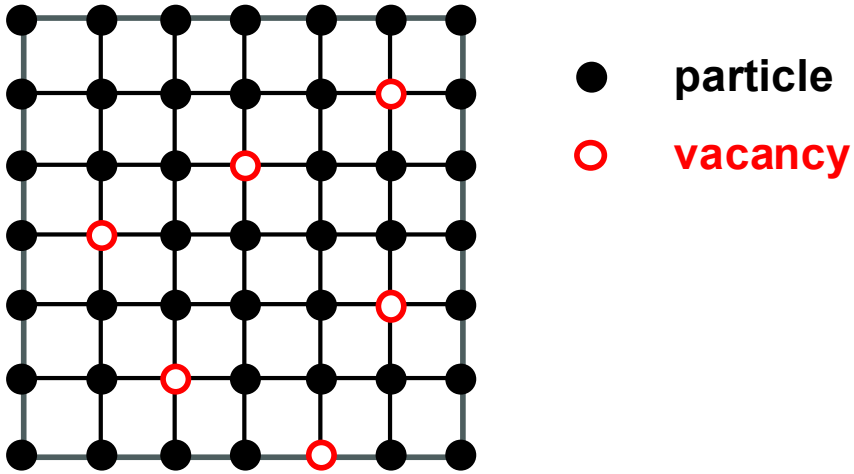
The difference between the thermodynamics of a crystal under hydrostatic stress and a liquid

The story of a collective variable from material science



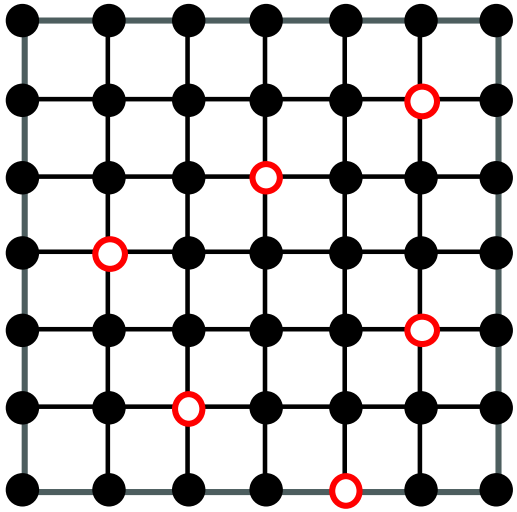
Number of vacancies not suitable as thermodynamic state variable

1.1: Larché-Cahn network constraint

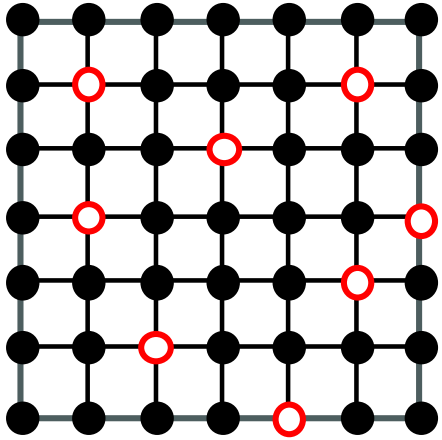
Central hypothesis of materials science

The lattice is preserved under deformation and creation of vacancies

Example: Open system compression



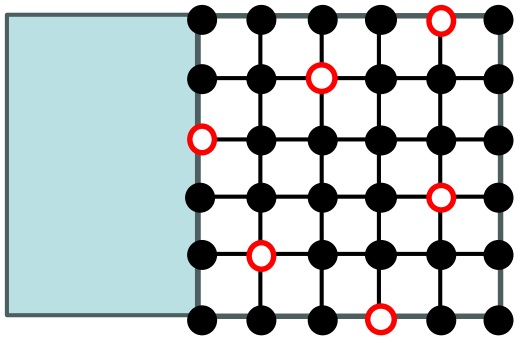
N particles
V volume
M lattice sites



N smaller
V smaller
M the same

F. Larché, J. W. Cahn *Acta Metall* **21** (1973) 1051-1063

1.2: Changing M by moving a liquid-solid interface

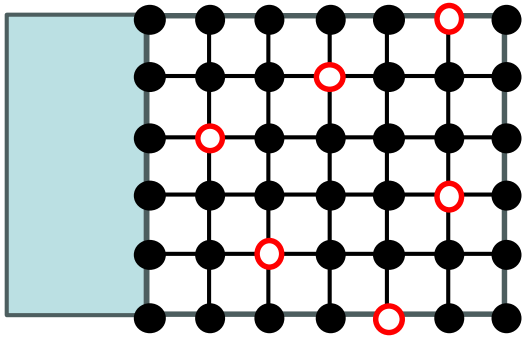


Volume of solid

$$V^{\mathsf{S}} = Mv^c, \quad v^c = \text{cell volume}$$

Displacing interface

$$\delta V^{\mathsf{S}} = -\delta V^{\mathsf{L}}, \quad \delta N^{\mathsf{S}} = -\delta N^{\mathsf{L}}$$

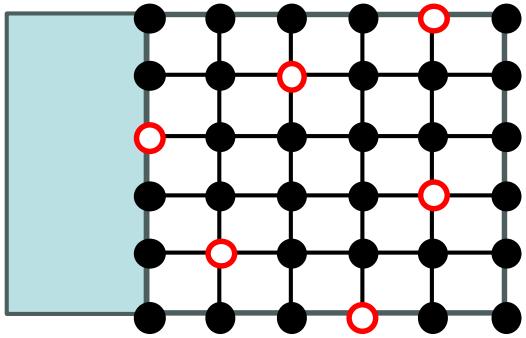


Accretion

$$\delta V^{\mathsf{S}} = v^c \delta M$$

Increasing M keeping cell volume v^c fixed

$$\delta N^{\mathsf{S}} \approx \delta M$$



Stretch

$$\delta V^{\mathsf{S}} = M \delta v^c$$

Increasing cell volume v^c keeping M fixed

$$\delta N^{\mathsf{S}} \approx 0$$

W. W. Mullins *J. Chem. Phys.* **81** (1984) 1436

1.3: Gibbs equation, one term more

Thermodynamics at constant temperature ($dT = 0$)

$$dF_l = -pdV + \mu dN + \nu dM$$

Pressure (no shear)

$$p = -\left(\frac{\partial F_l}{\partial V}\right)_{N,M}$$

Chemical potential

$$\mu = \left(\frac{\partial F_l}{\partial N}\right)_{V,M}$$

Lattice potential

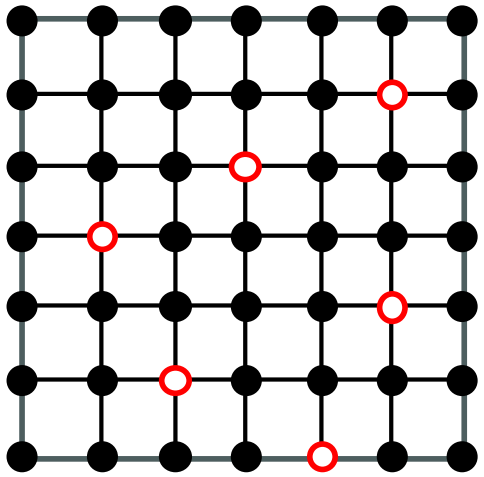
$$\nu = \left(\frac{\partial F_l}{\partial M}\right)_{N,V}$$

The question is now of course

How to interpret this ν and what can we do with it?

1.4: Three intensive state variables (densities)

Ratio's of particle number N, volume V and number of lattice sites M



$$\rho = \frac{N}{V} \qquad \text{particle density}$$

$$v^c = \frac{V}{M} \qquad \text{cell volume}$$

$$c = \frac{N}{M} \qquad \text{site occupation}$$

Two of them independent

$$\frac{c}{\rho} = \left(\frac{N}{M}\right)\left(\frac{V}{N}\right) = v^c$$

Note: Particle number N has been divided out

1.5: Free energy compressible lattice gas

Total free energy F_l is sum of three terms

$$F_l(N,V,M) = F_s(N,M) + F_e(V,M) + F_b(N,V)$$

$F_s(N,M) = Mf_s(c)$	entropy	$c = N/M$	site occupation
$F_e(V,M) = Mg_e(v^c)$	elastic energy	$v^c = V/M$	cell volume
$F_b(N,V) = -NI_b(\rho)$	molecular energy	$\rho = N/V$	particle density

Langmuir entropy per site

$$f_s(c) = k_B T\left(c\ln c + (1-c)\ln(1-c)\right)$$

Elastic energy per site

$$g_e(v^c) = \frac{\alpha_j}{2}(J-1)^2$$

is quadratic function of stretch J

$$J = \frac{v^c}{v_R^c} \qquad v_R^c = \text{reference cell volume}$$

$\epsilon = J - 1$ is the **volume strain**

1.6: Molecular interaction term

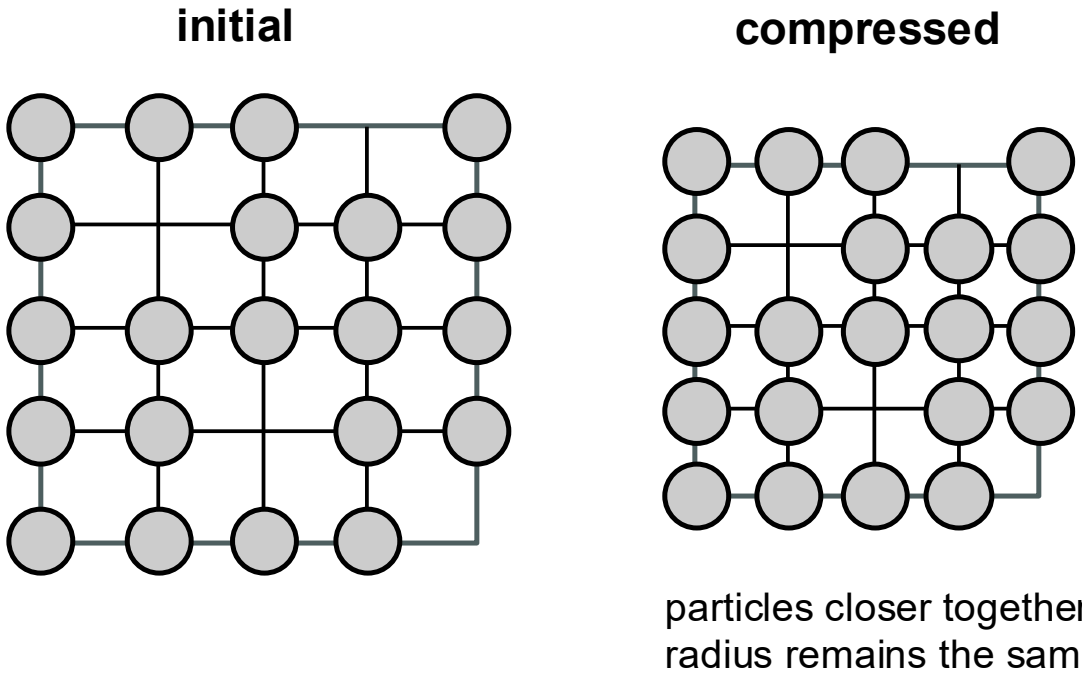
Total free energy

$$F_l(N,V,M) = F_s(N,M) + F_e(V,M) + F_b(N,V)$$

F_b accounts for short range pair interaction

$$F_b(N,V) = -NI_b(\rho), \qquad I_b(\rho) > 0$$

in mean field approximation



From per particle to per site representation

$$F_b(N,V) = -NI_b(\rho) = -McI_b(\rho)$$

1.7: Extensivity and per site representation

Free energy of compressible lattice gas

$$F_l\left(N,V,M\right)=F_s\left(N,M\right)+F_e\left(V,M\right)+F_b\left(N,V\right)$$

written as sum over energies per site

$$F_l\left(N,V,M\right)=M\big(f_s\left(c\right)+g_e\left(v\right)-cI_b\left(\rho\right)\big)$$

Scaling (N,V,M) by λ

$$F_l\left(\lambda N,\lambda V,\lambda M\right)=\lambda M\big(f_s\left(c\right)+g_e\left(v\right)-cI_b\left(\rho\right)\big)$$

Densities are invariant

$$F_l\left(\lambda N,\lambda V,\lambda M\right)=\lambda F_l\left(N,V,M\right)$$

Per site representation is **explicitly extensive**

1.8: Great grand potential

Combining

- **Gibbs equation**

$$dF_l = -pdV + \mu dN + \nu dM$$

- **Extensivity**

$$F_l(\lambda N, \lambda V, \lambda M) = \lambda F_l(N, V, M)$$

Applying the Euler theorem

$$F_l = -pV + \mu N + \nu M$$

or rearranged

$$\nu M = F_l + pV - \mu N$$

Great grand potential

$$\mathcal{E} = F + pV - \mu N \begin{cases} = 0 & \textit{liquid} \\ \neq 0 & \textit{crystal} \end{cases}$$

$\mathcal{E}$ was already introduced by **Guggenheim**

1.9: Chemical potential and pressure mismatch

Implications of a nonzero great grand potential

$$\nu M = F + pV - \mu N$$

for the standard "liquid phase" definitions of

- **Gibbs free energy** $G_l = F_l + pV$

$$G_l - \mu N = \nu M \quad \rightarrow \quad \frac{G_l}{N} - \mu = \frac{\nu}{c}$$

  where $c = N/M$ is the occupation

- **Grand potential** $\Omega_l = F_l - \mu N$

$$\Omega_l + pV = \nu M \quad \rightarrow \quad \frac{\Omega_l}{V} + p = \frac{\nu}{v^c}$$

  where $v^c = V/M$ is the volume of a lattice cell

The crystal thermodynamic gap (mismatch) is proportional to ν

1.10: Gibbs-Duhem equation and derivative isotherms

Isothermal Gibbs equation

$$dF_l = -pdV + \mu dN + \nu dM$$

Integral Gibbs-Duhem equation

$$F_l = -pV + \mu N + \nu M$$

Differential Gibbs-Duhem equation

$$Md\nu = -SdT + Vdp - Nd\mu$$

Absorption isotherm

$$\left(\frac{\partial \nu}{\partial \mu}\right)_{p,T} = -c$$

Cell volume isotherm

$$\left(\frac{\partial \nu}{\partial p}\right)_{\mu,T} = v^c$$

c and v^c are observables obtained from diffraction experiments

Changes in ν can be determined by thermodynamic integration

1.11: Chemical potential

Resolution free energy

$$F_l\left(N,V,M\right) = F_s\left(N,M\right) + F_e\left(V,M\right) + F_b\left(N,V\right)$$

$F_s\left(N,M\right) = Mf_s(c)$	Langmuir entropy	$c = N/M$	site occupation
$F_e\left(V,M\right) = Mg_e(v^c)$	elastic energy	$v^c = V/M$	cell volume
$F_b\left(N,V\right) = -NI_b\left(\rho\right)$	molecular energy	$\rho = N/V$	particle density

Chemical potential

$$\mu = \left(\frac{\partial F_l}{\partial N}\right)_{V,M} = \left(\frac{\partial F_s}{\partial N}\right)_{M} + \left(\frac{\partial F_b}{\partial N}\right)_{V}$$

Evaluating partial derivatives

$$\mu = k_{\mathrm{B}}T\ln\left(\frac{c}{1-c}\right) - I_b\left(\rho\right) - \rho\left(\frac{dI_b}{d\rho}\right)$$

Note

No elastic energy contribution to the chemical potential

1.12: Lattice potential

Resolution free energy

$$F_l\left(N,V,M\right)=F_s\left(N,M\right)+F_e\left(V,M\right)+F_b\left(N,V\right)$$

$F_s\left(N,M\right)=Mf_s(c)$	Langmuir entropy	$c=N/M$	site occupation
$F_e\left(V,M\right)=Mg_e(v^c)$	elastic energy	$v^c=V/M$	cell volume
$F_b\left(N,V\right)=-NI_b\left(\rho\right)$	molecular energy	$\rho=N/V$	particle density

Lattice potential

$$\nu=\left(\frac{\partial F_l}{\partial M}\right)_{N,V}=\left(\frac{\partial F_s}{\partial M}\right)_{N}+\left(\frac{\partial F_e}{\partial M}\right)_{V}$$

Evaluating partial derivatives

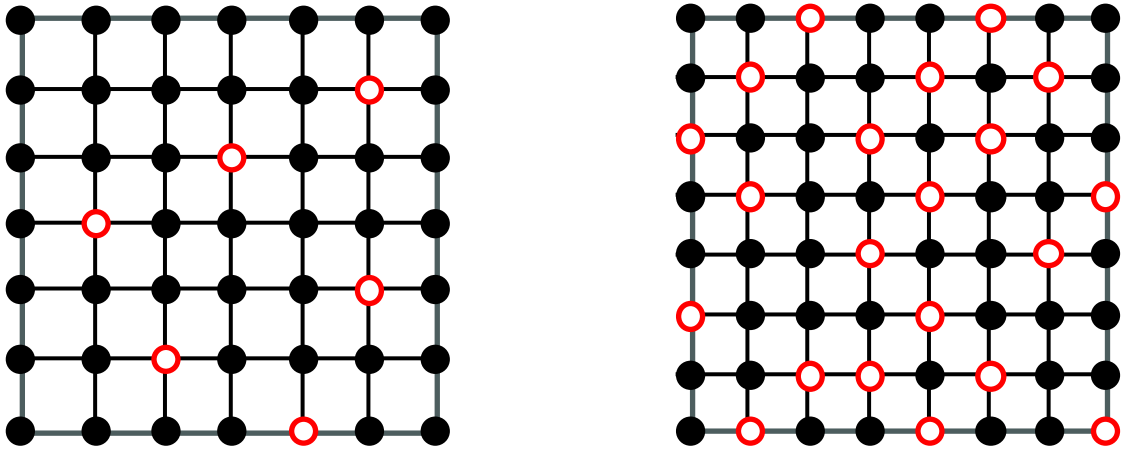
$$\nu=k_{\mathrm{B}}T\ln\left(1-c\right)-\frac{\alpha_j}{2}\left(J^2-1\right)$$

Note

No binding energy contribution to the lattice potential

1.13: Adding lattice sites at fixed N and V

N, V, M $\qquad$ $N, V, \lambda M$



Writing the lattice potential

$$\nu = k_{\mathrm{B}} T \ln h - \sigma_j$$

in the small deformation approximation

h	$=$	$1 - c$	vacancy population
σ_j	$=$	$\alpha_j \, (J - 1)$	elastic stress

ν links vacancies to volume elasticity

both of them absent in the liquid

1.14: Cancellation $c \to 1$ divergence

Lattice potential

$$\nu = k_{\mathsf{B}} T \ln (1 - c) - \sigma_j$$

Compare to chemical potential

$$\mu = k_{\mathsf{B}} T \ln \left(\frac{c}{1 - c} \right) - I_b (\rho) - \rho \left(\frac{dI_b}{d\rho} \right)$$

Singular terms cancel in integral Gibbs-Duhem energy relation

$$N\mu + \nu M = M (c\mu + \nu)$$

Substituting

$$\begin{aligned} c\mu + \nu &= k_{\mathsf{B}} T \big(c \ln \left(\frac{c}{1 - c} \right) + \ln (1 - c) \big) \\ &= k_{\mathsf{B}} T \big(c \ln c + (1 - c) \ln (1 - c) \big) = f_s (c) \end{aligned}$$

Ideal crystal limit of Langmuir entropy is finite

$$\lim_{c \to 1} f_s(c) = 0$$

1.15: Pressure

Resolution free energy

$$F_l\left(N,V,M\right)=F_s\left(N,M\right)+F_e\left(V,M\right)+F_b\left(N,V\right)$$

Pressure determined by elastic energy and molecular interactions

$$p=-\left(\frac{\partial F_l}{\partial V}\right)_{N,M}=-\left(\frac{\partial F_e}{\partial V}\right)_{M}-\left(\frac{\partial F_b}{\partial V}\right)_{N}$$

Defining the scaled pressure

$$p^{\star}=v_R^c\,p$$

and evaluating partial derivatives

$$p^{\star}=p_c^{\star}-\sigma_j \qquad \text{total pressure}$$

$$p_c^{\star}=-v_R^c\,\rho^2\left(\frac{dI}{d\rho}\right) \qquad \text{molecular pressure} \qquad \rho=\frac{N}{V}$$

$$\sigma_j=\alpha_j\left(J-1\right) \qquad \text{elastic volume stress} \qquad J=\frac{V}{v_R^c M}=\frac{v^c}{v_R^c}$$

Now f_s missing

No (configurational) entropy contribution to the pressure

1.16: Residual deformation under zero external pressure

Mechanical equilibrium under applied pressure $\bar{p}^\star = v_R^c \bar{p}$

$$p_c^\star(\rho) - \sigma_j(J) = \bar{p}^\star$$

Density ρ is a function of occupation c and stretch J

$$\left.\begin{aligned} c &= \frac{N}{M} \\ J &= \frac{V}{v_R^c M} \end{aligned}\right\} \rightarrow \rho = \left(\frac{N}{M}\right)\left(\frac{M}{V}\right) = \frac{c}{v_R^c J}$$

Changing variables

$$\tilde{p}_c^\star(c, J) = p_c^\star(\rho(c, J))$$

Setting $\bar{p}^\star = 0$ substituting for σ_j

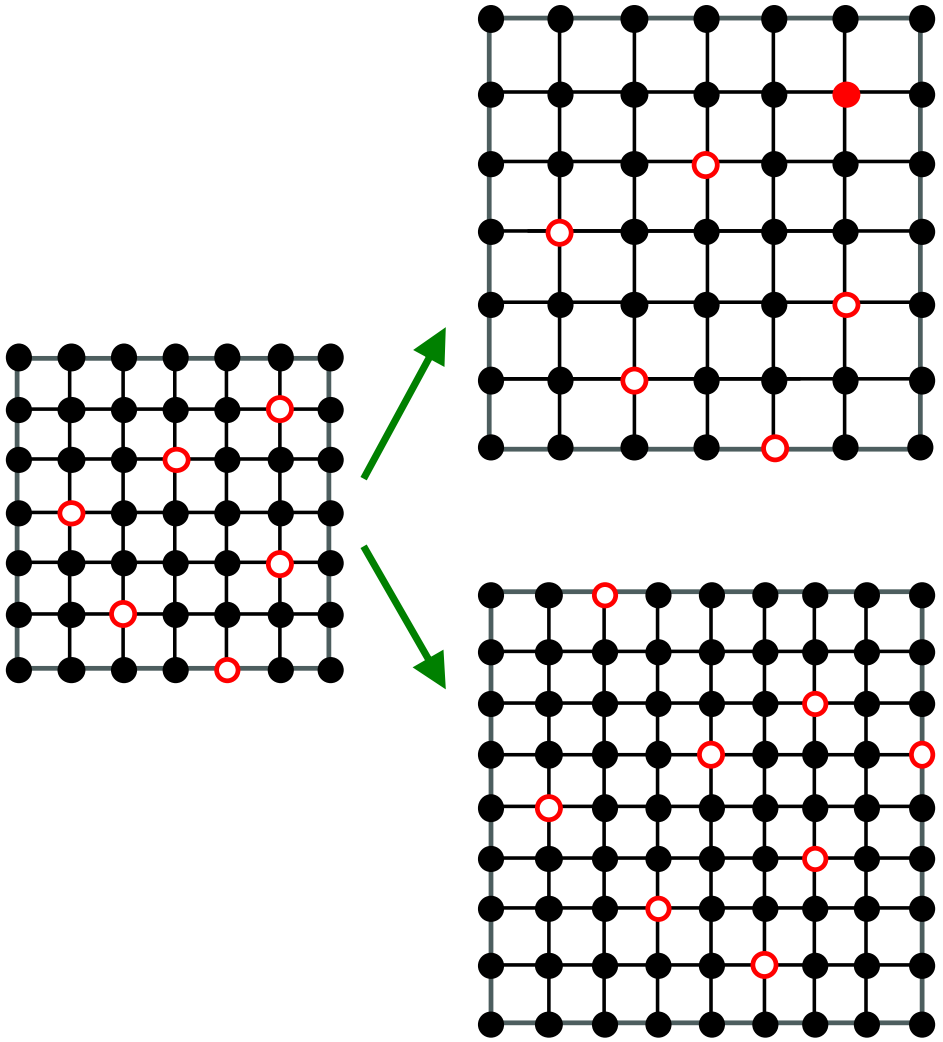
$$\tilde{p}_c^\star(c, J_0) = \alpha_j(J_0 - 1)$$

Crystal left with a finite strain ϵ_0 at zero applied (external) pressure

$$J_0 = 1 + \epsilon_0 \qquad \begin{cases} \epsilon_0 > 0 & \text{expansion} \\ \epsilon_0 < 0 & \text{compression} \end{cases}$$

also called **eigenstrain**

1.17: Larché-Cahn network principle for open systems



Open system **expansion**

$$(\mu, V, M) \to (\mu, \lambda V, M)$$

induced change in density

$$\frac{d\rho}{\rho} = \left(2\beta\gamma_b\,(1-c) - \frac{1}{J}\right) dJ$$

instead of **accretion**

$$(\mu, V, M) \to (\mu, \lambda V, \lambda M)$$

No change in density

$$\frac{d\rho}{\rho} = 0$$

MS *J. Chem. Phys.* (in press), also on *arXiv*

Dear Michele

Congratulations and carry on

leading us with your example of

never giving up on a difficult problem