} = 1 - y_{22,z}$, it becomes

$v_{11}\, dp_z + RT_z\, dy_z/y_z = -M_1 g\, dz$ and $v_{22}\, dp_z - RT_z\, dy_z/(1 - y_z) = -M_2 g\, dz$ which combined yield

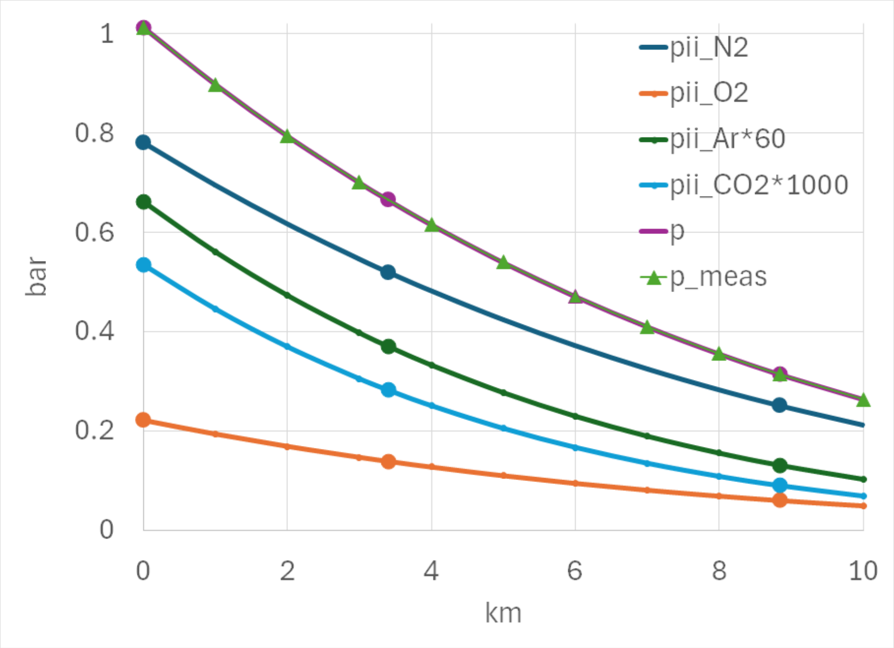
$$\frac{1}{v_{11}}\frac{dy_z}{y_z} + \frac{1}{v_{22}}\frac{dy_z}{1 - y_z} = (\rho_{22} - \rho_{11})\frac{g}{R}\frac{dz}{T_z} \quad \text{integrated} \quad \frac{y_z}{y_0}\left(\frac{1 - y_0}{1 - y_z}\right)^{v_{11}/v_{22}} = \exp\left(\frac{(\rho_{22} - \rho_{11})M_1 g}{\rho_{11} R}\int_0^z \frac{dz}{T_z}\right)$$

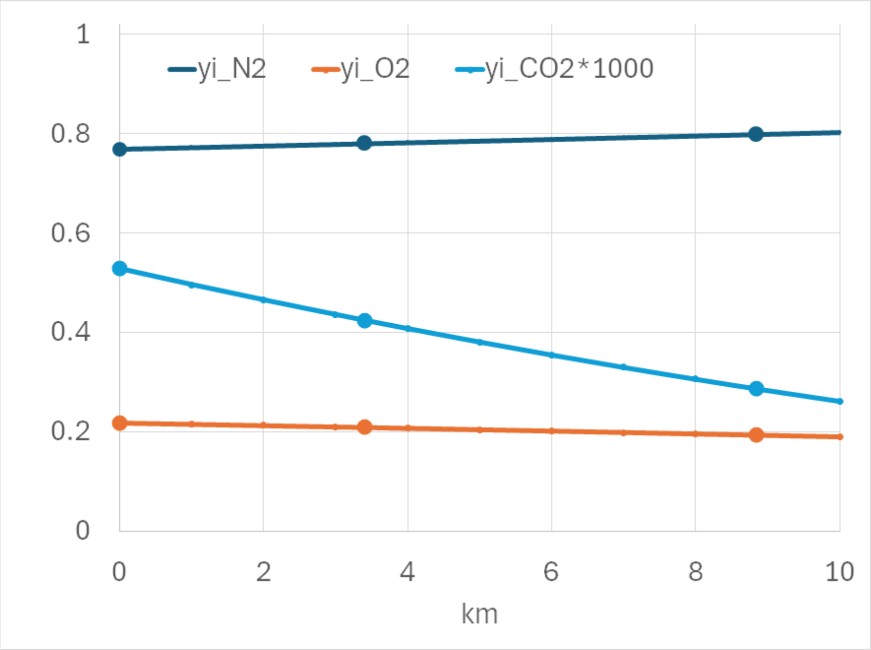
Example: Stratification in the atmosphere (if we neglect turbulent mixing)

Empirical correlations for T_z and p_z are $T_z = T_0 - az$ and $p_z = p_0\,(1 - 0.02256\,z)^{5.256}$ with $T_0 = 288\,\mathrm{K}$, $p_0 = 1.01325\,\mathrm{bar}$, $a = 6.5\,\mathrm{K/km}$, and z in km. Let us use our result, written as

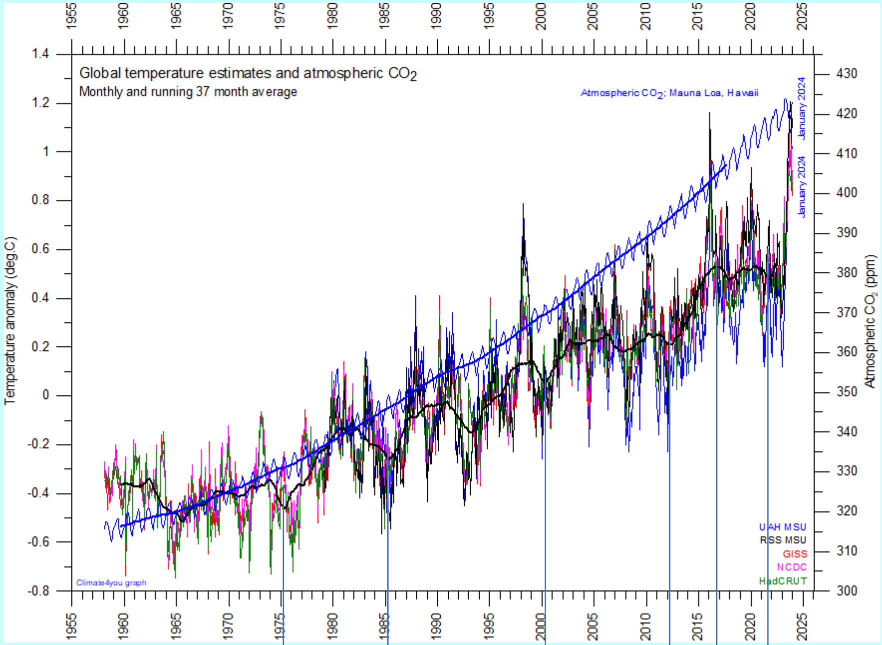
$$p_{ii,z} = p_{ii,0} \exp\left(-\frac{M_i g z}{R T_0} C_z\right) \qquad \text{where} \quad C_z = \frac{T_0}{z}\int_0^z \frac{dz}{T_0 - az} = -\frac{T_0}{az}\ln\left(1 - \frac{az}{T_0}\right)$$

We assume the atmosphere is a mixture of only four constituents, 1=N2, 2=O2, 3=Ar, 4=CO2, with concentrations at Mauna Loa ($z = 3400$ m) in ppm, respectively: 780900, 209360, 9300, 425. The resulting calculation (see Excel file stratificationAtmosphere.xlsx) are plotted here. The resulting pressure distribution is in excellent agreement with the empirical correlation for p_z.

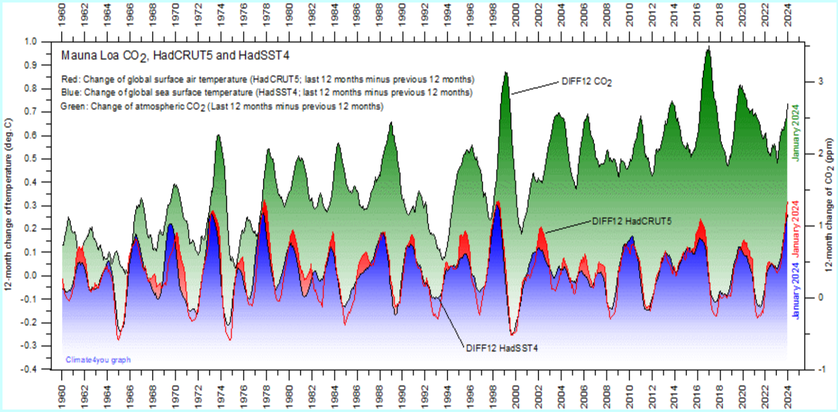




Relevance of mutual equilibrium between ocean and atmosphere

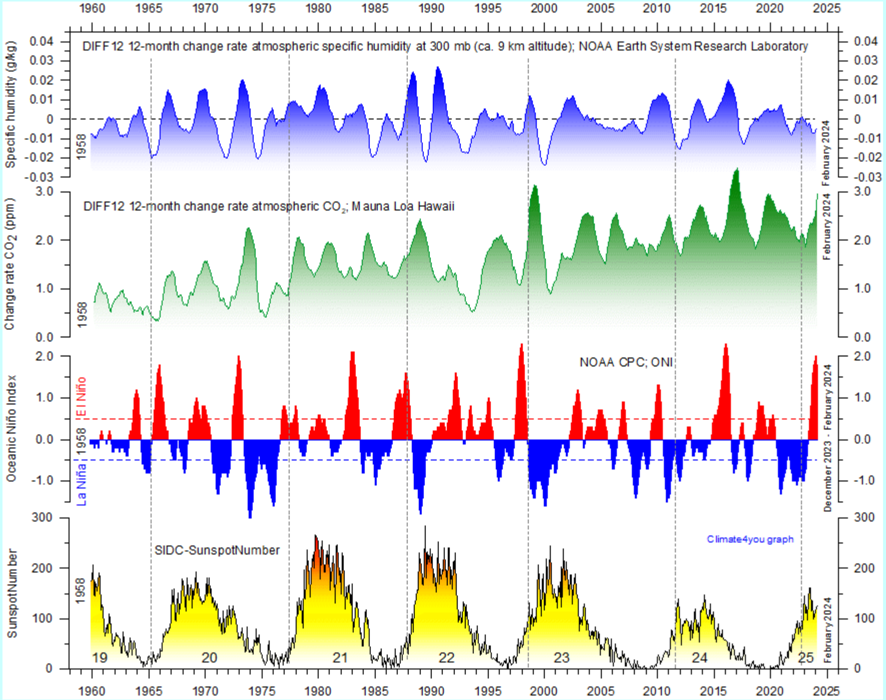


Global temperature estimates and atmospheric CO$_2$
Monthly and running 37 month average



Mauna Loa CO$_2$, HadCRUT5 and HadSST4

Red: Change of global surface air temperature (HadCRUT5; last 12 months minus previous 12 months)
Blue: Change of global sea surface temperature (HadSST4; last 12 months minus previous 12 months)
Green: Change of atmospheric CO$_2$ (Last 12 months minus previous 12 months)

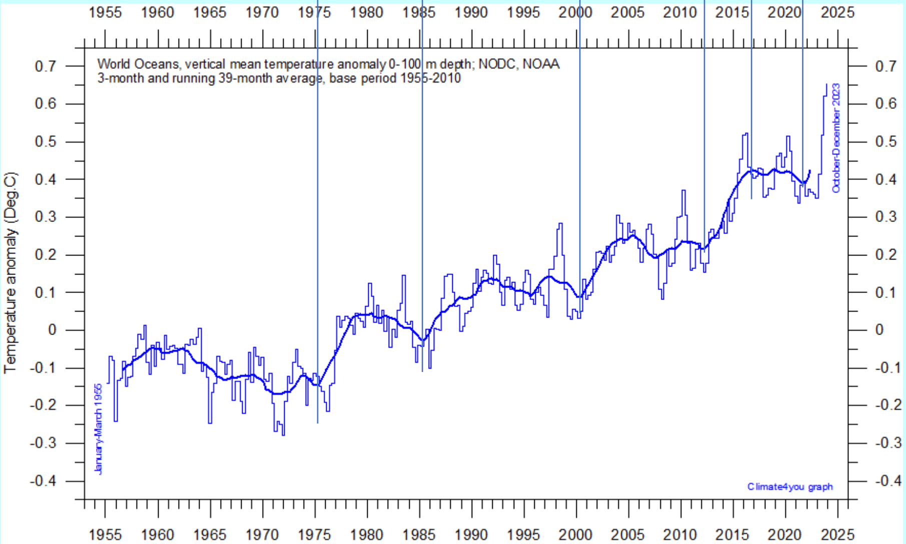


DIFF 12 12-month change rate atmospheric specific humidity at 300 mb (ca. 9 km altitude); NOAA Earth System Research Laboratory

DIFF12 12-month change rate atmospheric CO$_2$; Mauna Loa Hawaii

NOAA CPC; ONI

SIDC-SunspotNumber



World Oceans, vertical mean temperature anomaly 0-100 m depth; NODC, NOAA
3-month and running 39-month average, base period 1955-2010

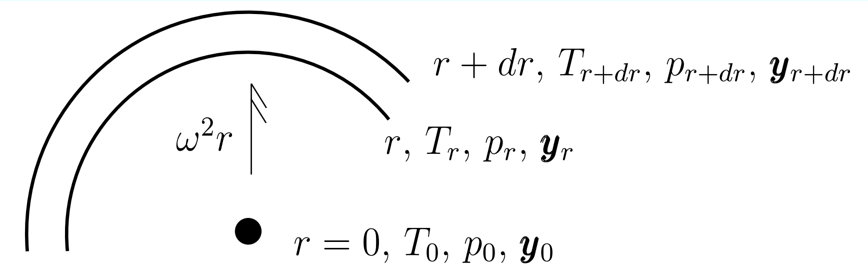
Figures taken from: https://www.climate4you.com/ on March 17, 2024

Stratification of ideal gas and liquid mixtures at rest inside a centrifuge

$$E_r = U(S_r, V_r, \boldsymbol{n}_r) - \frac{1}{2} m_r \omega^2 r^2 \qquad m_r = \sum_i n_{ir} M_i$$

$$\mu^{\text{tot}}_{i,r} = \left(\frac{\partial E_r}{\partial n_{ir}}\right)_{S_r, V_r, \boldsymbol{n}'_{ir}} = \mu_i(T_r, p_r, \boldsymbol{y}_r z) - \frac{1}{2} M_i \omega^2 r^2$$

$=$ total potential of constituent i



$\omega^2 r$

$r + dr,\ T_{r+dr},\ p_{r+dr},\ \boldsymbol{y}_{r+dr}$

$r,\ T_r,\ p_r,\ \boldsymbol{y}_r$

$r = 0,\ T_0,\ p_0,\ \boldsymbol{y}_0$

Assume (locally only) $T_{r+dr} \approx T_r$ and impose,

for every constituent i, the equality of total potentials, $\mu^{\text{tot}}_{i,r+dr} = \mu^{\text{tot}}_{i,r}$, between adjacent layers

$$\mu^{\text{tot}}_{i,r+dr} \approx \mu_i(T_r, p_{r+dr}, \boldsymbol{y}_{r+dr}) - \tfrac{1}{2} M_i \omega^2 (r + dr)^2 = \mu_{ii}(T_r, p_{r+dr}) + RT_r \ln y_{i,r+dr} - \tfrac{1}{2} M_i \omega^2 (r^2 + 2r\, dr)$$

$$\mu^{\text{tot}}_{i,r} = \mu_i(T_r, p_r, \boldsymbol{y}_r) - \tfrac{1}{2} M_i \omega^2 r^2 = \mu_{ii}(T_r, p_r) + RT_r \ln y_{i,r} - \tfrac{1}{2} M_i \omega^2 r^2 \text{ (assumed ideal solution).}$$

Therefore, $\mu^{\text{tot}}_{i,r+dr} = \mu^{\text{tot}}_{i,r}$ implies $\mu_{ii}(T_r, p_{r+dr}) + RT_r \ln(y_{i,r} + dy_{i,r}) - M_i \omega^2 r\, dr = \mu_{ii}(T_r, p_r) + RT_r \ln y_{i,r}$

Finally, $v_{ii}(T_r, p_r)\, dp_r + RT_r\, dy_{i,r}/y_{i,r} - M_i \omega^2 r\, dr = 0$ where we used $\ln(1 + dy_{i,r}/y_{i,r}) = dy_{i,r}/y_{i,r}$

For a pure substance this is $v(T, p)\, dp = M\omega^2 r\, dr$ and yields the hydrostatic pressure distributions $\Rightarrow$

$$\begin{cases} \text{ideal gas } p_r = p_0 \exp\left(\dfrac{M\omega^2}{R} \displaystyle\int_0^r \dfrac{r\, dr}{T_r}\right) \\ \text{incompr.liquid } p_r = p_0 + \rho\omega^2 r^2/2 \qquad \rho = M/v \end{cases}$$

For a mixture of ideal gases, instead, recalling that under ideal behavior $y_{i,r} p_r = p_{ii,r}$, it becomes

$$RT_r\, dp_r/p_r + RT_r\, dy_{i,r}/y_{i,r} = RT_r\, dp_{ii,r}/p_{ii,r} = M_i \omega^2 r\, dr \quad \Rightarrow \quad p_{ii,r} = p_{ii,0} \exp\left(\frac{M_i \omega^2}{R} \int_0^r \frac{r\, dr}{T_r}\right)$$

so that, once we have the $p_{ii,r}$'s, we find $p_r = \sum_i p_{ii,r}$ and $y_{i,r} = p_{ii,r}/p_r$.

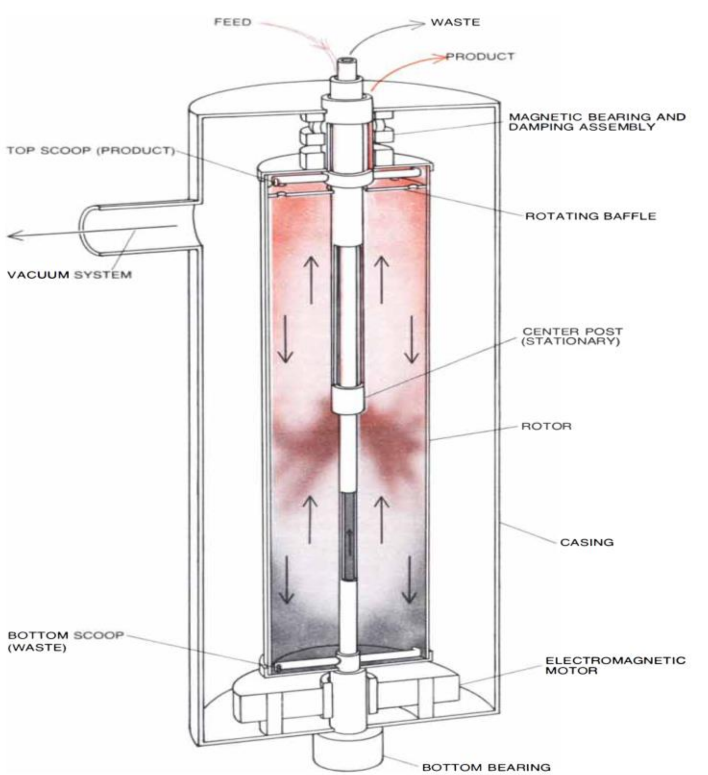
For a binary mixture of incompressible liquids, setting $y_r = y_{11,r} = 1 - y_{22,r}$, it becomes

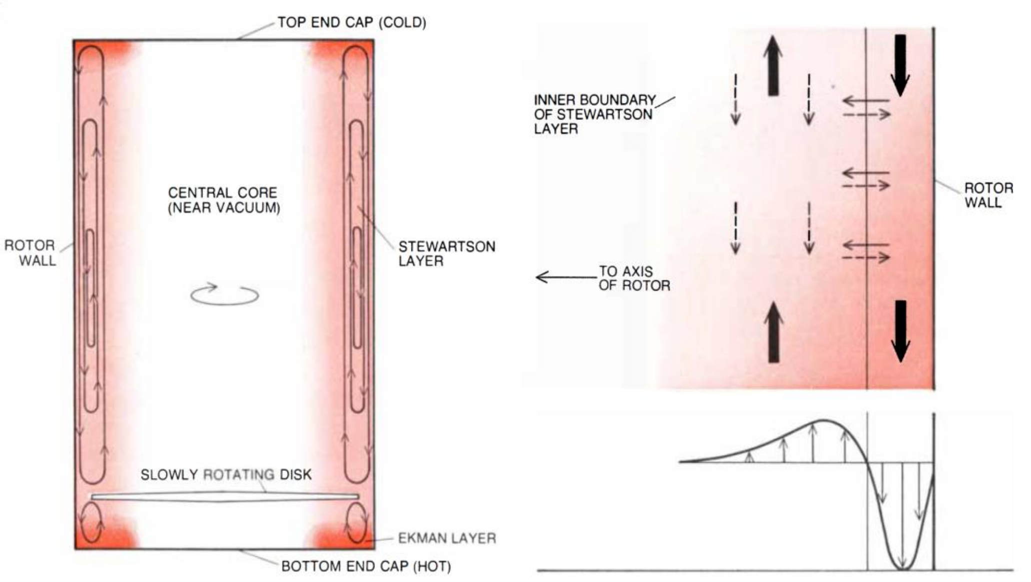
$v_{11}\, dp_r + RT_r\, dy_r/y_r = M_1 \omega^2 r\, dr$ and $v_{22}\, dp_r - RT_r\, dy_r/(1 - y_r) = M_2 \omega^2 r\, dr$ which combined yield

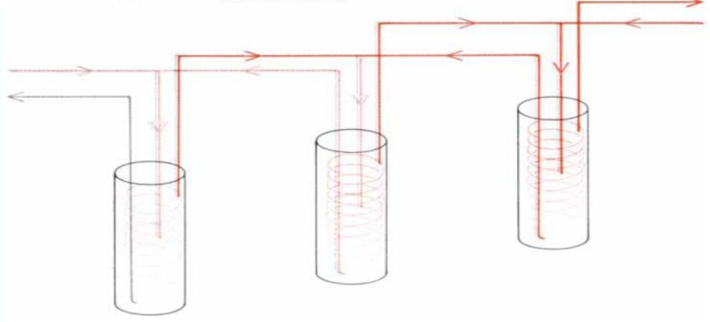
$$\frac{1}{v_{11}} \frac{dy_r}{y_r} + \frac{1}{v_{22}} \frac{dy_r}{1 - y_r} = (\rho_2 - \rho_1) \frac{\omega^2}{R} \frac{r\, dr}{T_r} \quad \text{and} \quad \frac{y_r}{y_0} \left(\frac{1 - y_0}{1 - y_r}\right)^{v_{11}/v_{22}} = \exp\left((\rho_2 - \rho_1) \frac{\omega^2 v_{11}}{R} \int_0^r \frac{r\, dr}{T_r}\right)$$

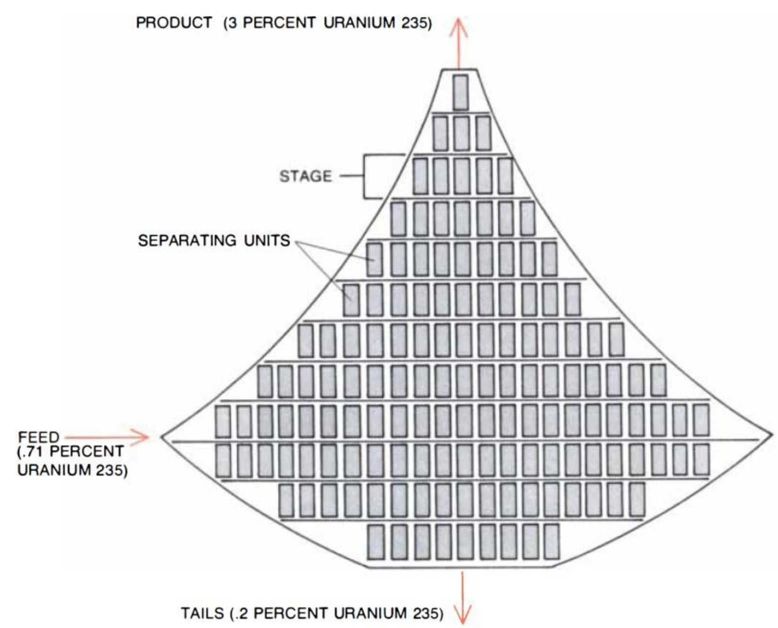
Fission reactors need enrichment in ^{235}U from 0.71% to 3%. This is done with ^{235}UF$_6$ (uranium hexafluoride)

gas centrifuges on gaseous uranium hexafluoride (mixture of ^{235}UF$_6$ and ^{238}UF$_6$)









Figures from: D.R. Olander, The Gas Centrifuge, Scientific American, 239, 37 (1978).

Stratification of charge carriers in a uniform electric field

$E_{\boldsymbol{x}} = U(S_{\boldsymbol{x}}, V_{\boldsymbol{x}}, \boldsymbol{n}_{\boldsymbol{x}}) + q_{\boldsymbol{x}}\,\varphi(\boldsymbol{x}) \qquad q_{\boldsymbol{x}} = \sum_i n_{i\boldsymbol{x}} z_i F$

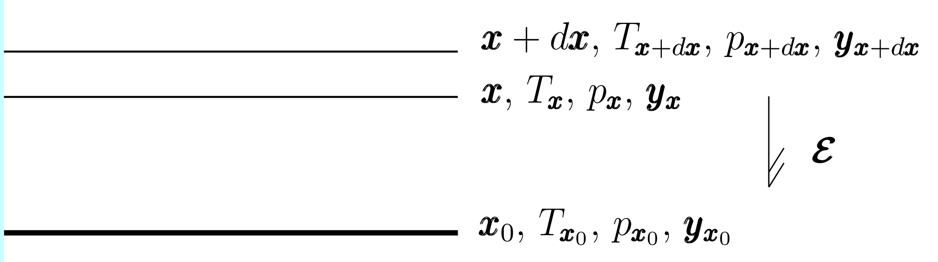
$F = N_{\rm Av}\, e \qquad e = 1.602176634^{-19}\,\mathrm{C} \qquad R = N_{\rm Av} k_{\rm B}$

$N_{\rm Av} = 6.02214076 \times 10^{23}\,\mathrm{mol}^{-1} \qquad \boldsymbol{\mathcal{E}} = -\boldsymbol{\nabla}\varphi$

$k_{\rm B} = 1.380649 \times 10^{-23}\,\mathrm{J/K} \qquad F/R = e/k_{\rm B}$

$$\mu^{\rm tot}_{i,\boldsymbol{x}} = \left(\frac{\partial E_{\boldsymbol{x}}}{\partial n_{i\boldsymbol{x}}}\right)_{S_{\boldsymbol{x}}, V_{\boldsymbol{x}}, \boldsymbol{n}'_{i\boldsymbol{x}}} = \mu_i(T_{\boldsymbol{x}}, p_{\boldsymbol{x}}, \boldsymbol{y}_{\boldsymbol{x}}) + z_i F \varphi(\boldsymbol{x})$$

$=$ electrochemical potential of constituent i



$\boldsymbol{x} + d\boldsymbol{x},\ T_{\boldsymbol{x}+d\boldsymbol{x}},\ p_{\boldsymbol{x}+d\boldsymbol{x}},\ \boldsymbol{y}_{\boldsymbol{x}+d\boldsymbol{x}}$

$\boldsymbol{x},\ T_{\boldsymbol{x}},\ p_{\boldsymbol{x}},\ \boldsymbol{y}_{\boldsymbol{x}}$

$\boldsymbol{\mathcal{E}}$

$\boldsymbol{x}_0,\ T_{\boldsymbol{x}_0},\ p_{\boldsymbol{x}_0},\ \boldsymbol{y}_{\boldsymbol{x}_0}$

Assume (locally only) $T_{\boldsymbol{x}+d\boldsymbol{x}} \approx T_{\boldsymbol{x}}$ and impose, $\mu^{\rm tot}_{i,\boldsymbol{x}+d\boldsymbol{x}} = \mu^{\rm tot}_{i,\boldsymbol{x}}\ \forall i$, between adjacent parcels.

$\mu^{\rm tot}_{i,\boldsymbol{x}+d\boldsymbol{x}} \approx \mu_i(T_{\boldsymbol{x}}, p_{\boldsymbol{x}+d\boldsymbol{x}}, \boldsymbol{y}_{\boldsymbol{x}+d\boldsymbol{x}}) + z_i F \varphi(\boldsymbol{x} + d\boldsymbol{x}) = \mu_{ii}(T_{\boldsymbol{x}}, p_{\boldsymbol{x}+d\boldsymbol{x}}) + RT_{\boldsymbol{x}} \ln y_{i,\boldsymbol{x}+d\boldsymbol{x}} + z_i F \varphi(\boldsymbol{x} + d\boldsymbol{x})$

$\mu^{\rm tot}_{i,\boldsymbol{x}} = \mu_i(T_{\boldsymbol{x}}, p_{\boldsymbol{x}}, \boldsymbol{y}_{\boldsymbol{x}}) + z_i F \varphi(\boldsymbol{x}) = \mu_{ii}(T_{\boldsymbol{x}}, p_{\boldsymbol{x}}) + RT_{\boldsymbol{x}} \ln y_{i,\boldsymbol{x}} + z_i F \varphi(\boldsymbol{x})$ (we assumed ideal mixture behavior).

Therefore, $\mu^{\rm tot}_{i,\boldsymbol{x}+d\boldsymbol{x}} = \mu^{\rm tot}_{i,\boldsymbol{x}}$ implies $\mu_{ii}(T_{\boldsymbol{x}}, p_{\boldsymbol{x}+d\boldsymbol{x}}) + RT_{\boldsymbol{x}} \ln(y_{i,\boldsymbol{x}} + dy_{i,\boldsymbol{x}}) + z_i F\, \boldsymbol{\nabla}\varphi \cdot d\boldsymbol{x} = \mu_{ii}(T_{\boldsymbol{x}}, p_{\boldsymbol{x}} z) + RT_{\boldsymbol{x}} \ln y_{i,\boldsymbol{x}}$

Finally, $v_{ii}(T_{\boldsymbol{x}}, p_{\boldsymbol{x}})\, dp_{\boldsymbol{x}} + RT_{\boldsymbol{x}}\, dy_{i,\boldsymbol{x}}/y_{i,\boldsymbol{x}} + z_i F\, \boldsymbol{\nabla}\varphi \cdot d\boldsymbol{x} = 0$ where we used $\ln(1 + dy_{i,\boldsymbol{x}}/y_{i,\boldsymbol{x}}) = dy_{i,\boldsymbol{x}}/y_{i,\boldsymbol{x}}$

For a pure substance this is $v(T,p)\, dp = -zF\, \boldsymbol{\nabla}\varphi \cdot d\boldsymbol{x}$ and integration yields Boltzmann (plasma) relations

$$\Rightarrow \begin{cases} \text{ideal gas } p_z = p_0 \exp\left(-\dfrac{zF}{R} \displaystyle\int_{\boldsymbol{x}_0}^{\boldsymbol{x}} \dfrac{\boldsymbol{\nabla}\varphi \cdot d\boldsymbol{x}}{T_{\boldsymbol{x}}}\right) \\ \text{incompr.liquid } p_z = p_0 - zF\,[\varphi(\boldsymbol{x}) - \varphi(\boldsymbol{x}_0)] \end{cases}$$

For a mixture of ideal gases, instead, recalling that under ideal behavior $y_{i,\boldsymbol{x}} p_{\boldsymbol{x}} = p_{ii,\boldsymbol{x}}$, it becomes

$$RT_{\boldsymbol{x}}\, dp_{\boldsymbol{x}}/p_{\boldsymbol{x}} + RT_{\boldsymbol{x}}\, dy_{i,\boldsymbol{x}}/y_{i,\boldsymbol{x}} = RT_{\boldsymbol{x}}\, dp_{ii,\boldsymbol{x}}/p_{ii,\boldsymbol{x}} = -z_i F\, \boldsymbol{\nabla}\varphi \cdot d\boldsymbol{x} \quad \Rightarrow \quad p_{ii,\boldsymbol{x}} = p_{ii,0} \exp\left(-\frac{z_i F}{R} \int_{\boldsymbol{x}_0}^{\boldsymbol{x}} \frac{\boldsymbol{\nabla}\varphi \cdot d\boldsymbol{x}}{T_{\boldsymbol{x}}}\right)$$

so that, once we have the $p_{ii,\boldsymbol{x}}$'s, we find $p_{\boldsymbol{x}} = \sum_i p_{ii,\boldsymbol{x}}$ and $y_{i,\boldsymbol{x}} = p_{ii,\boldsymbol{x}}/p_{\boldsymbol{x}}$. Notice the identity $\boldsymbol{\nabla}\varphi \cdot d\boldsymbol{x} = d\varphi$.

For a binary mixture of incompressible liquids, setting $y_{\boldsymbol{x}} = y_{11,\boldsymbol{x}} = 1 - y_{22,\boldsymbol{x}}$, it becomes

$v_{11}\, dp_{\boldsymbol{x}} + RT_{\boldsymbol{x}}\, dy_{\boldsymbol{x}}/y_{\boldsymbol{x}} = -z_1 F\, d\varphi$ and $v_{22}\, dp_{\boldsymbol{x}} - RT_{\boldsymbol{x}}\, dy_{\boldsymbol{x}}/(1 - y_{\boldsymbol{x}}) = -z_2 F\, d\varphi$ which combined yield

$$\frac{1}{v_{11}} \frac{dy_{\boldsymbol{x}}}{y_{\boldsymbol{x}}} + \frac{1}{v_{22}} \frac{dy_{\boldsymbol{x}}}{1 - y_{\boldsymbol{x}}} = \left(\frac{z_2}{v_{22}} - \frac{z_1}{v_{11}}\right) \frac{F}{R} \frac{d\varphi}{T_{\boldsymbol{x}}} \quad \text{and} \quad \frac{y_{\boldsymbol{x}}}{y_{\boldsymbol{x}_0}} \left(\frac{1 - y_{\boldsymbol{x}_0}}{1 - y_{\boldsymbol{x}}}\right)^{v_{11}/v_{22}} = \exp\left[\left(\frac{z_2}{v_{22}} - \frac{z_1}{v_{11}}\right) \frac{F v_{11}}{R} \int_{\boldsymbol{x}_0}^{\boldsymbol{x}} \frac{\boldsymbol{\nabla}\varphi \cdot d\boldsymbol{x}}{T_{\boldsymbol{x}}}\right]$$

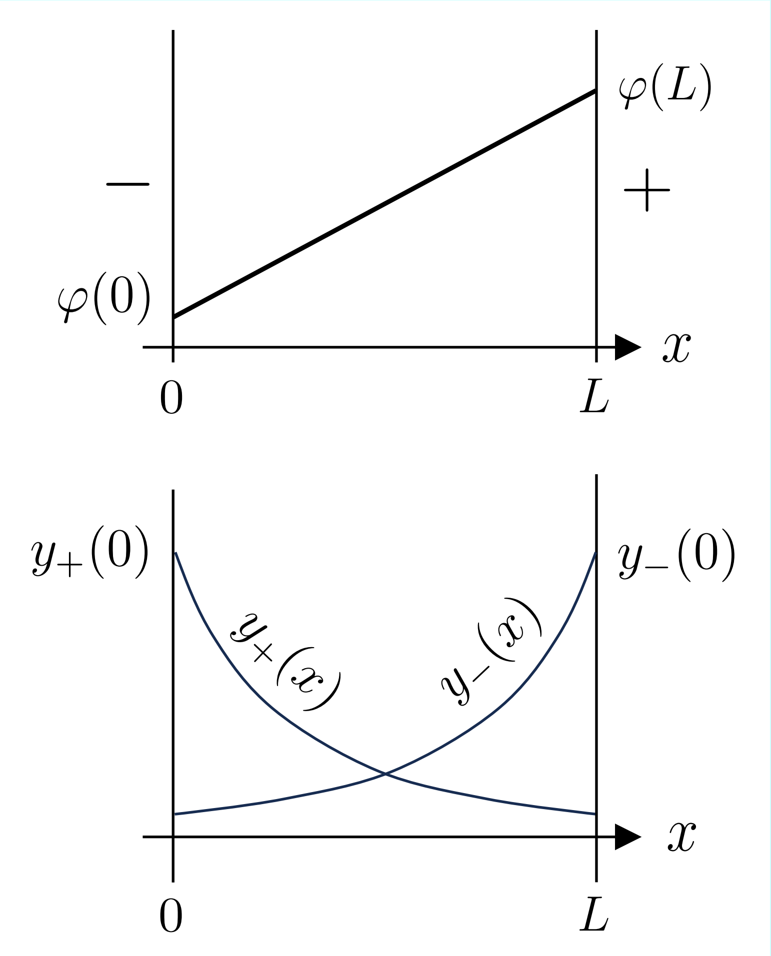
Example: Charge carriers concentration in a charged capacitor

$$\mu_{i,\text{tot}} = \mu_i + z_i F \varphi \qquad \mu_i = \mu_{ii}^o + RT \ln y_i \qquad \varphi(x) - \varphi(0) = E\, x$$

Impose $\mu_{i,\text{tot}}(x) = \mu_{ii}^o + RT \ln y_i(x) + z_i F \varphi(x) = \text{indep of } x$

$$RT \ln \frac{y_i(x)}{y_i(0)} = -z_i F[\varphi(x) - \varphi(0)]$$

$$y_i(x) = y_i(0) \exp\left[-\frac{z_i F E\, x}{RT}\right]$$



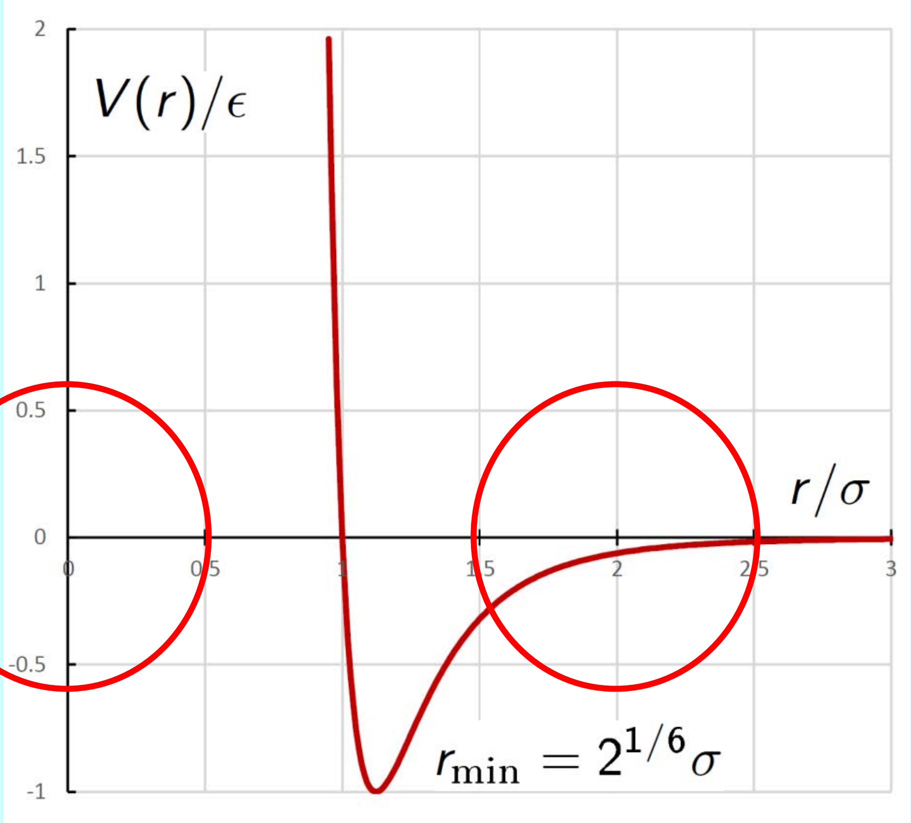
Liquid-vapor equilibria in pure substances

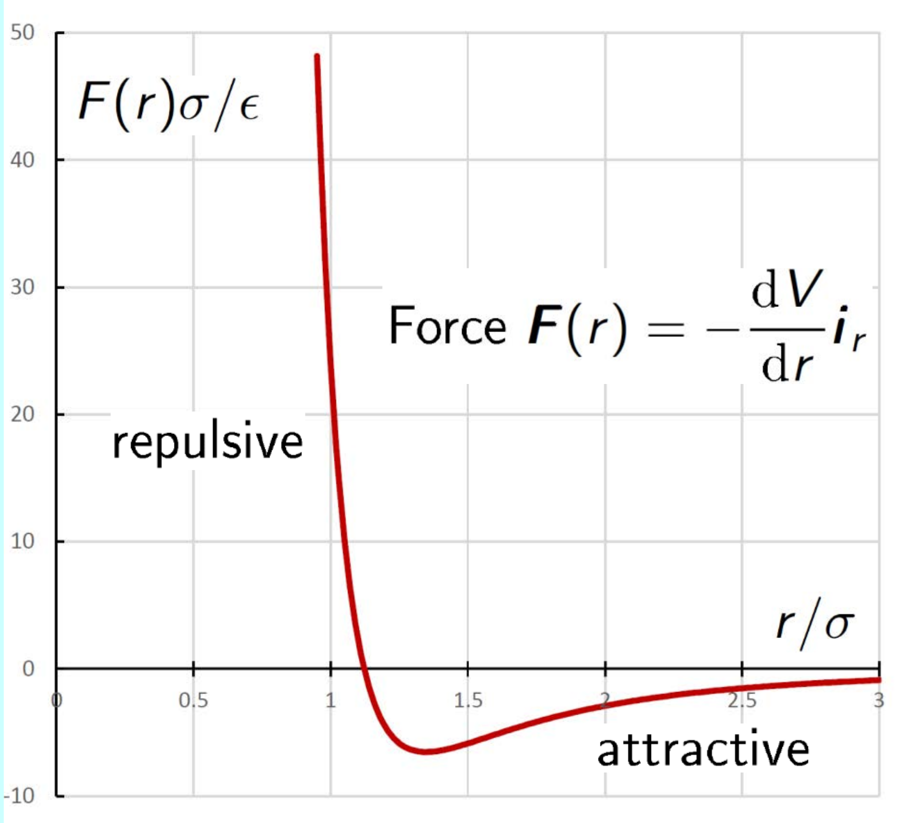
Lennard-Jones pure fluid model
van der Waals liquid-vapor model
stability
metastable states
liquid-vapor spinodal decomposition

Lennard-Jones potential (model of intermolecular forces)

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$
$$= \epsilon\left[\left(\frac{r_{\min}}{r}\right)^{12} - 2\left(\frac{r_{\min}}{r}\right)^{6}\right]$$

$$F(r) = 24\frac{\epsilon}{\sigma}\left(\frac{\sigma}{r}\right)^{3}\left[2\left(\frac{\sigma}{r}\right)^{6} - 1\right]$$
$$= 12\frac{2^{2/3}\epsilon}{r_{\min}}\left(\frac{r_{\min}}{r}\right)^{3}\left[\left(\frac{r_{\min}}{r}\right)^{6} - 1\right]$$





MD and MC modeling of non-ideal SES behavior:

Lennard-Jones pure substance ("Lennardjonesium")

Critical point

$T_c = 1.321\,\epsilon/k_{\rm B}$

$p_c = 0.129\,\epsilon/\sigma^3$

$v_c = 3.16\,\sigma^3$

Notice: $\frac{3}{2}k_{\rm B}T_c = 1.98\,\epsilon$

also: $v_c = 4.47\,v_{\rm c.p.spheres}$ where

$$v_{\rm c.p.spheres} = \frac{3\sqrt{2}}{\pi}\frac{\pi\sigma^3}{6} = 0.707\,\sigma^3$$

$$\mathcal{Z}_c = \frac{p_c v_c}{k_{\rm B}T_c} = 0.309$$

$\mathcal{Z}_c$ for real substances differ

0.23 for H_2O, 0.275 for CO_2

0.29 for Ar, 0.31 for ^{4}He

From given T_c and p_c:

$\epsilon = k_{\rm B}T_c/1.321$

$\sigma = 0.46\sqrt[3]{k_{\rm B}T_c/p_c}$

Triple point

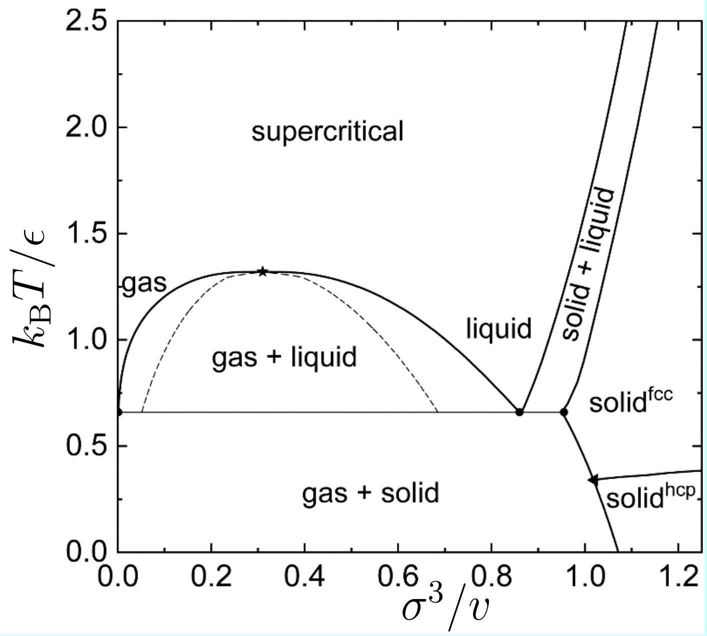
$\frac{3}{2}k_{\rm B}T_{\rm tp} = 1.035\,\epsilon$

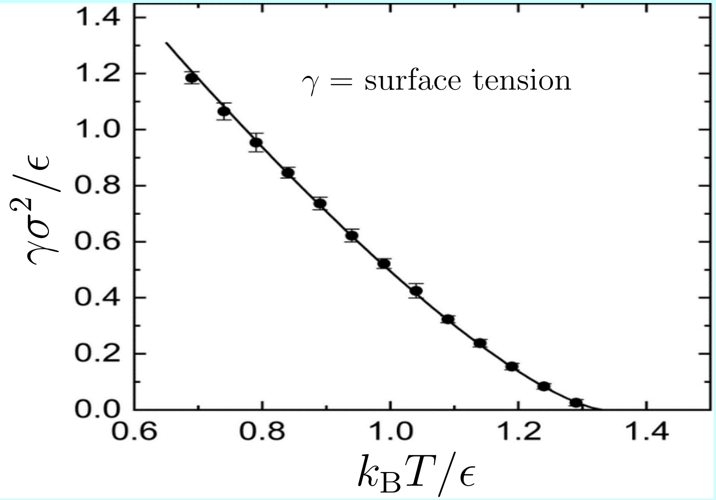
$v_{\rm tp,solid} = 1.04\,\sigma^3 = 1.47\,v_{\rm c.p.spheres}$

$v_{\rm tp,liquid} = 1.18\,\sigma^3 = 1.7\,v_{\rm c.p.spheres}$

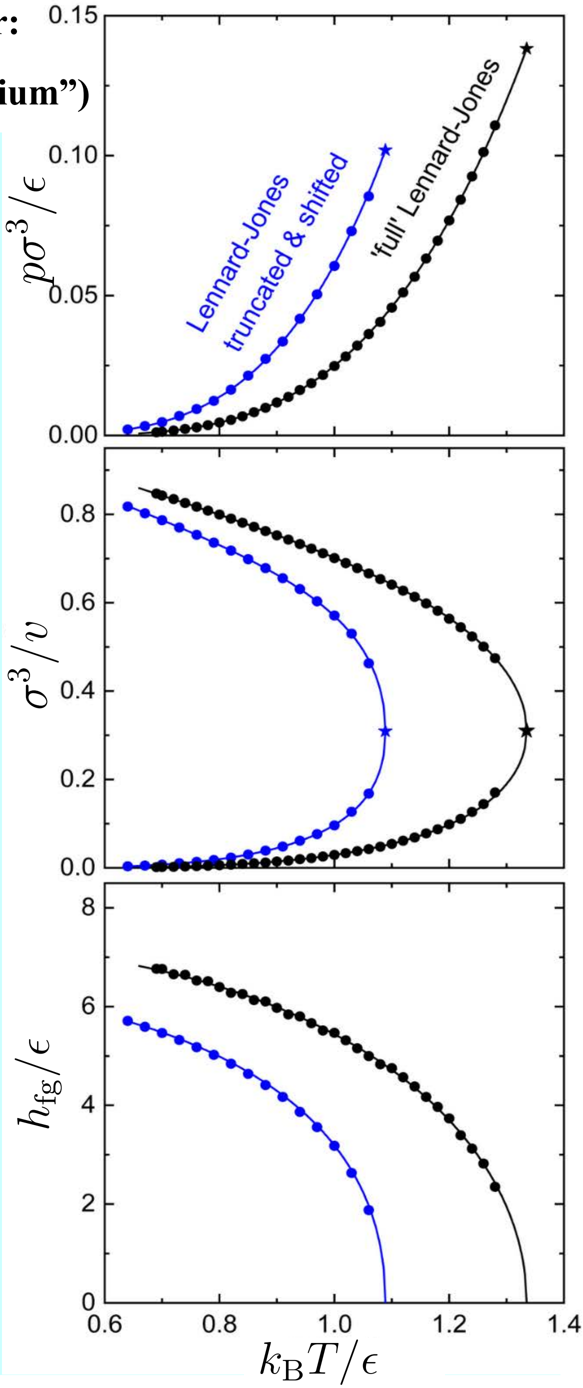
$v_{\rm tp,vapor} = 588\,\sigma^3 = 832\,v_{\rm c.p.spheres}$

$$\mathcal{Z}_{\rm tp,vapor} = \frac{p_{\rm tp}v_{\rm tp,vapor}}{k_{\rm B}T_{\rm tp}} = 1.023$$





Figures adapted from Wikipedia, TimeStep89, CC BY 4.0.



Modeling non-ideal SES behavior:

van der Waals (PhD 1873, Nobel 1910) model of liquid/vapor SES of pure substances

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

The expressions for κ_T and α_p that follow, can be used to compute u, s, h

$$\kappa_T = \frac{1}{p}\frac{1-b/v}{1-a/v^2p+2ab/v^3p} \quad \alpha_p = \frac{1}{T}\frac{(1-b/v)(1+a/v^2p)}{1-a/v^2p+2ab/v^3p} \quad c_p - c_v = R\,\frac{1+a/v^2p}{1-a/v^2p+2ab/v^3p}$$

For vapor states, where generally $v \gg b$ and $v^2p \gg a$, the following approximations hold

$$\begin{array}{lll} pv \approx RT & (p\kappa_T - T\alpha_p)\,v \approx -a/RT & \alpha_p/\kappa_T \approx p/T \\ c_p - c_v \approx R & (1-T\alpha_p)\,v \approx b - 2a/RT & \mu_{JT} \approx (2a/RT - b)/c_p \end{array}$$

The critical isotherm (temperature T_c) exhibits a horizontal tangent flex at the critical point. Imposing $(\partial p/\partial v)_T = 0$ and $(\partial^2 p/\partial v^2)_T = 0$ yields the critical parameters

$$T_c = 8a/27Rb \qquad p_c = a/27b^2 \qquad (\text{also } v_c = 3b\text{, but using this leads to imprecisions})$$

The chemical potential can be obtained by integrating by parts $(\partial\mu/\partial p)_T = v$,

$$\mu = c(T) + \int v\,dp = c(T) + pv - \int p\,dv = c(T) + f(T,v) \quad \text{where} \quad f(T,v) = \frac{RTv}{v-b} - RT\ln(v-b) - \frac{2a}{v}$$

and $c(T)$ is an integration constant, which can be evaluated at saturation, where liquid and vapor in MSE have the same pressure, $p_{\rm sat}(T)$, and chemical potential, $\mu_{\rm sat}(T)$, i.e.,

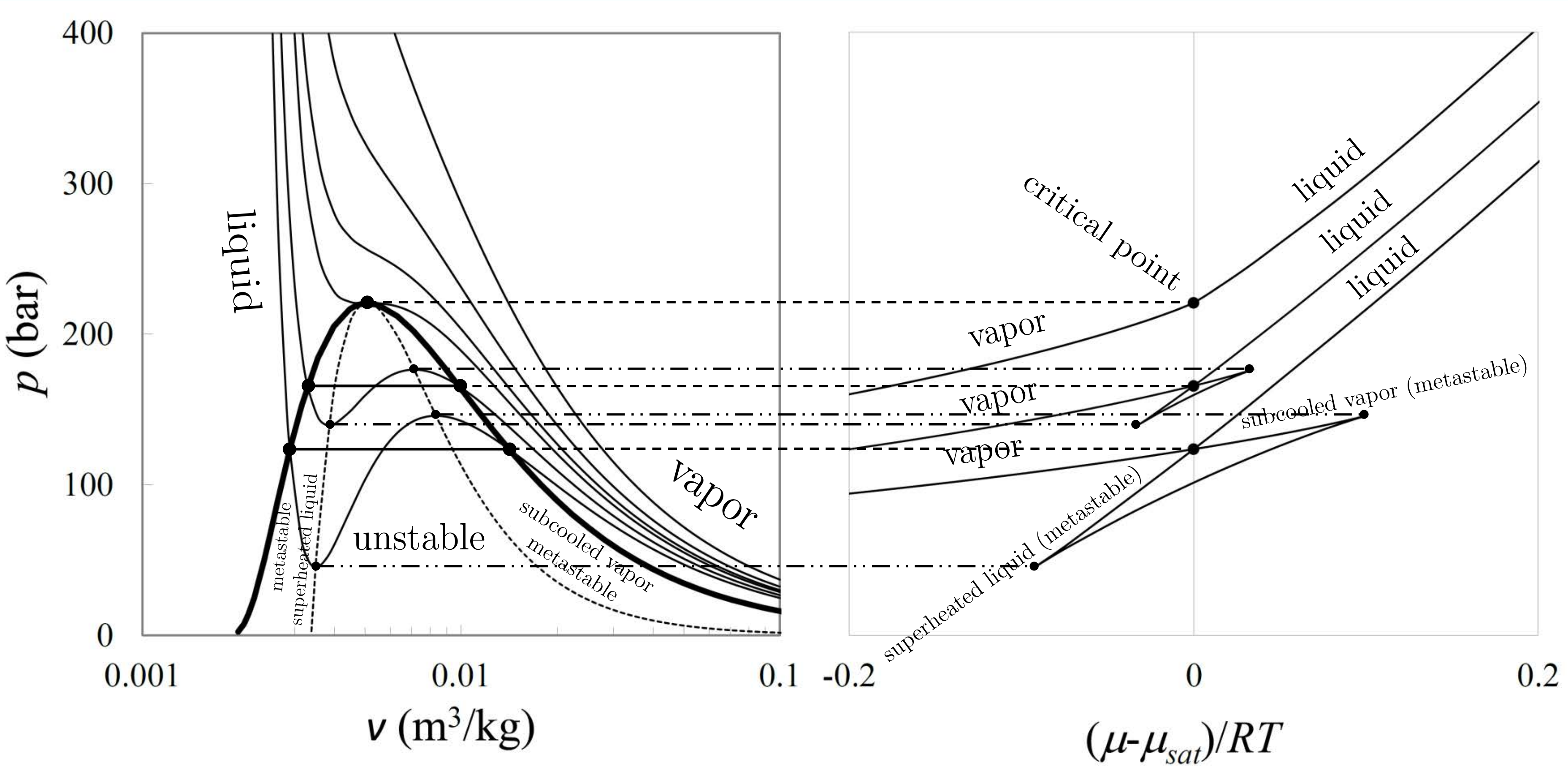
$$p_f = p_{\rm vdW}(T,v_f) = p_{\rm sat}(T) = p_g = p_{\rm vdW}(T,v_g) \quad \text{or} \quad p_{\rm vdW}(T,v_f(T)) = p_{\rm vdW}(T,v_g(T)) \qquad (1)$$

$$\mu_f = c(T) + f(T,v_f) = \mu_{\rm sat}(T) = \mu_g = c(T) + f(T,v_g) \quad \text{or} \quad f(T,v_f(T)) = f(T,v_g(T)) \qquad (2)$$

Solving the system (1)-(2) yields the values of $v_f(T)$ and $v_g(T)$, which define the saturation curve, and the value of $\mu_{\rm sat}(T) - c(T) = f(T,v_g(T))$, so that we have $\mu - \mu_{\rm sat}(T) = f(T,v) - f(T,v_g(T))$.

Modeling non-ideal SES behavior:

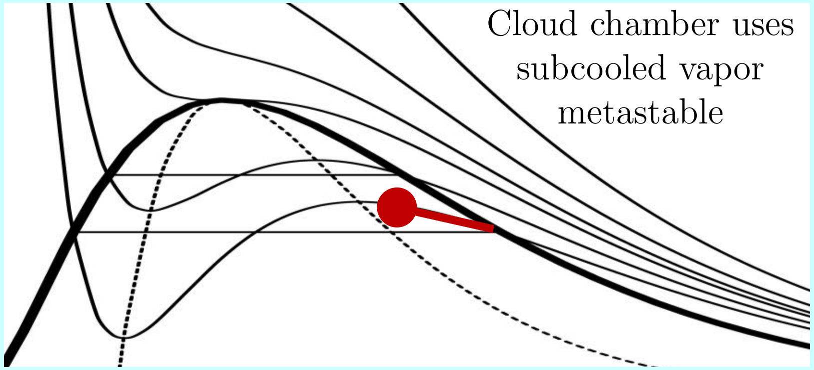
van der Waals isotherms, metastable and unstable states

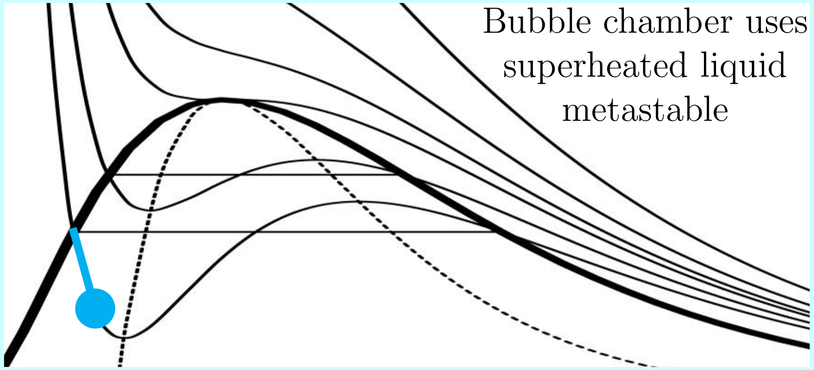


The critical isotherm (temperature T_c) exhibits a horizontal tangent flex at the critical pressure p_c. For $T < T_c$, each vdW isotherm has a minimum and a maximum. The spinodal curve (dashed), with equation $p = (v - 2b)a/v^3$, is the locus of these minima and maxima. Below it, for $p < (v - 2b)a/v^3$, the vdW model violates the stability condition $(\partial p/\partial v)_T \leq 0$ (see LeChatelier Braun, $\kappa_T \geq 0$).

Historical applications of subcooled vapor and superheated liquid metastable states:

Wilson (1911, Nobel 1927) **cloud chamber** and **Glaser** (1952, Nobel 1960) **bubble chamber**





https://upload.wikimedia.org/wikipedia/commons/0/03/CloudChamberRadium226.gif

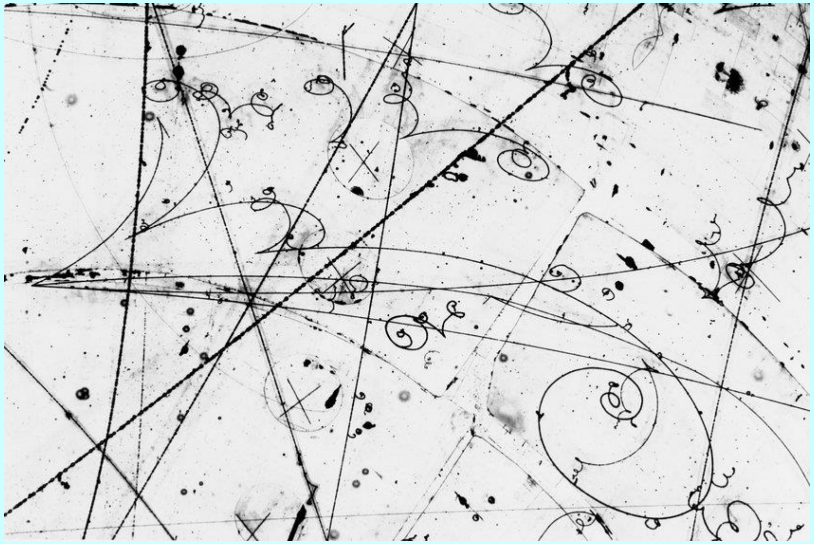
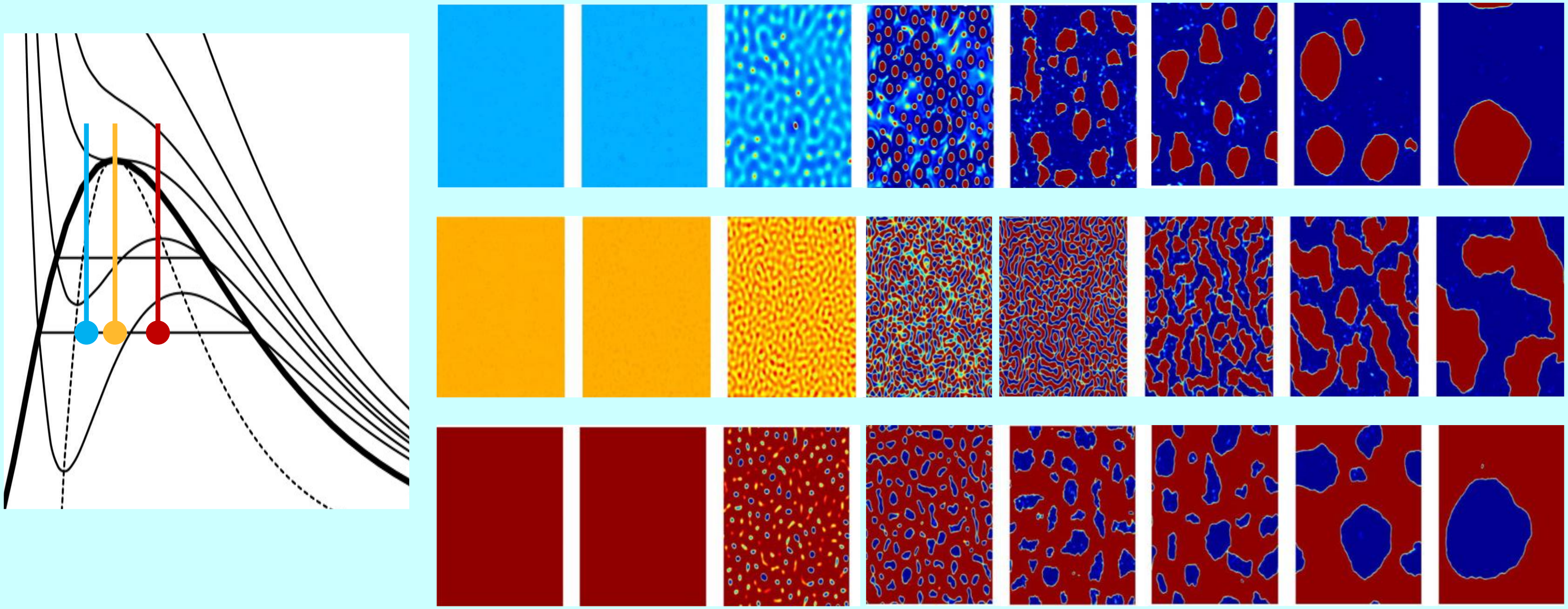


Fig.1 from A. Aurisano, L.H. Whitehead, End-to-End Analyses Using Image Classification, Artificial Intelligence For High Energy Physics (Edited by P. Calafiura, D. Rousseau, K. Terao), 313 (2022).

Modeling non-ideal SES behavior (diffuse interface numerical simulations):

liquid-vapor spinodal decomposition of a van der Waals fluid



Figures adapted from A.G. Lamorgese, R. Mauri, Diffuse-interface modeling of liquid-vapor phase separation in a van der Waals fluid, Physics of Fluids 21, 044107 (2009).

For quench at the critical density, the phase-ordering process is characterized by the formation of bicontinuous structures, which subsequently grow and coalesce.

For off-critical quenches, the phase separation pattern consists of a random collection of rapidly coalescing pseudospherical nuclei of the minority phase, surrounded by the majority phase. As can be seen, only after the first spinodal pattern is formed, i.e., a bicontinuous pattern for the critical quench, or a random collection of nuclei for the off-critical quenches, do the single-phase domains start to grow and coalesce.

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