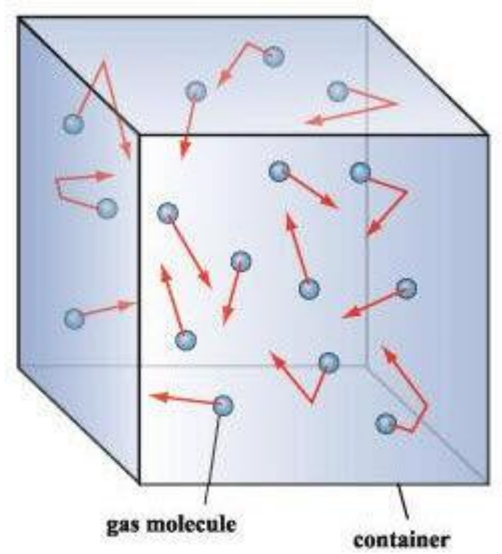
Five little stories about liquids

Matteo Baggioli (SJTU Shanghai)

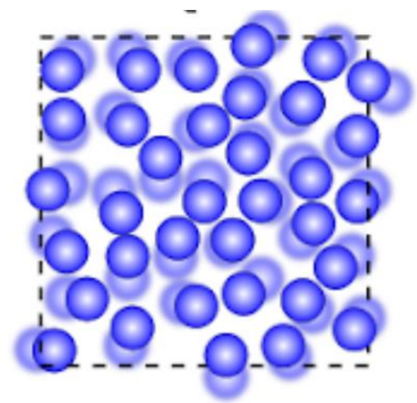
"perdersi in un bicchere d'acqua"

gases



solids

liquids



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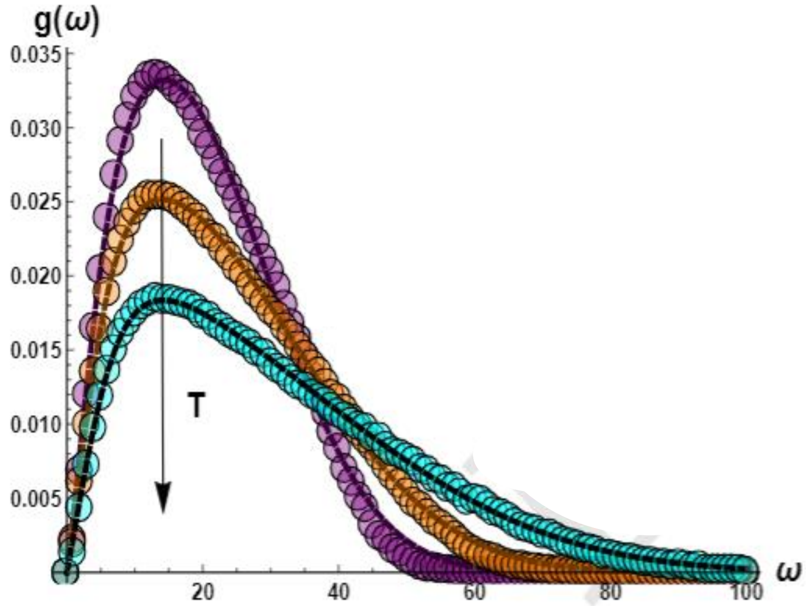
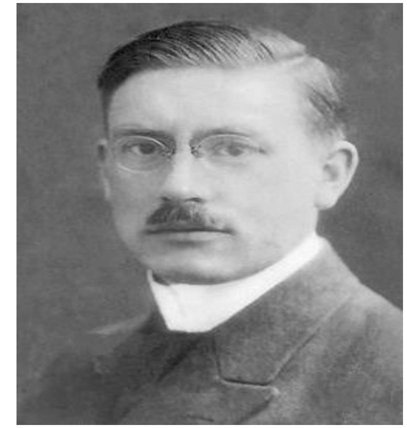
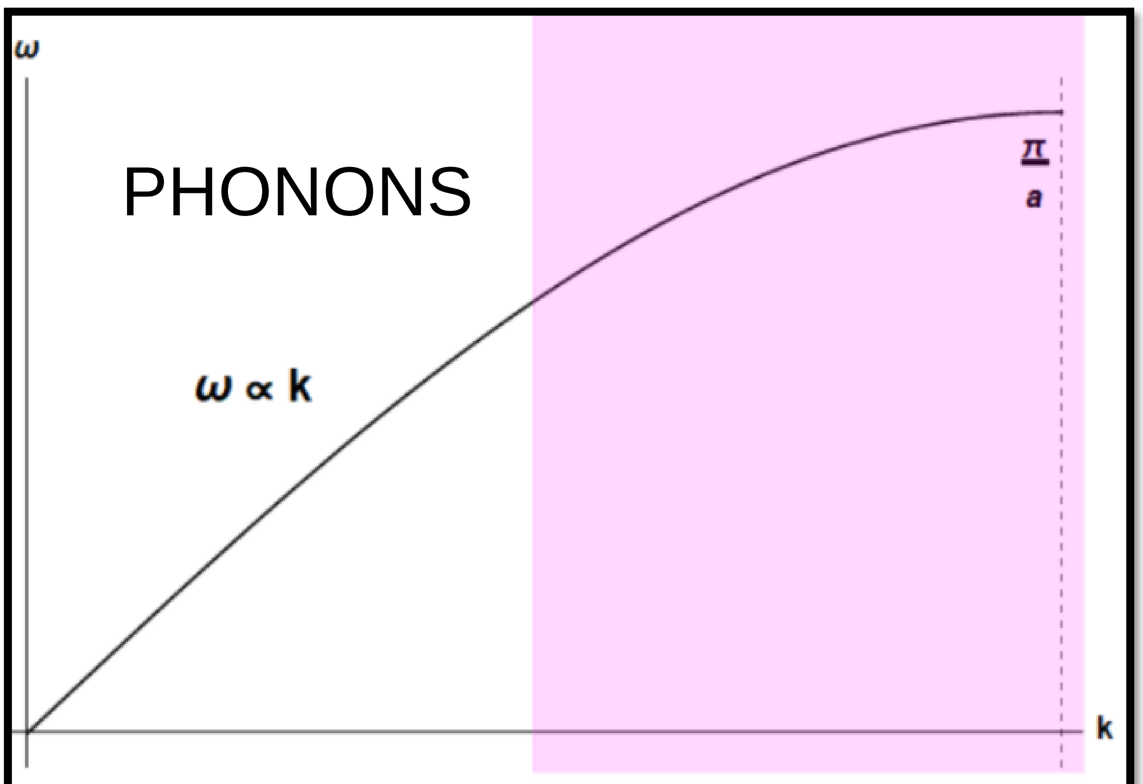
Zaccone
PNAS
2021



Density of States

The  **:** 



Simple counting argument
+
dispersion relation

$$g(\omega)\, d\omega \;=\; f(k)\, dk \;=\; \frac{k^2}{2\,\pi^2}\, dk$$

$$g(\omega) \;=\; \frac{1}{2\,\pi^2\, v^3}\,\omega^2$$

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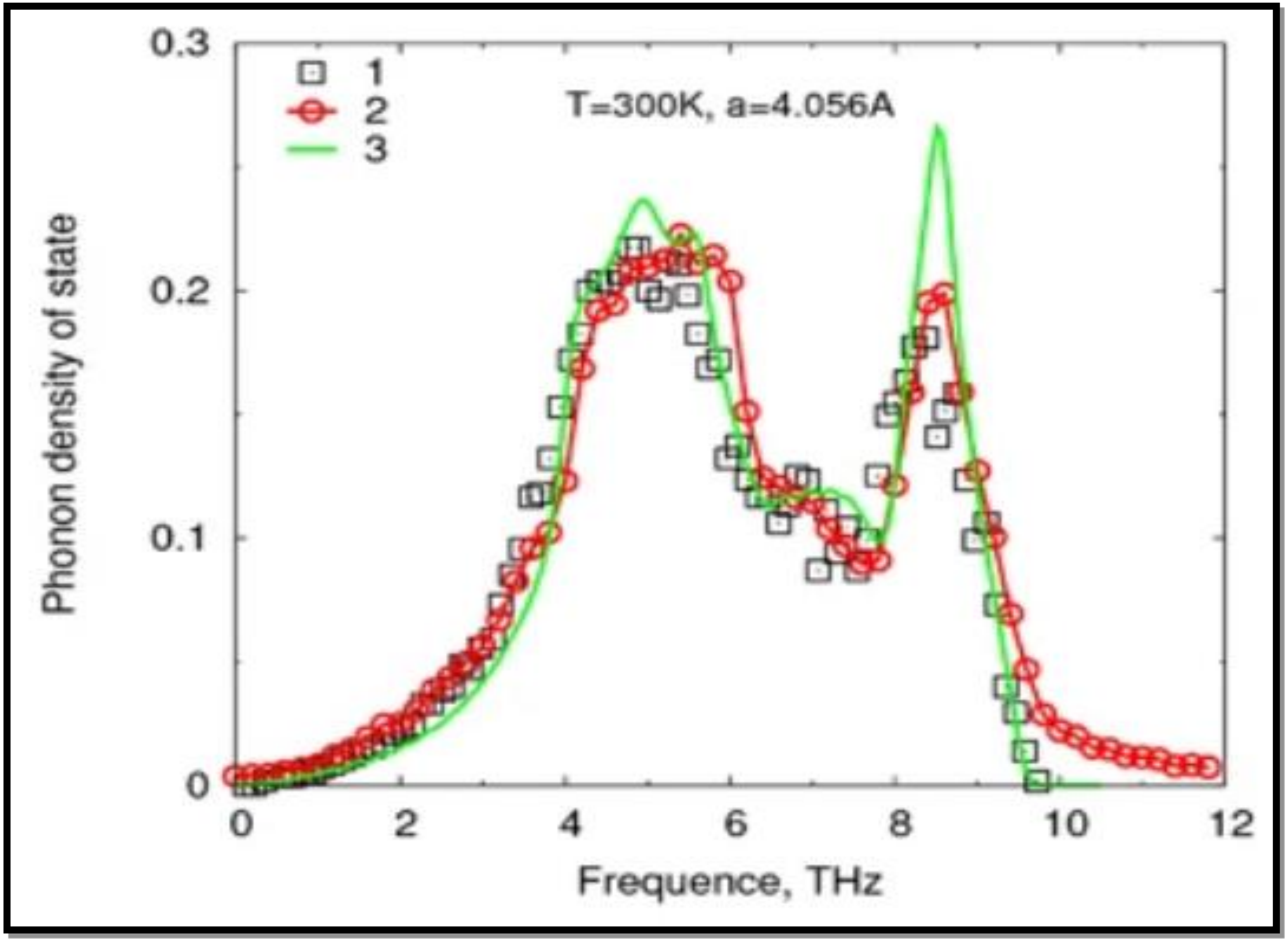
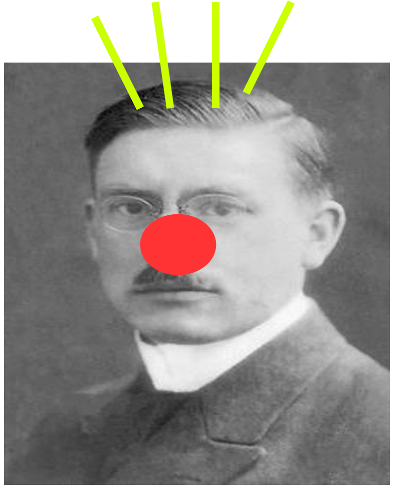
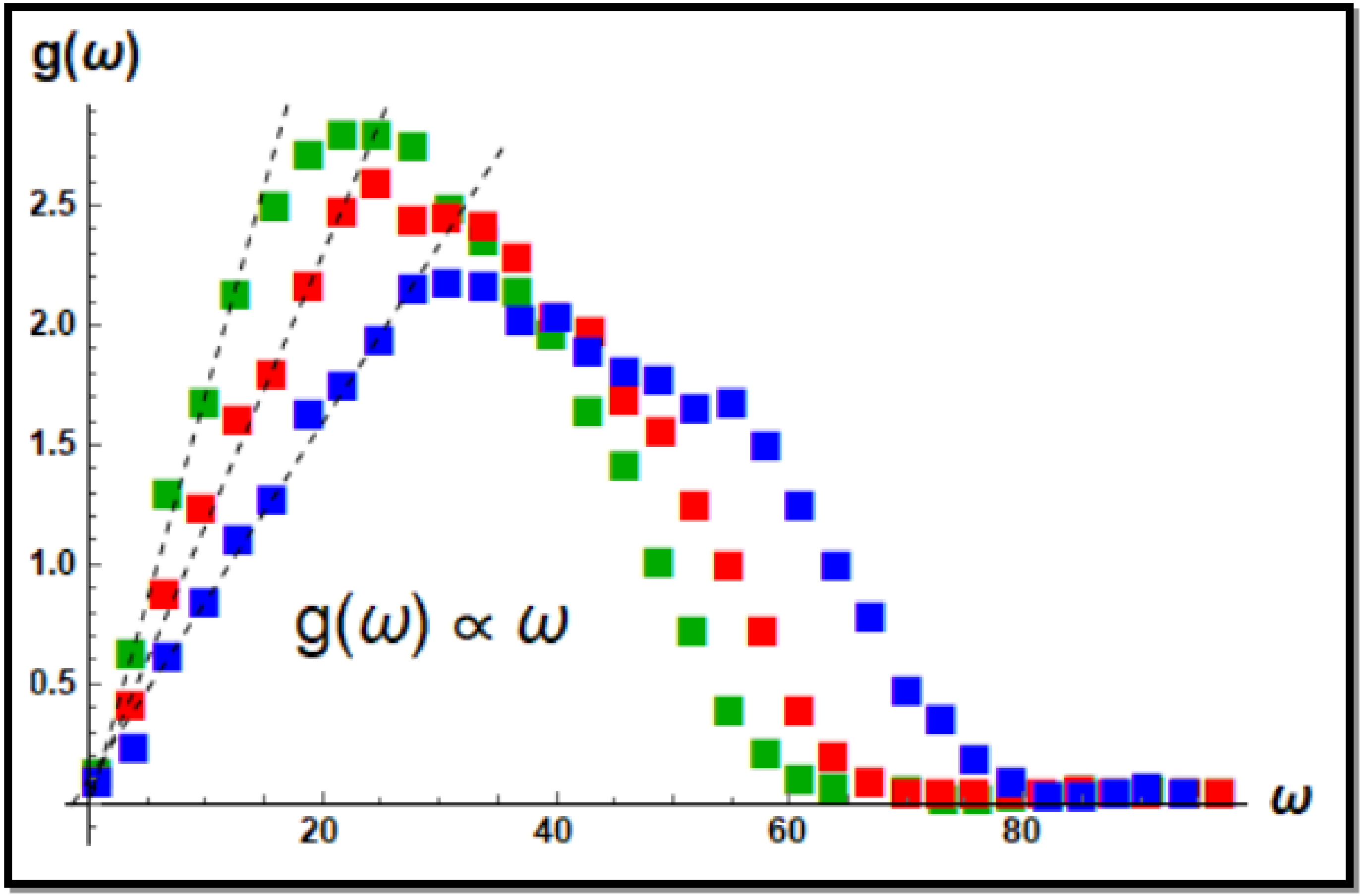


TEXTBOOK MATERIAL

The  **:** 



Explanation not in textbooks

MAY 1995

The Instantaneous Normal Modes of Liquids

RICHARD M. STRATT

Department of Chemistry, Brown University, Providence, Rhode Island 02912

Received December 22, 1994

I. Liquids Are Not Held Together by Springs

It hardly needs saying that the presence, and indeed the dynamics, of liquids plays a crucial role in chemical processes ranging from electron transfer[1] to acid–base chemistry.[2] Sometimes this role is merely the result of the solvent's availability as a reactant present in huge excess, but more generically, it arises becauses solvents can *solvate*: they can alter the energy of a

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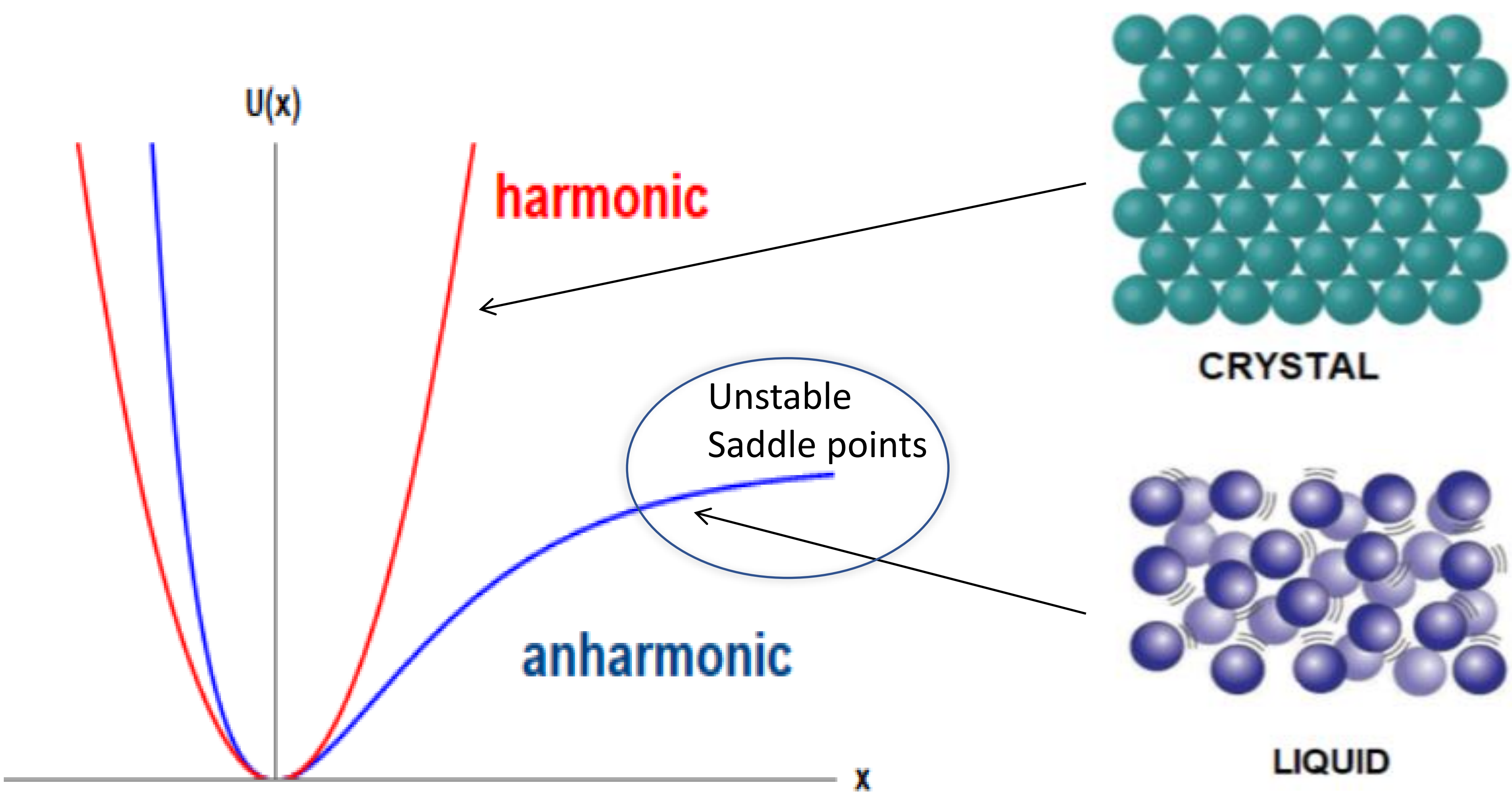
Instantaneous normal modes (INMs)

The locally anharmonic dynamics of atoms in liquids leads to many saddle points in the energy landscape. These saddle points are associated with localized unstable (exponentially decaying) modes, with purely imaginary frequency.



$$\frac{d\mathbf{v}}{dt} = -\Gamma\mathbf{v}, \quad \Gamma \equiv 1/\tau$$

[Langevin equation]

Large amount of purely relaxational modes

Starting point

$$g(\omega) = \frac{1}{3\mathcal{N}} \sum_j \delta(\omega - \omega_j) \qquad G(\omega) = \frac{1}{i\,\omega + \Gamma}$$

Some math after (complex Plemeji identity)

J Julve, R Cepedello, FJ de Urries, The complex Dirac Delta, Plemelj formula, and integral representations. *arXiv e-prints*, arXiv:1603.05530 (2016).

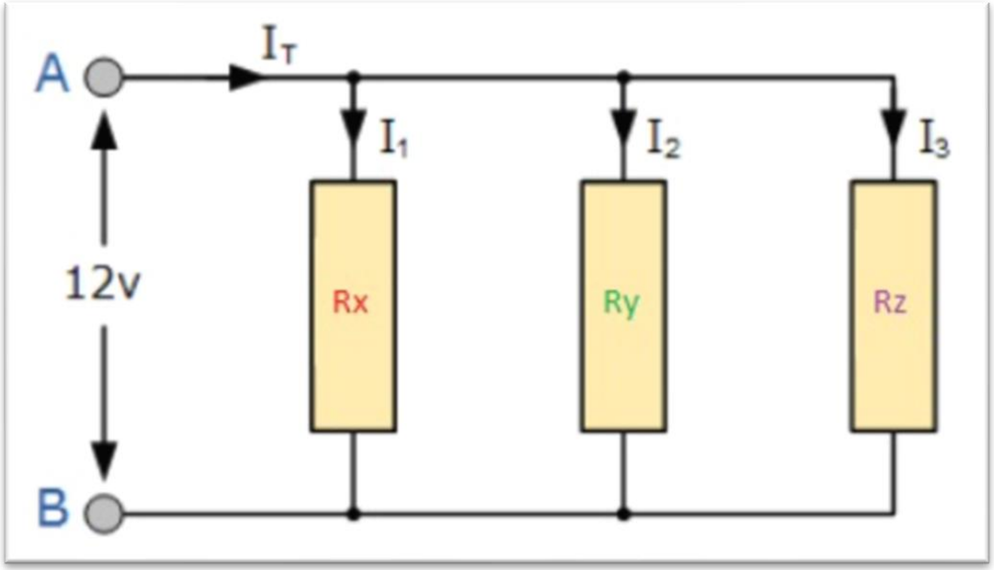
J Julve, FJ de Urríes, Inner products of resonance solutions in 1d quantum barriers. *J. Phys. A: Math. Theor.* **43**, 175301 (2010).

$$g(z) \equiv \delta(z - z') = -\frac{1}{3\,\pi\,\mathcal{N}}\,\mathrm{Im}\left[\frac{1}{i\omega - (-\Gamma) + i\,0^+}\right]$$

$$= \frac{1}{3\,\pi\,\mathcal{N}}\,\frac{\omega}{\omega^2 + \Gamma^2}\,.$$

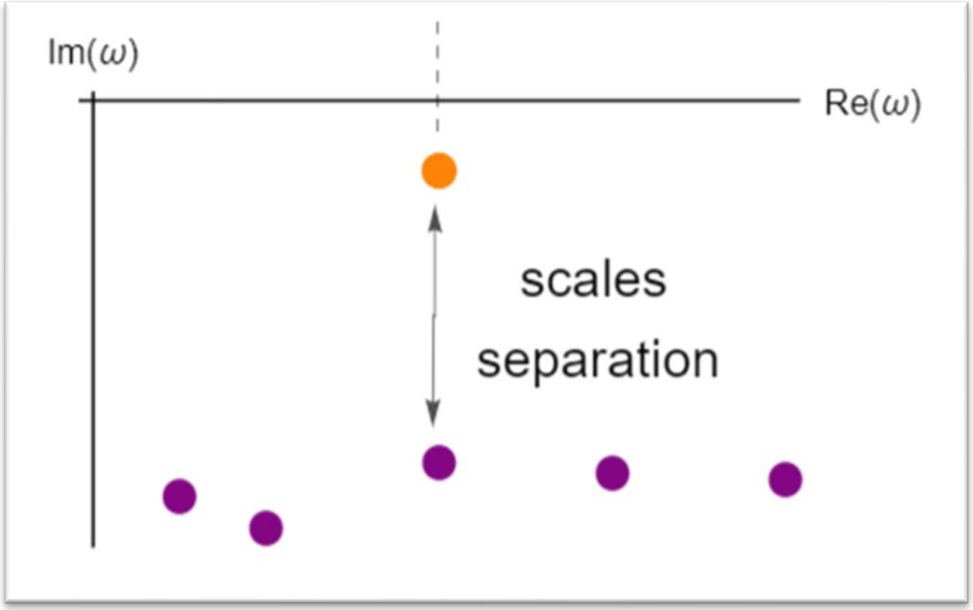
Caveat

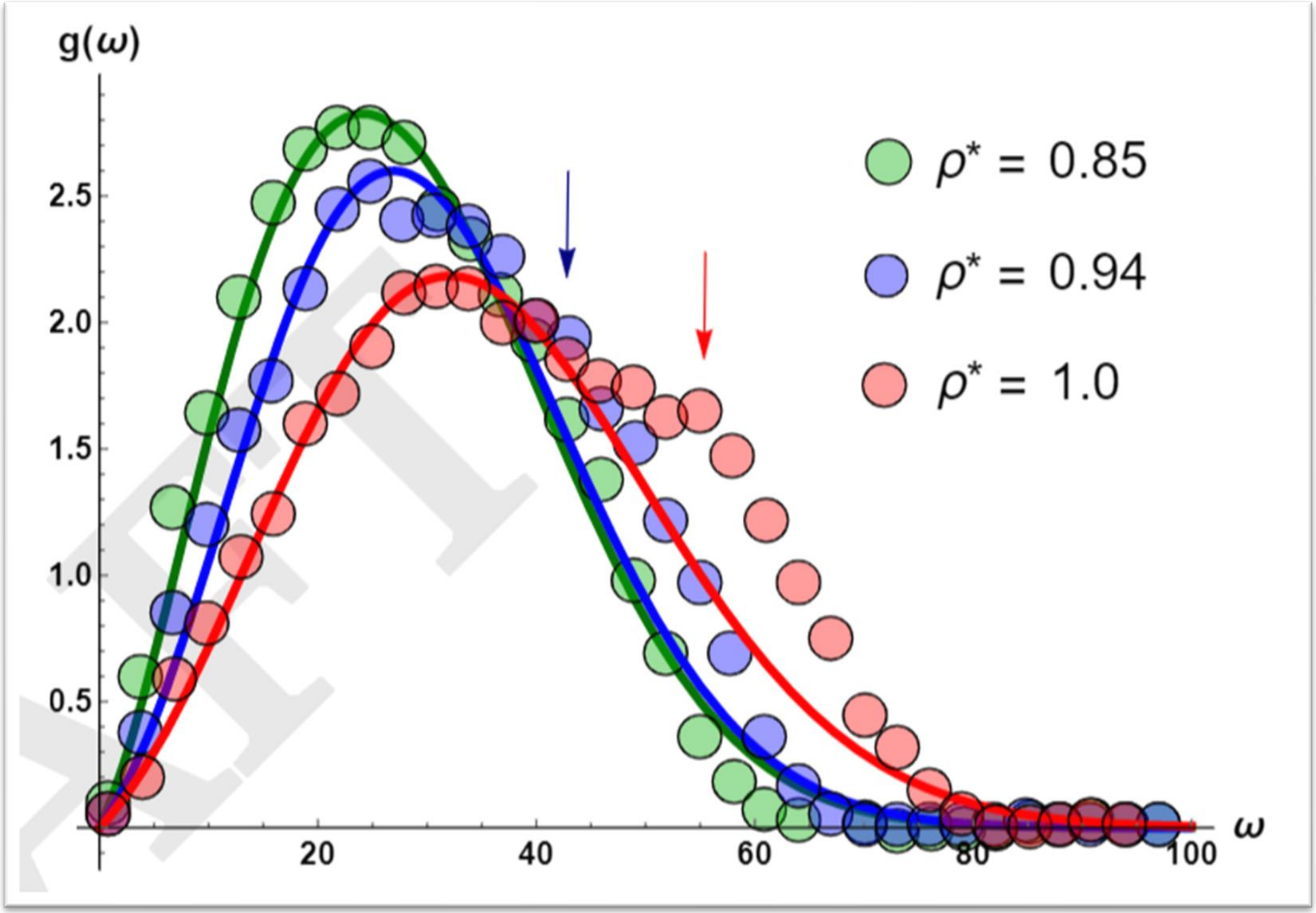
$$\frac{1}{\Gamma^2} = \sum_i \frac{1}{\Gamma_i^2}$$



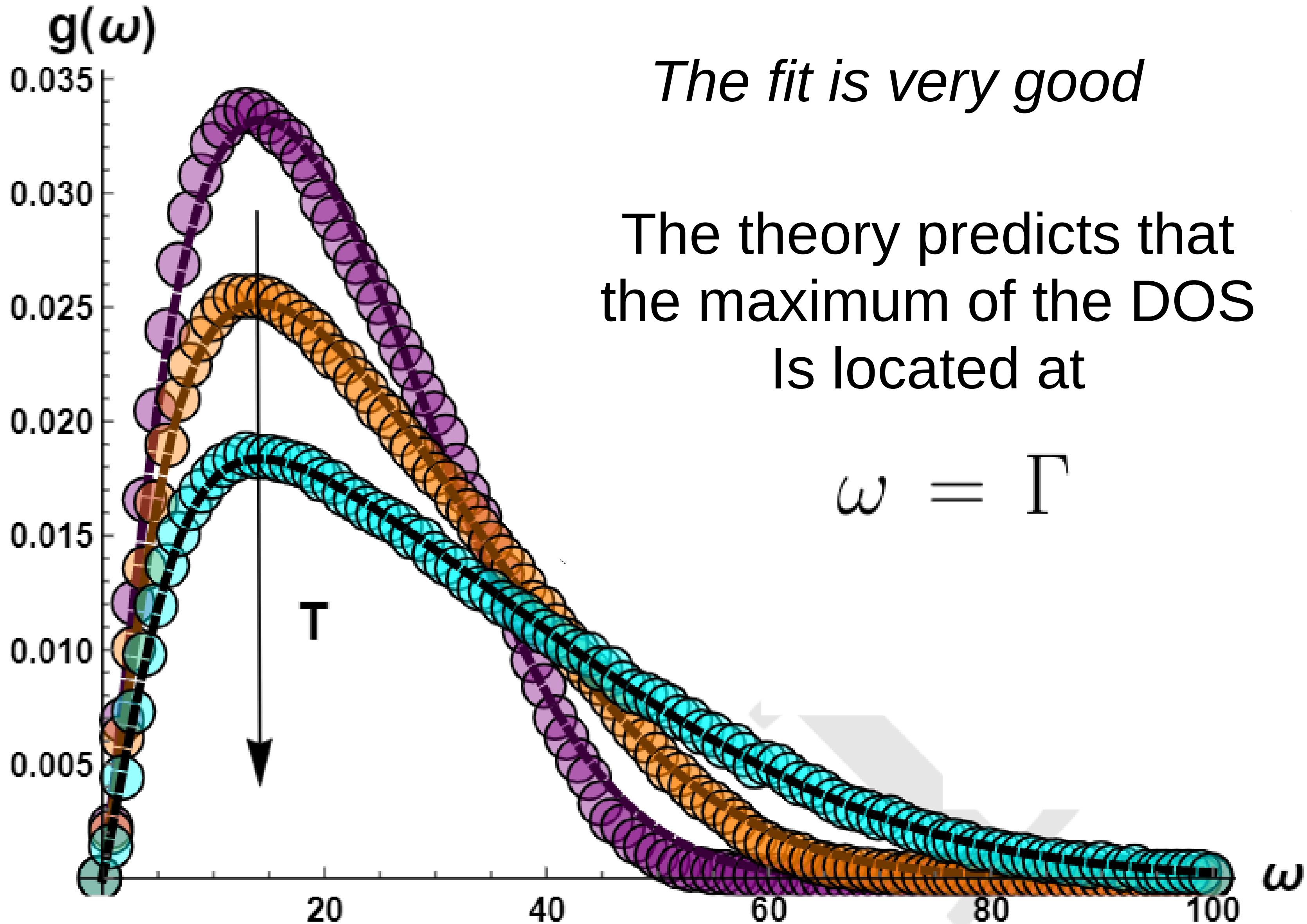
IF separation of scales

$$\Gamma^* \ll \Gamma_2, \Gamma_3, \ldots$$





[Red line is close to the glass transition. The system is becoming solid. See the low regime becomes quadratic and a relic of the Van-Hove singularity is appearing]



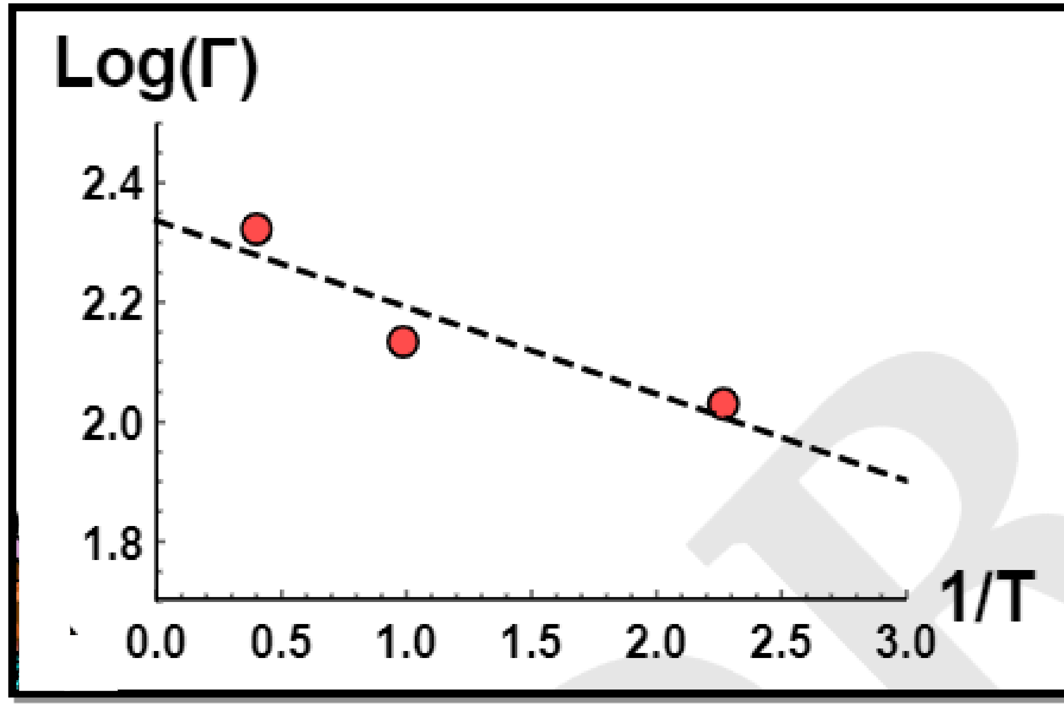
The fit is very good

The theory predicts that the maximum of the DOS Is located at

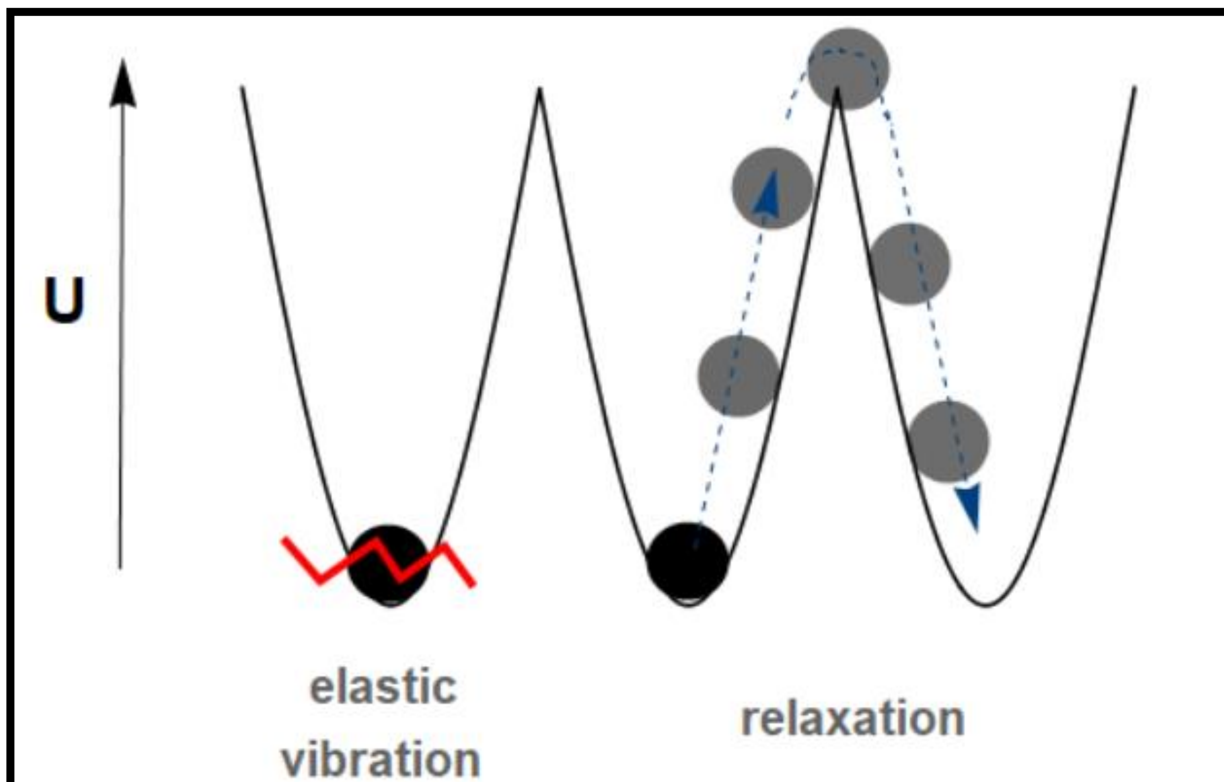
$$\omega = \Gamma$$

From the fit of the DOS we obtain

$$\Gamma(T) = \Gamma_0 e^{-U/T}$$



Famous Arrhenius law



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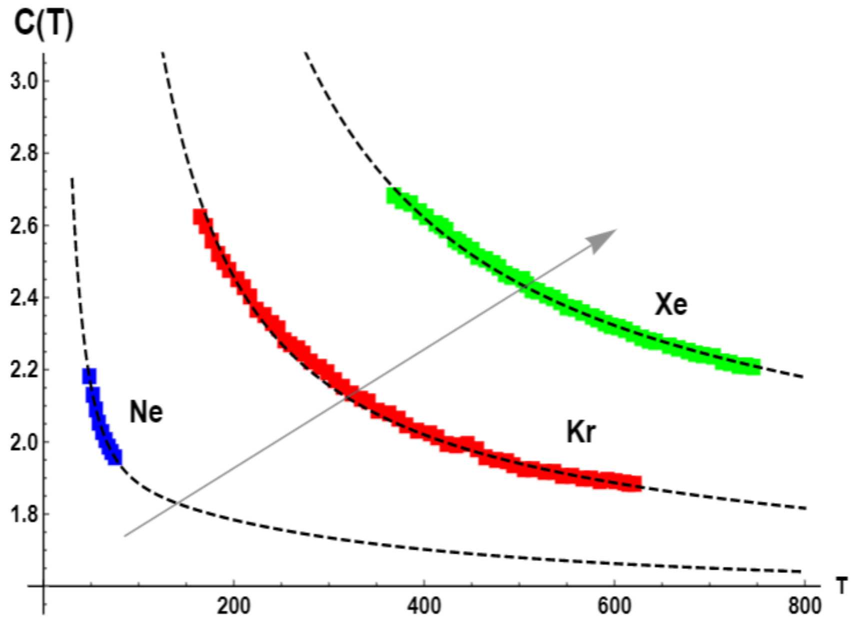
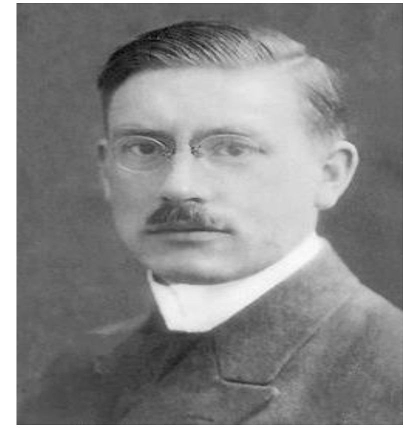
Zaccone
2021
[submitted]

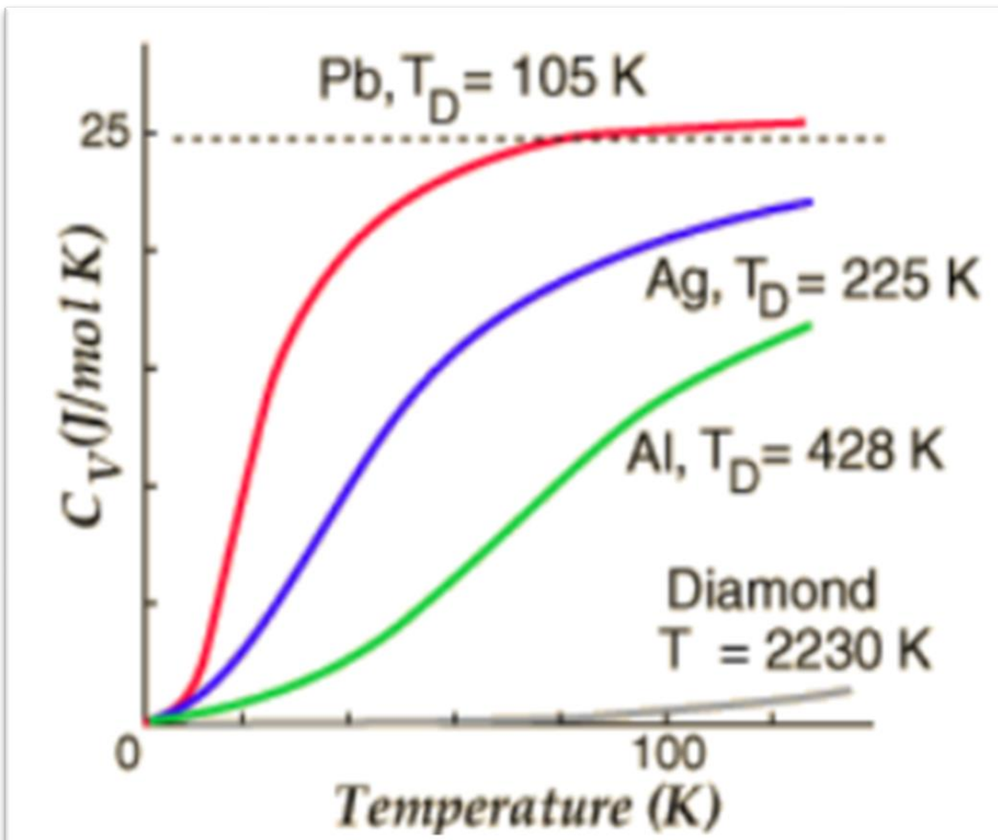


Specific Heat

The

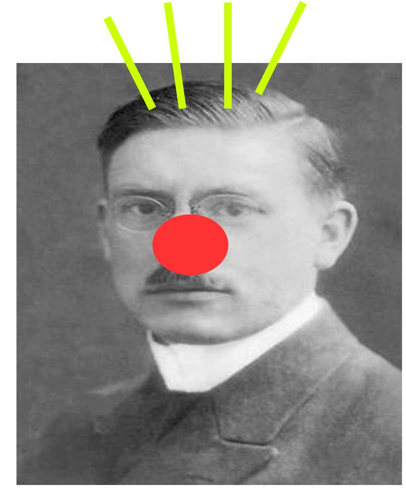
:

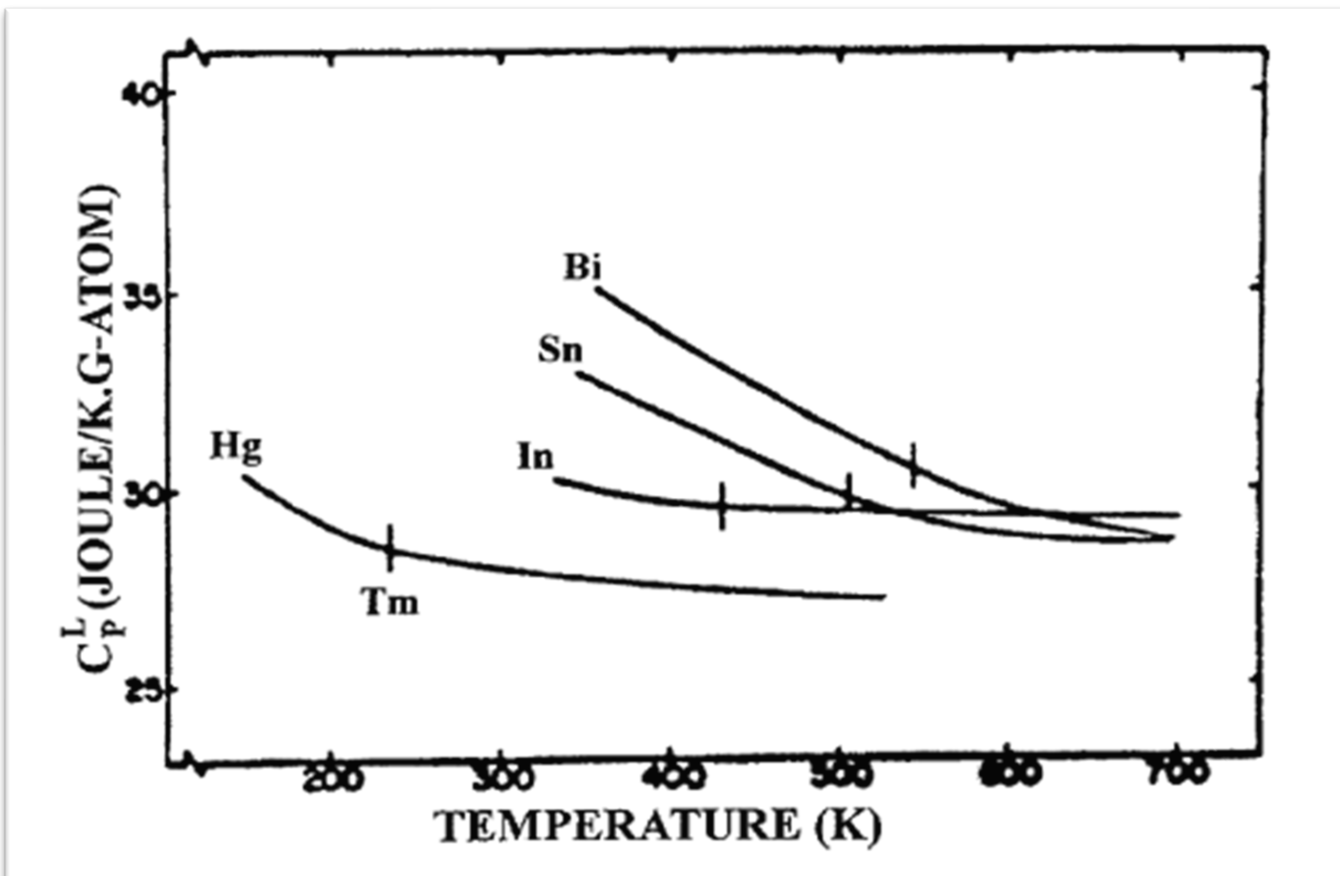




$$C(T) \sim T^d$$

TEXTBOOK
MATERIAL

The  ***:*** 



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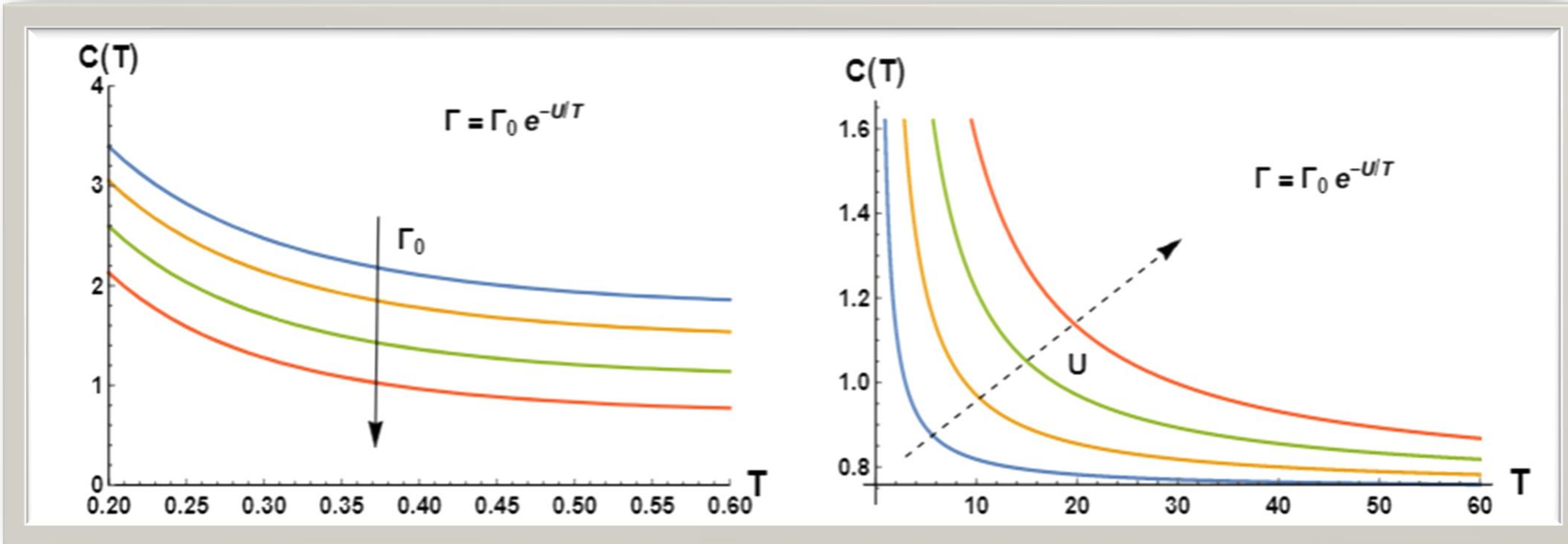
Standard derivation for bosonic fields

$$C_V(T) = \left(\frac{\partial E}{\partial T}\right)_V = 3N\int_0^\infty \frac{(\omega/T)^2 e^{\omega/T}}{(e^{\omega/T}-1)^2} g(\omega)\,d\omega = 3N\int_0^\infty \left(\frac{\omega}{2T}\right)^2 \sinh\left(\frac{\omega}{2T}\right)^{-2} g(\omega)\,d\omega$$

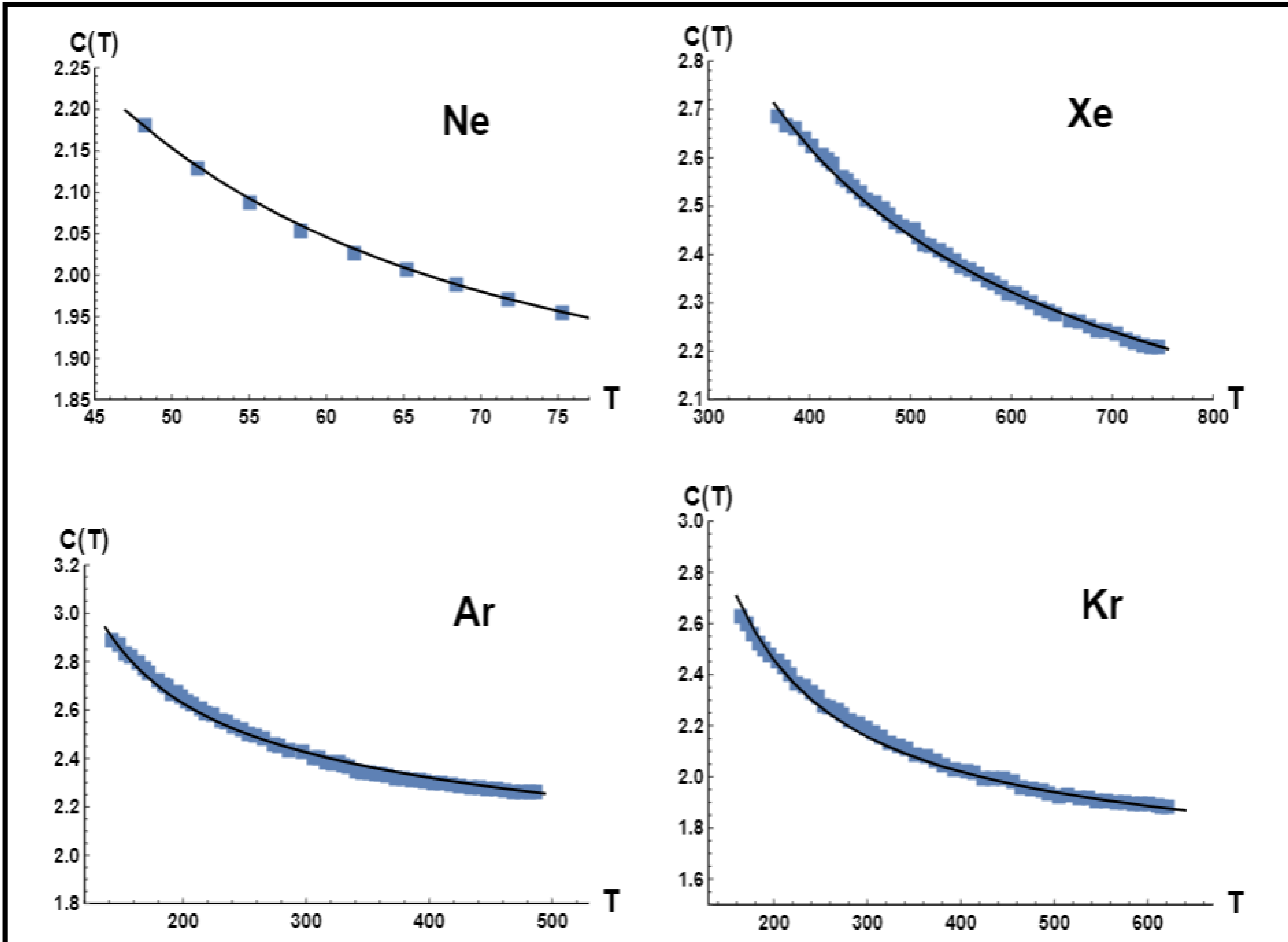
+ use our previous result

$$g_{liq}(\omega) \sim \frac{\omega}{\omega^2+\Gamma^2}\, e^{-\omega^2/\omega_D^2}\,,$$



The smaller the relaxation rate:

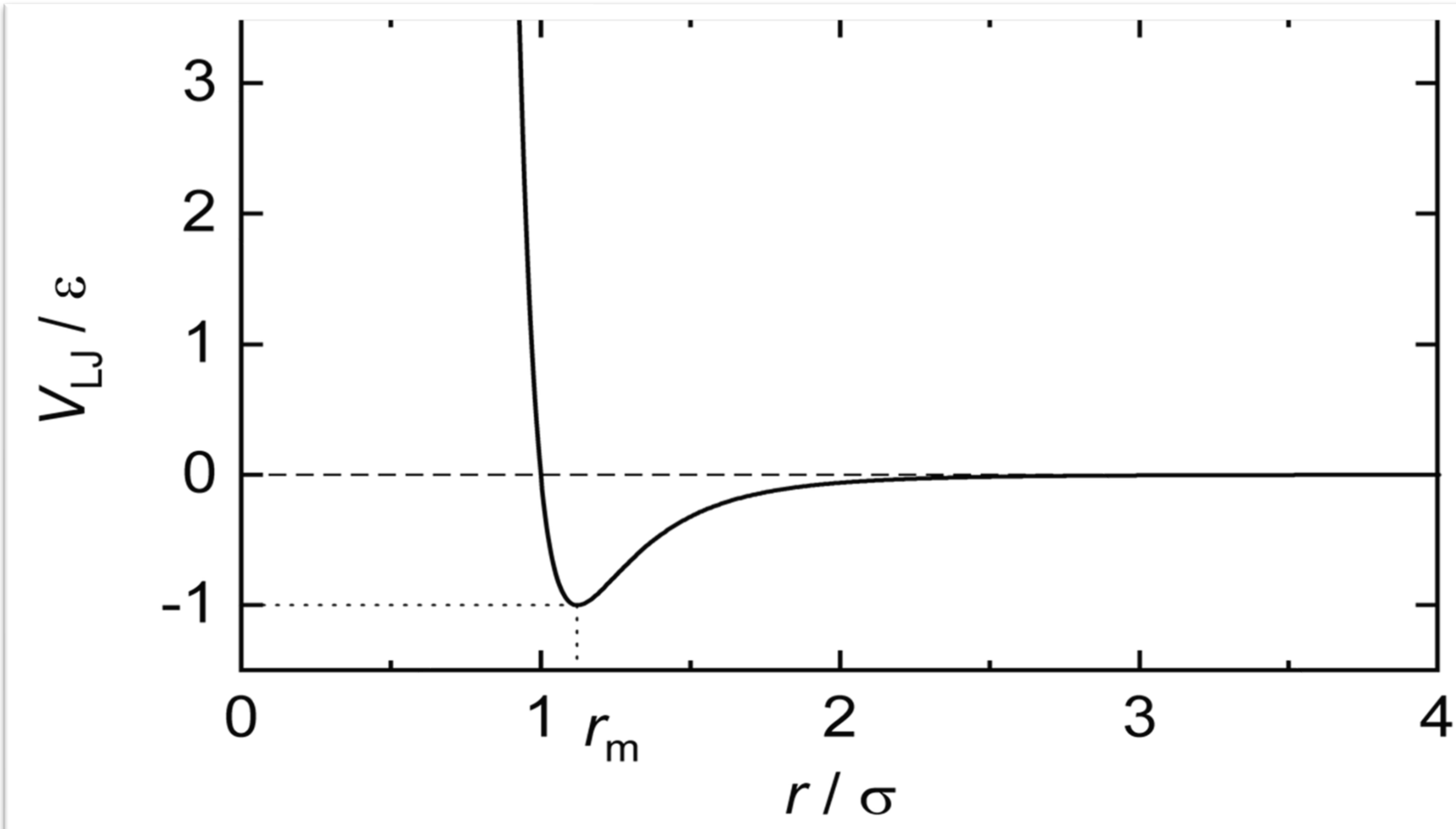
1) the lower the specific heat
2) the later it bends and the lower the curvature with the temperature

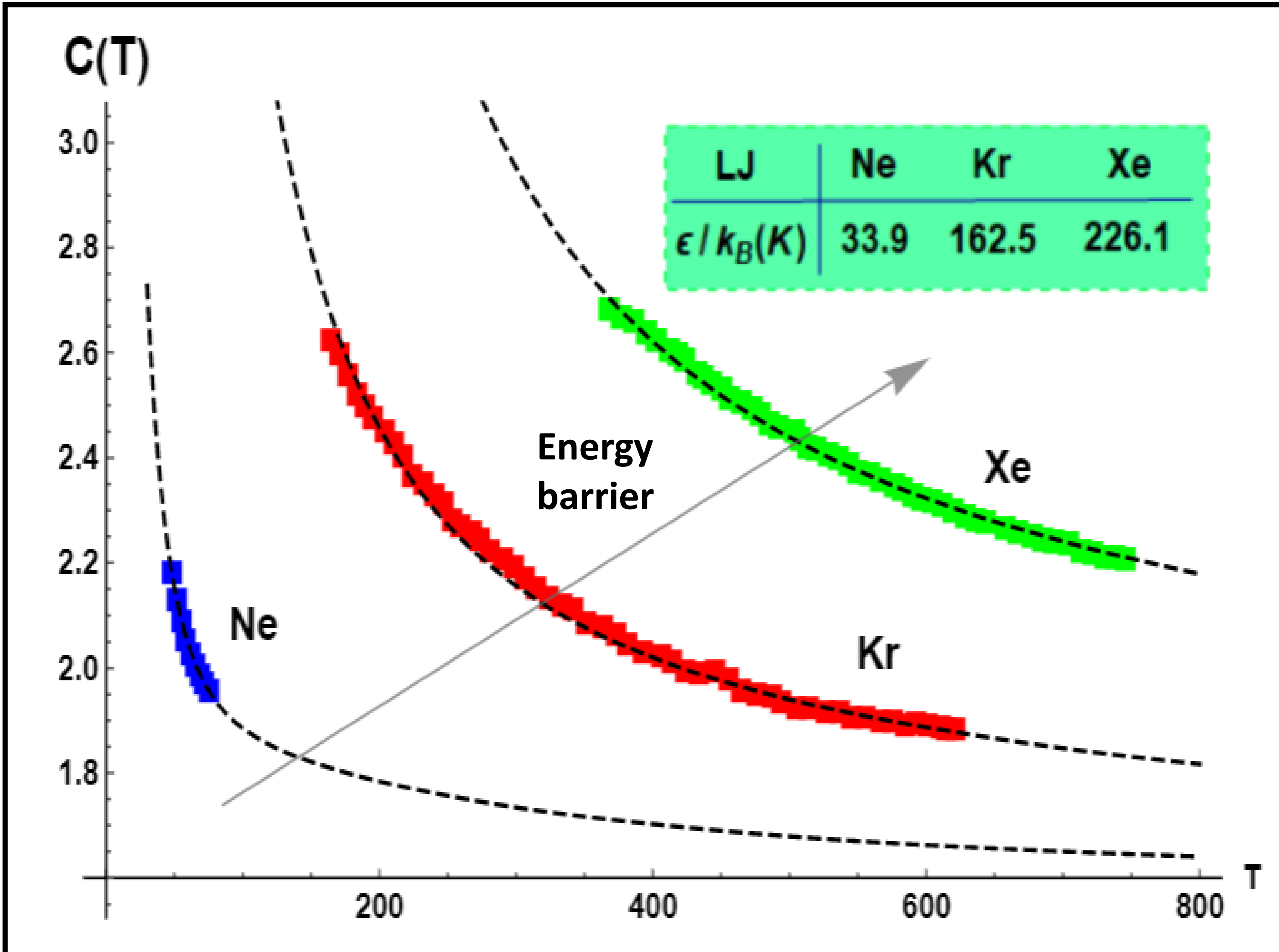


Ne
C(T)
T
Xe
C(T)
T
Ar
C(T)
T
Kr
C(T)
T

LENNARD-JONES POTENTIAL

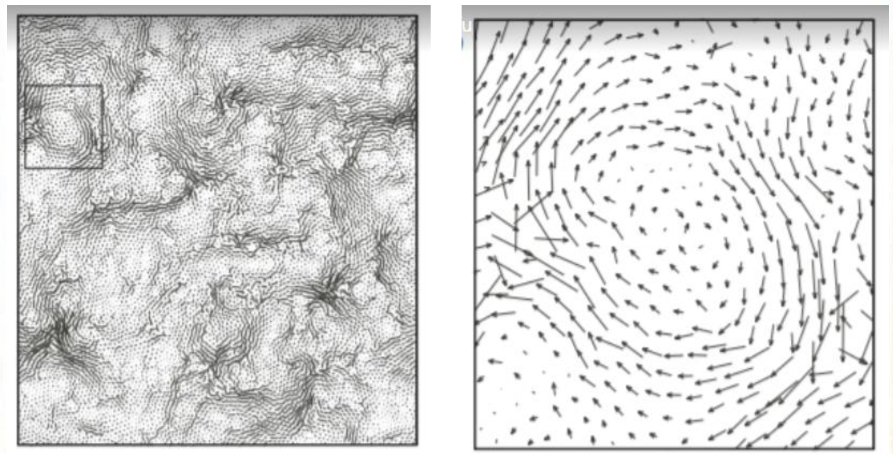
$$V_{\mathrm{LJ}} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right],$$





C(T)
3.0
2.8
2.6
2.4
2.2
2.0
1.8
200
400
600
800
T
LJ
Ne
Kr
Xe
ϵ / kB(K)
33.9
162.5
226.1
Energy
barrier
Xe
Ne
Kr

Baggioli,
Landry,
Zaccone,
2021
[Arxiv Today]



Fluids vs Solids

Shear Waves

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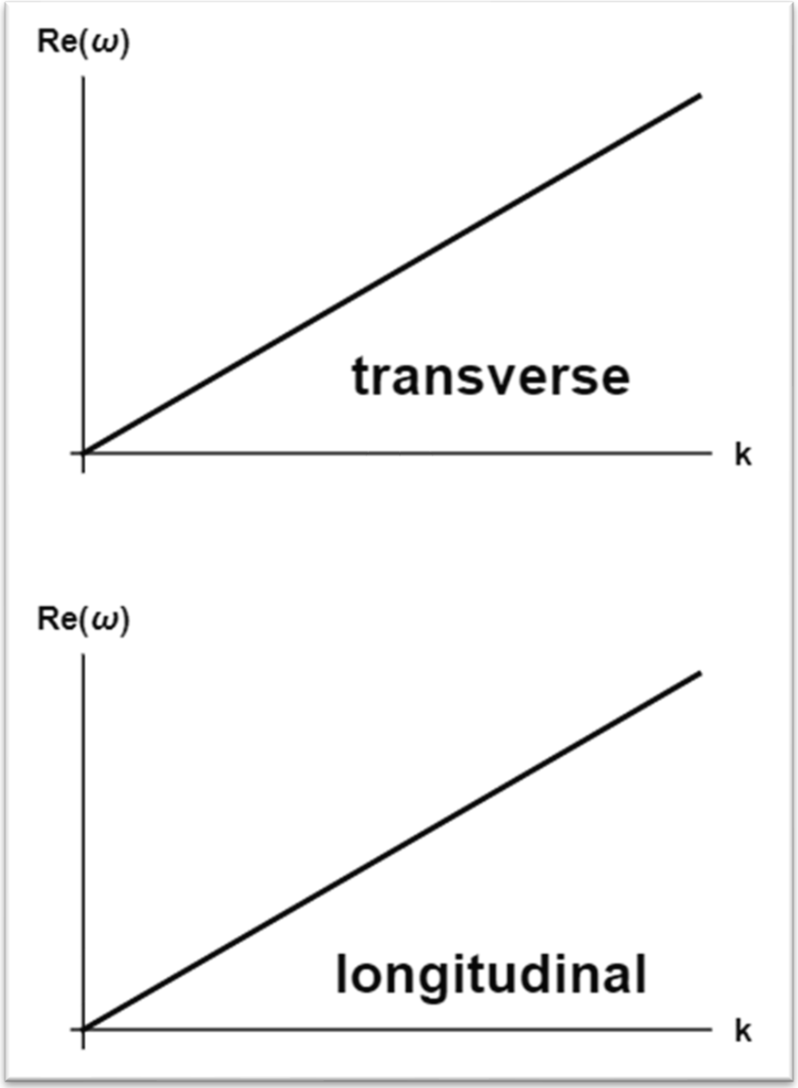

TEXTBOOK MATERIAL

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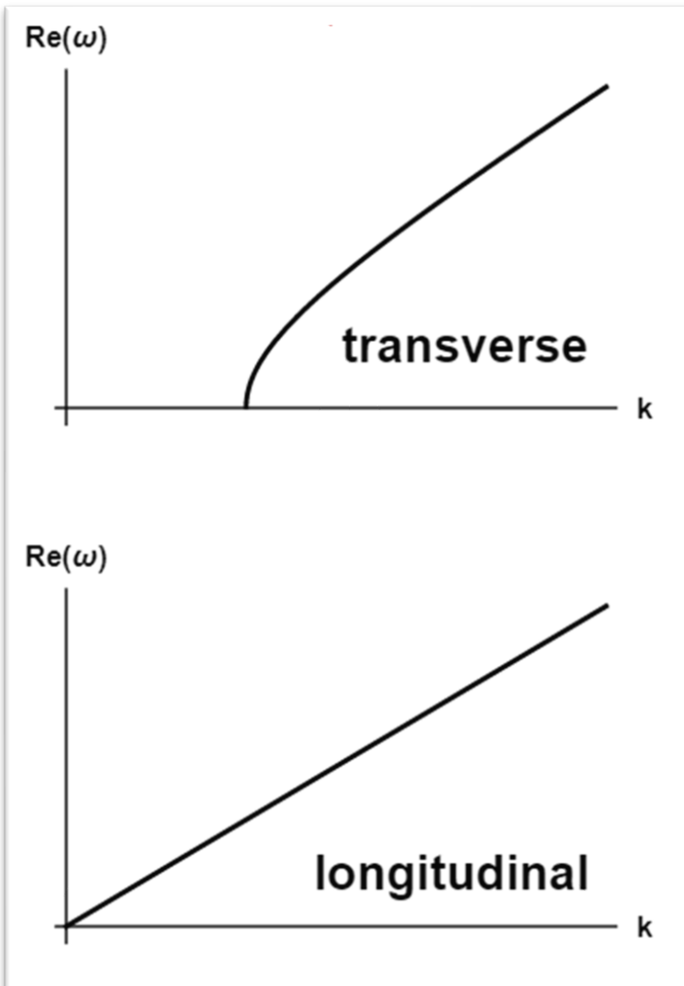
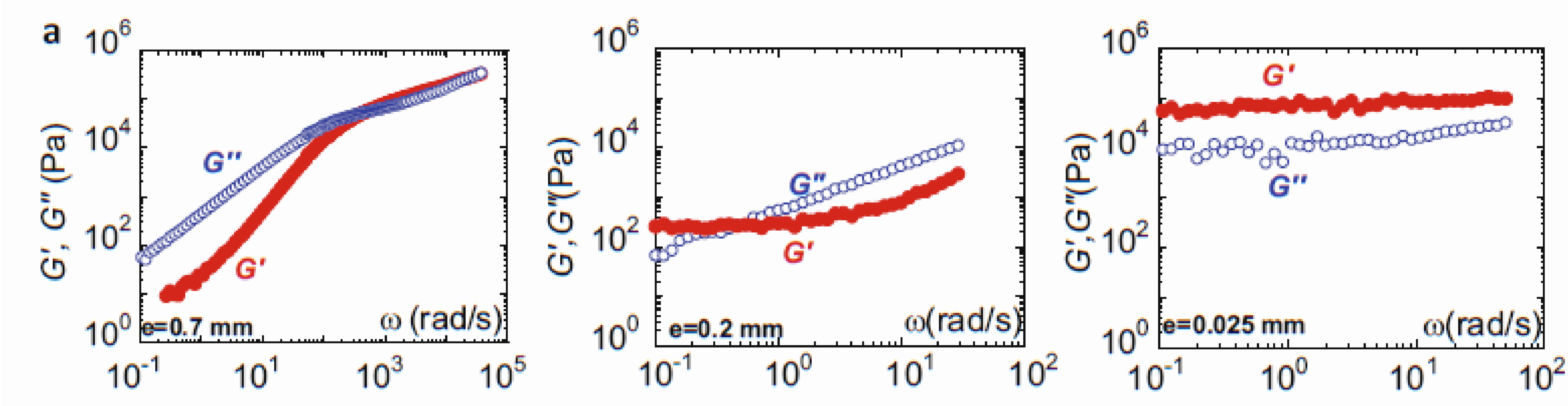
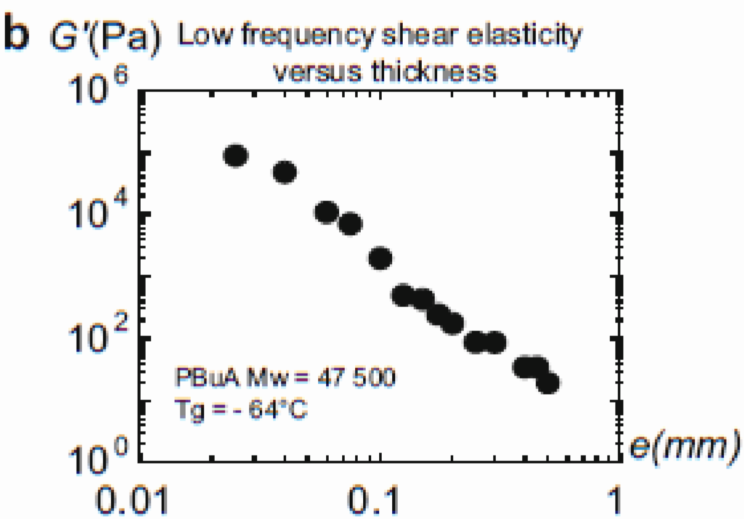


Explanation not in Textbooks



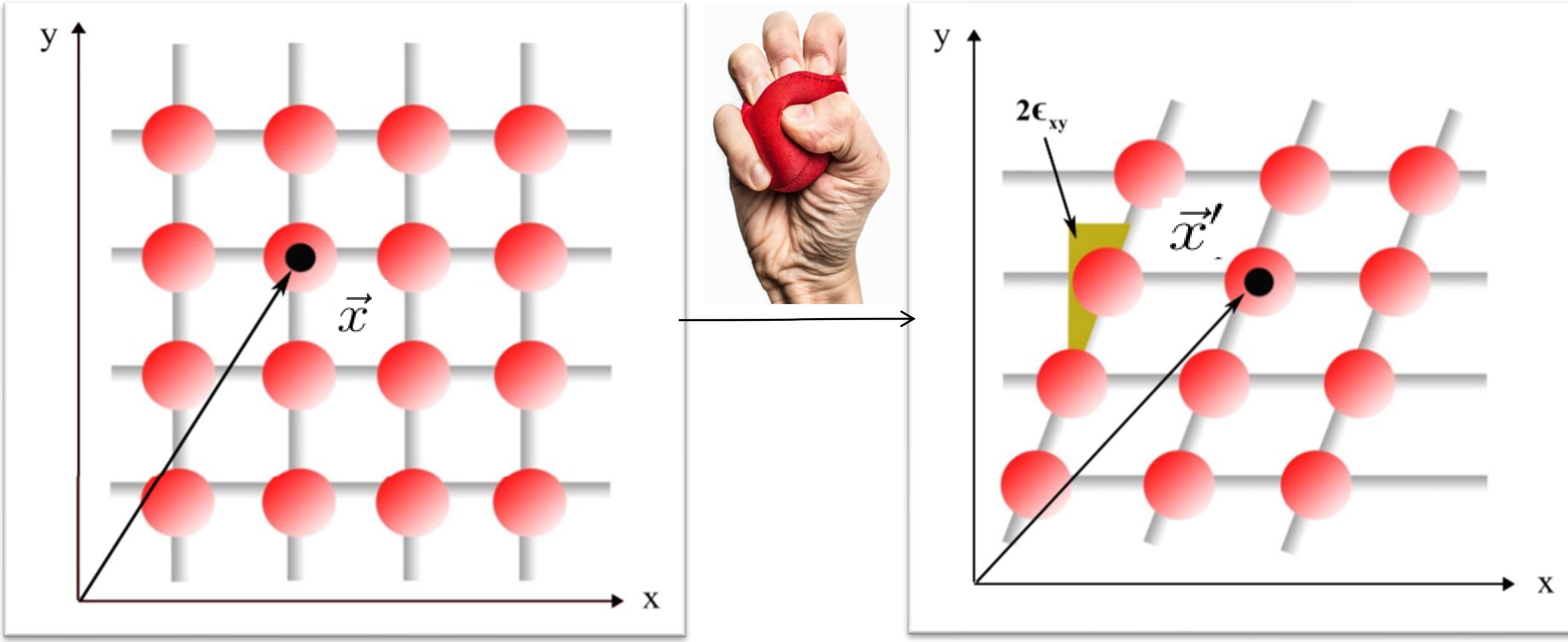


There is a liquid to solid crossover going to small sizes (or large momenta)

Identification of a low-frequency elastic behaviour in liquid water

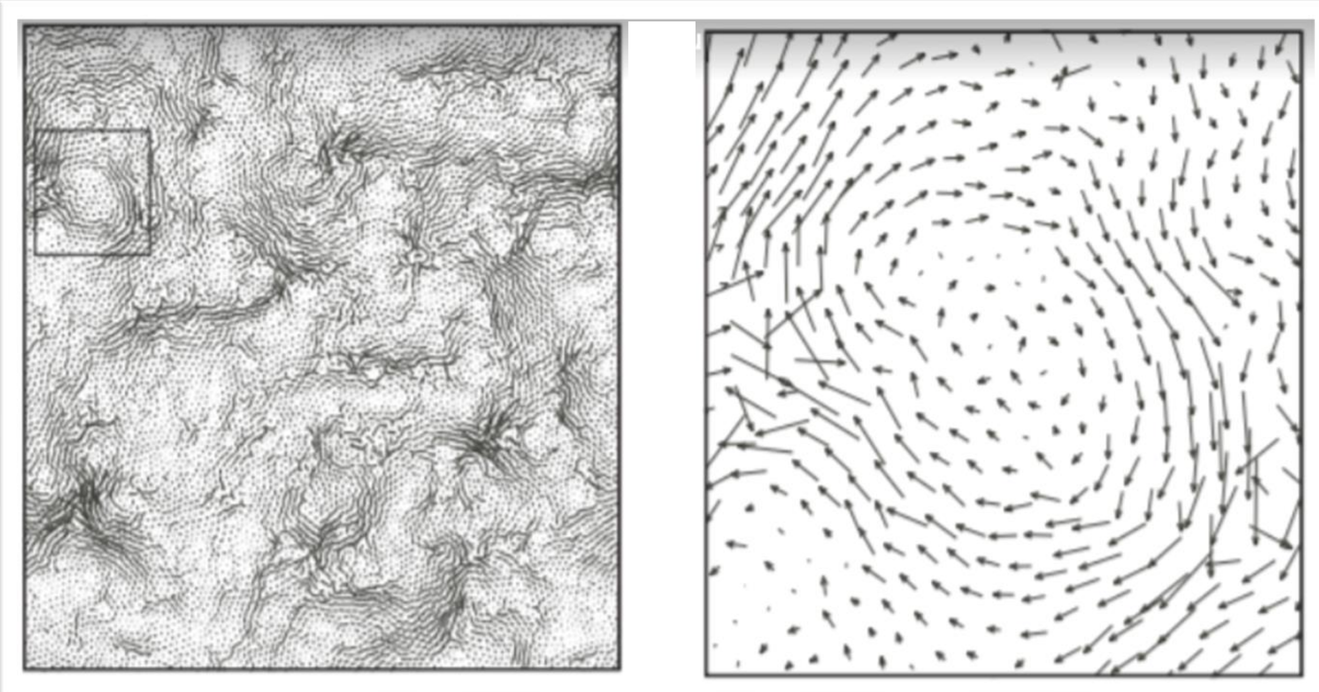
Laurence Noirez[1] and Patrick Baroni[1]

Theory of elasticity



$$\text{displacement } \vec{u} \equiv \vec{x}' - \vec{x}$$

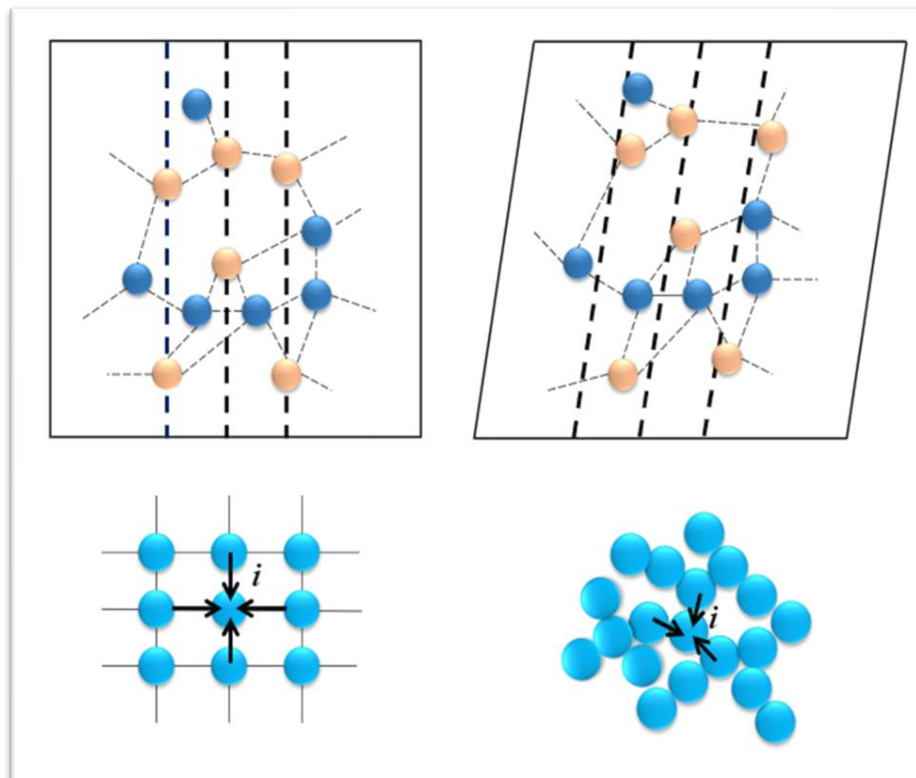
$$\text{strain tensor } \epsilon_{ij} \equiv \frac{1}{2}(\partial_i u_j + \partial_j u_i) \qquad u_i = \epsilon_{ij}\, dx^j$$



Non-affine displacements

Singular parts of the displacements (cf.dislocations and vortices)

$$u_i(\mathbf{x}) = \underbrace{\gamma_{ij}\, x^j}_{\text{affine}} + \underbrace{u'_i(\mathbf{x})}_{\text{non-affine}} \;,$$



Compatibility constraint

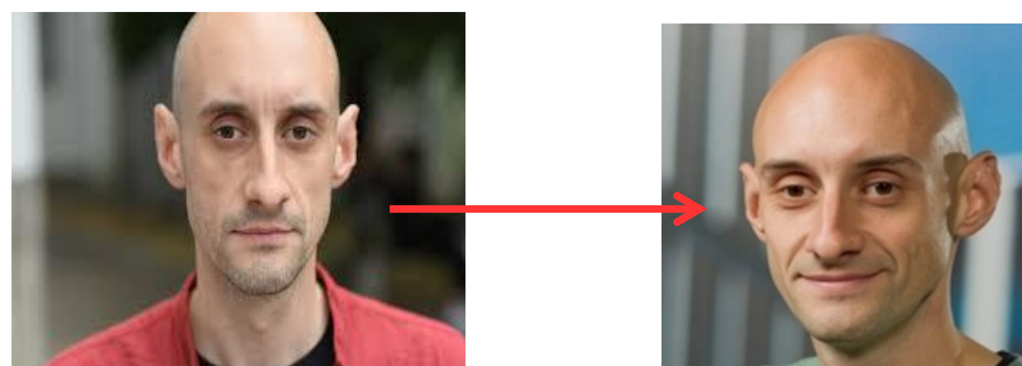
$$\oint_L du_i = 0 .$$

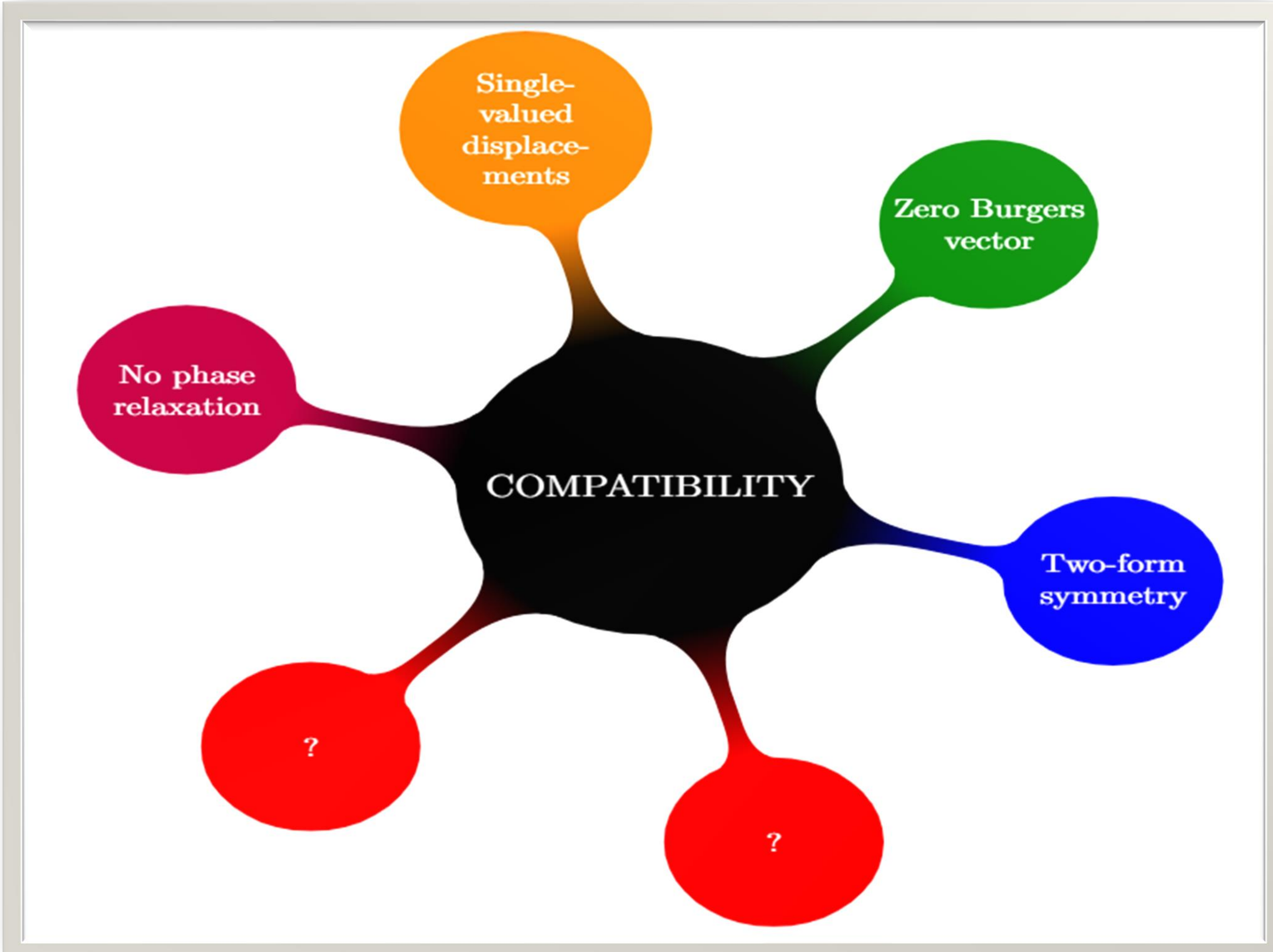
$$\nabla \times \nabla \times \epsilon = 0$$

$$[\partial, \partial] \, \phi = 0$$

$$\partial_\mu J_I^{\mu\nu} = \partial_\mu \, \epsilon^{\mu\nu\rho} \, \partial_\rho \phi_I = 0$$

Global two-form symmetry




Single-valued displacements
Zero Burgers vector
No phase relaxation
COMPATIBILITY
Two-form symmetry
?
?

$$u_i(\mathbf{x}) = \underbrace{\gamma_{ij}\, x^j}_{\text{affine}} + \underbrace{u'_i(\mathbf{x})}_{\text{non-affine}} \longrightarrow \oint_L du'_i = -\, b_i$$

Non-affine displacement *produces a finite* ***Burgers vector***

Using Stokes' theorem

$$\epsilon^{abj}\,\partial_b\,\partial_j\, u'_i \equiv -\,\alpha^a_i \neq 0$$

Moving to the dual picture

$$\alpha^a_i = \partial_\mu J^{\mu a}_i = -\,\Omega\, J^{ta}_i \neq 0$$

NON-AFFINE DISPLACEMENTS

MACROSCOPIC PHASE RELAXATION

Hydrodynamics

Goldstone field $\phi_I(t,x)$ $(\lambda_\perp = \nabla \times \phi,\, \lambda_\parallel = \nabla \cdot \phi)$

Modified (relaxed) Josephson relations

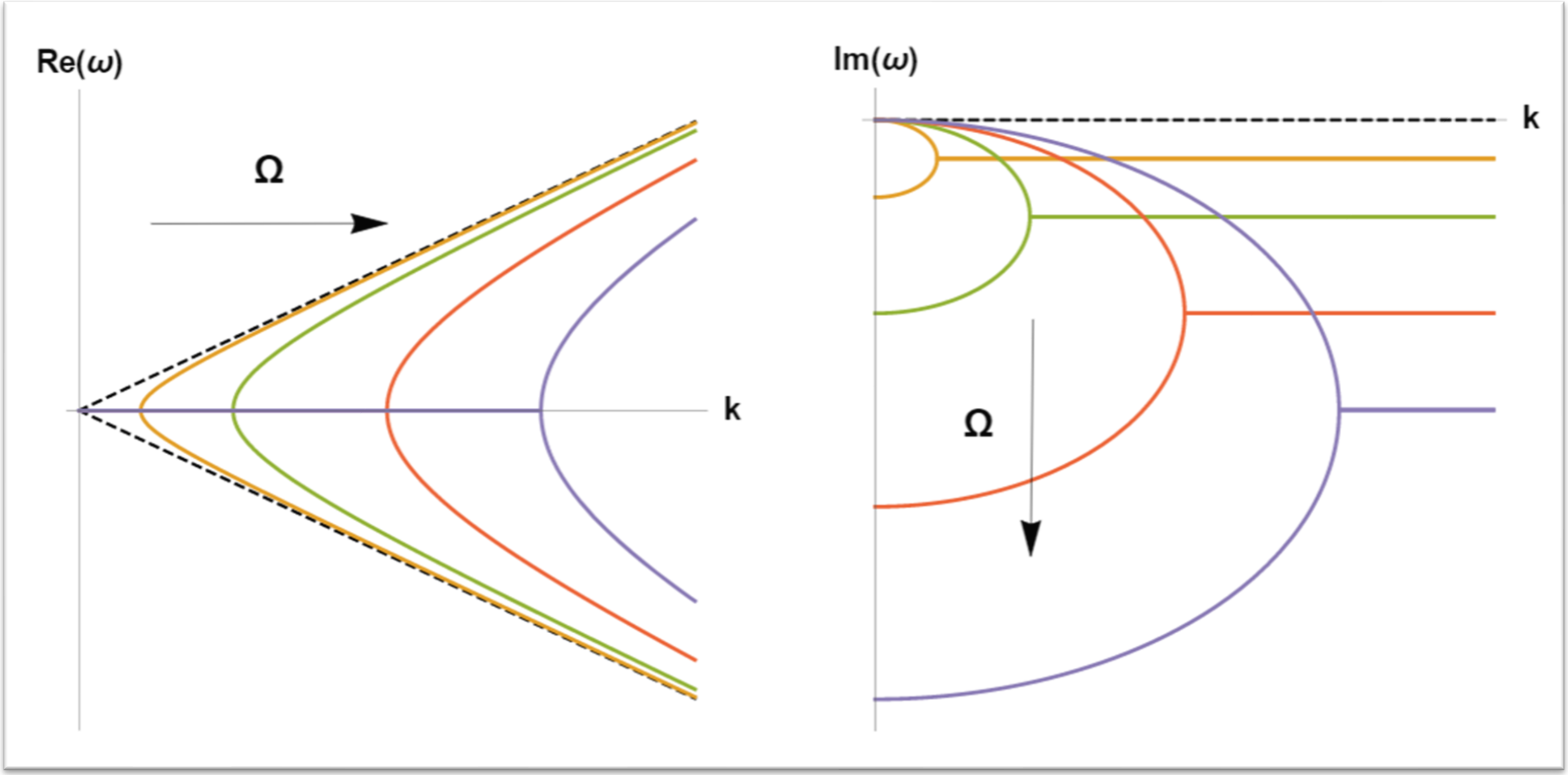
$$\partial_t \lambda_\perp(t,x) - \partial \times \vec{v}(t,x) - \xi_\perp \partial_i \partial^i u_\perp(t,x) = -\Omega_\perp \, \lambda_\perp(t,x);$$

$$\partial_t \lambda_\parallel(t,x) - \partial \cdot \vec{v}(t,x) - \gamma_2 \, \partial_j \partial^j T(t,x) - \xi_\parallel \, \partial_k \partial^k u_\parallel(t,x) = -\Omega_\parallel \, \lambda_\parallel(t,x) \, .$$

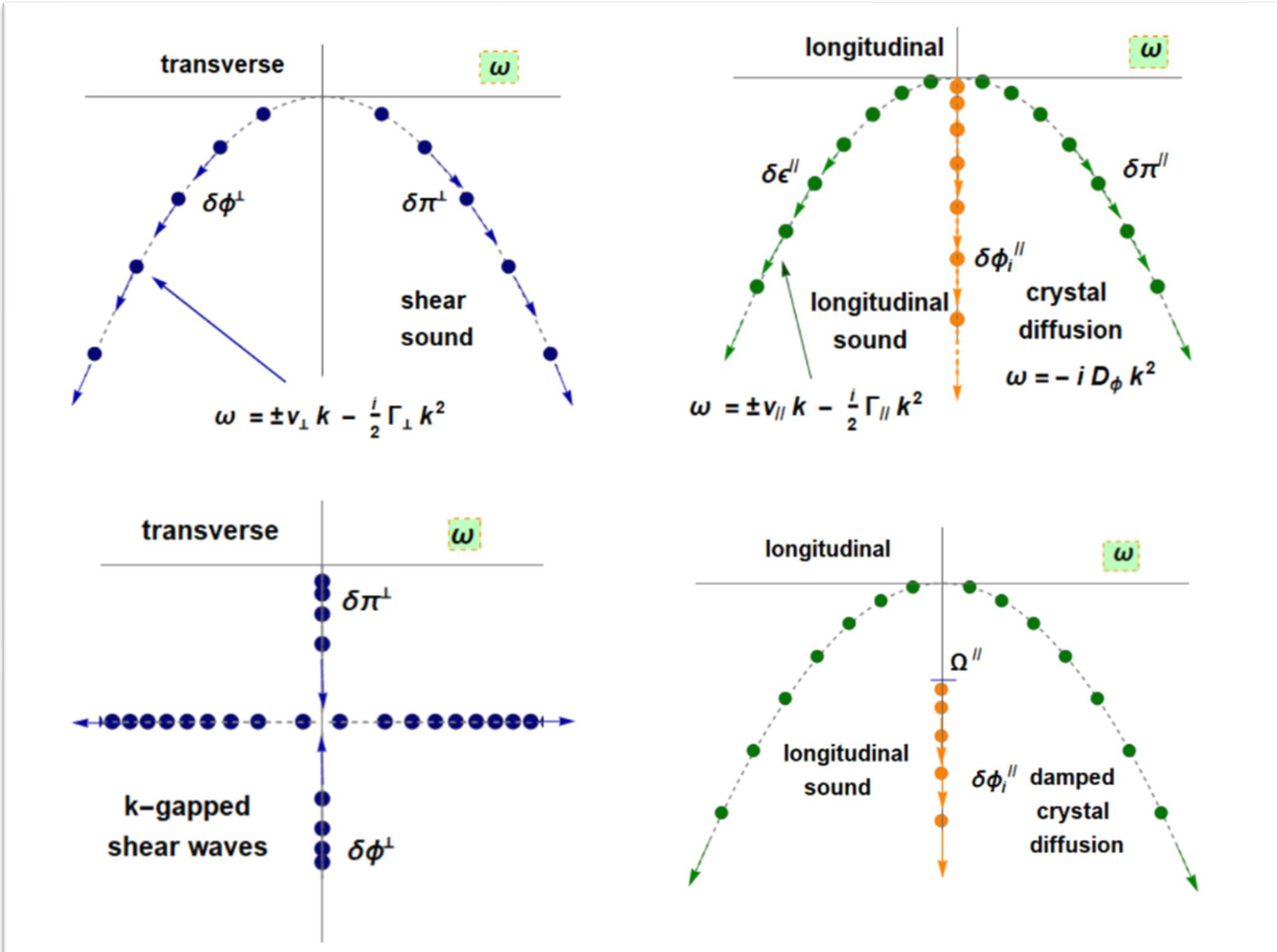
and one finds

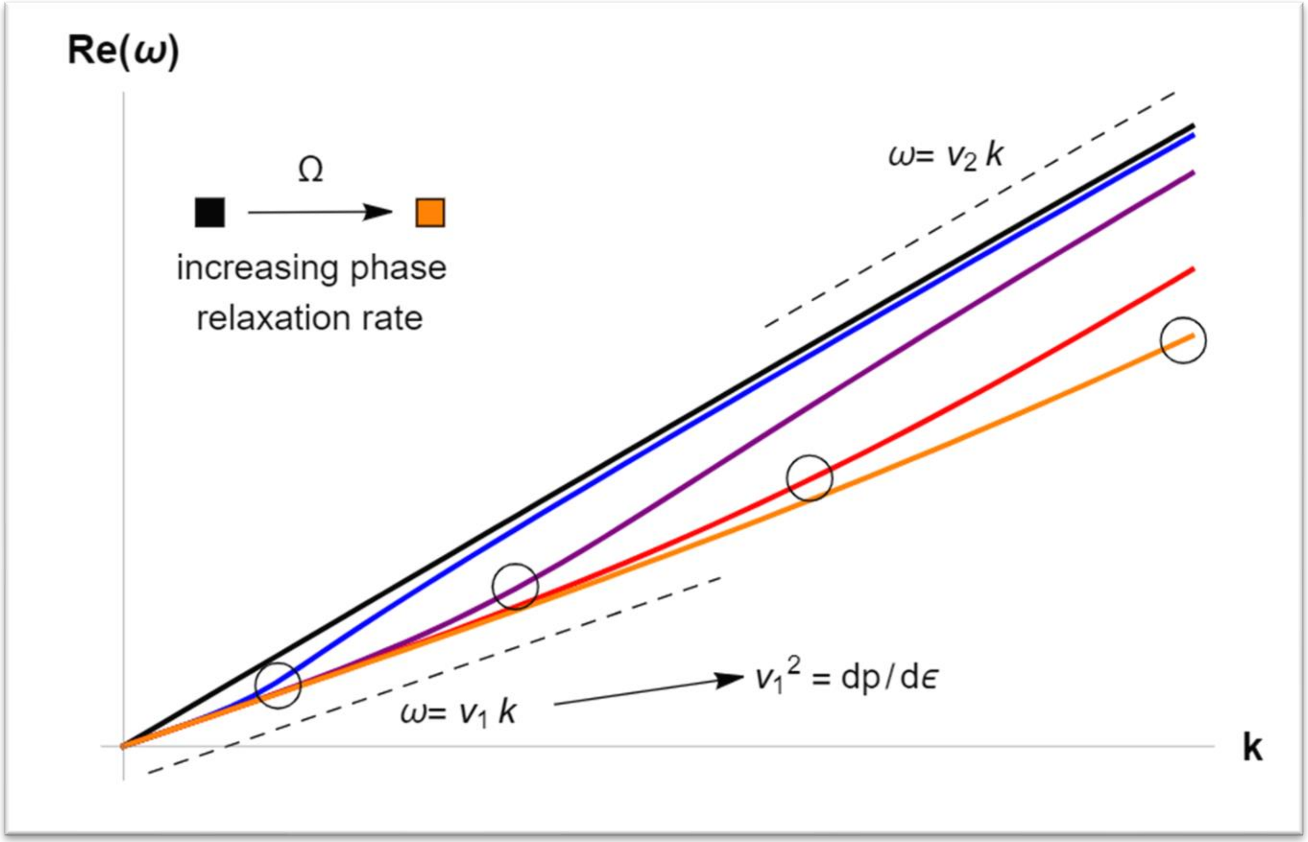
$$\omega_\pm = -\frac{i}{2}\Omega_\perp \pm \frac{1}{2\,\chi_{\pi\pi}} \sqrt{k^2 \chi_{\pi\pi} \left[4\,G - 2\,(\xi_\perp - \eta)\,\Omega_\perp\right] - \chi_{\pi\pi}^2 \, \Omega_\perp^2 + \mathcal{O}(k^4)}$$

Exactly what we were after for the shear waves dynamics !

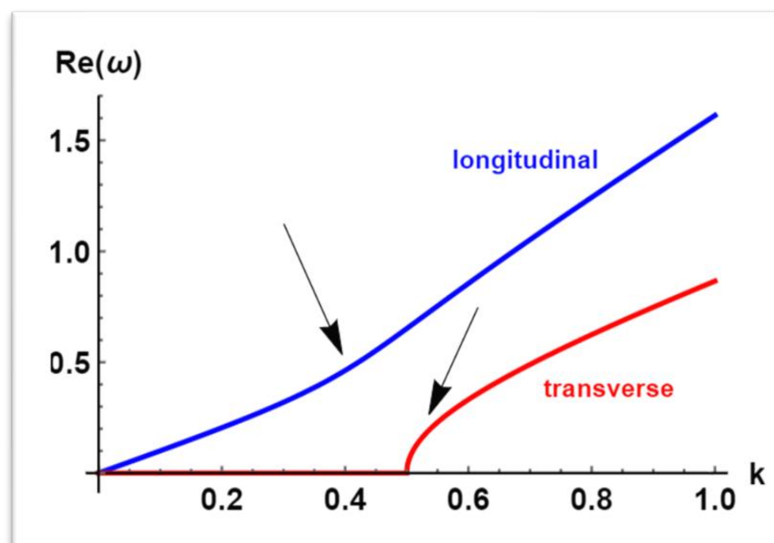


It explains also why in glasses shear waves are back!
Because the relaxation timescale becomes huge!


transverse
ω
δφ⊥
δπ⊥
shear
sound
$\omega = \pm v_\perp k - \frac{i}{2}\Gamma_\perp k^2$
longitudinal
ω
δε//
δπ//
δφi//
longitudinal
sound
crystal
diffusion
$\omega = -i D_\phi k^2$
$\omega = \pm v_{//} k - \frac{i}{2}\Gamma_{//} k^2$
transverse
ω
δπ⊥
k−gapped
shear waves
δφ⊥
longitudinal
ω
Ω//
longitudinal
sound
δφi//
damped
crystal
diffusion



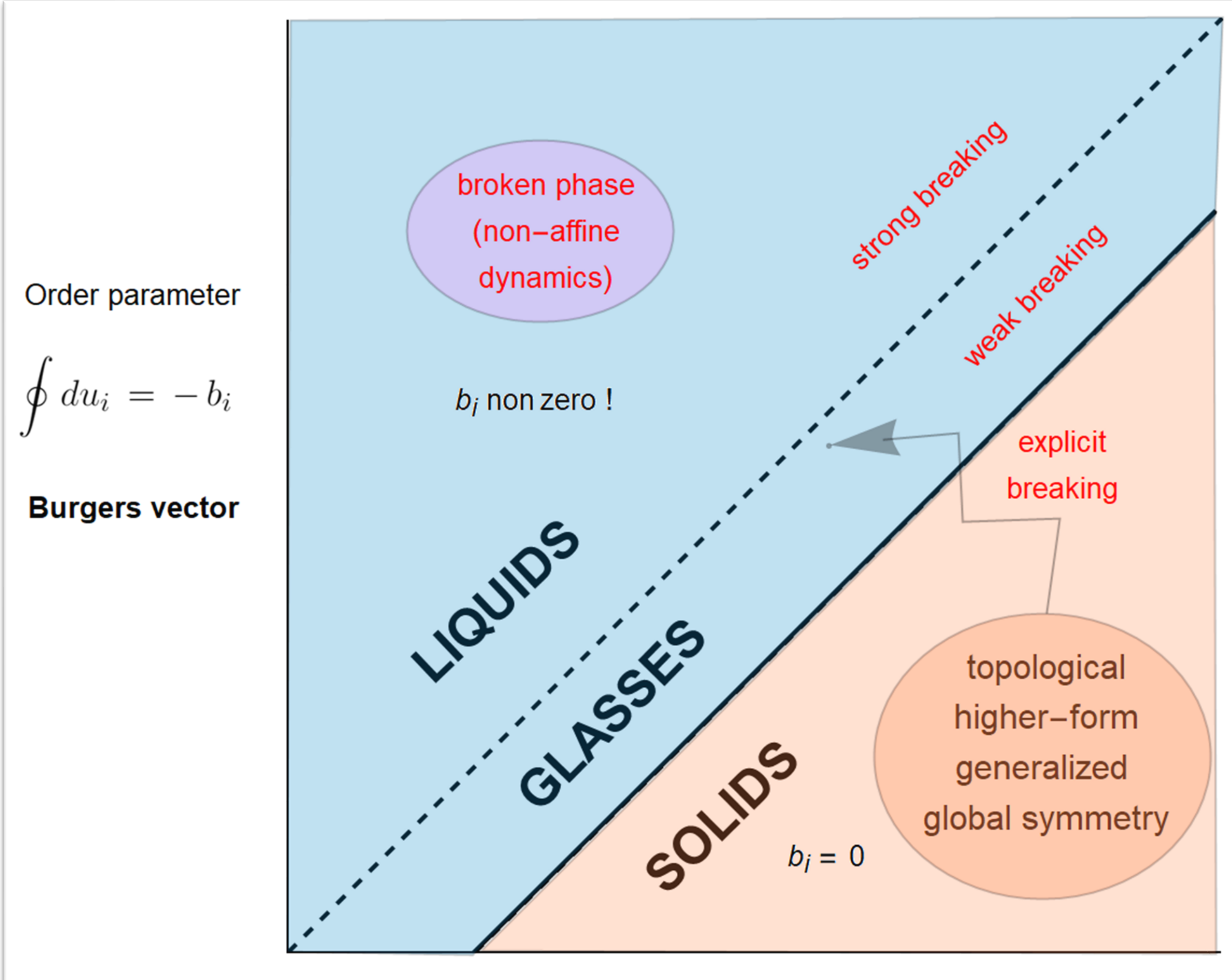
From the same theory
We can predict also
The so-called
<u>Positive-sound-dispersion</u>
phenomenon

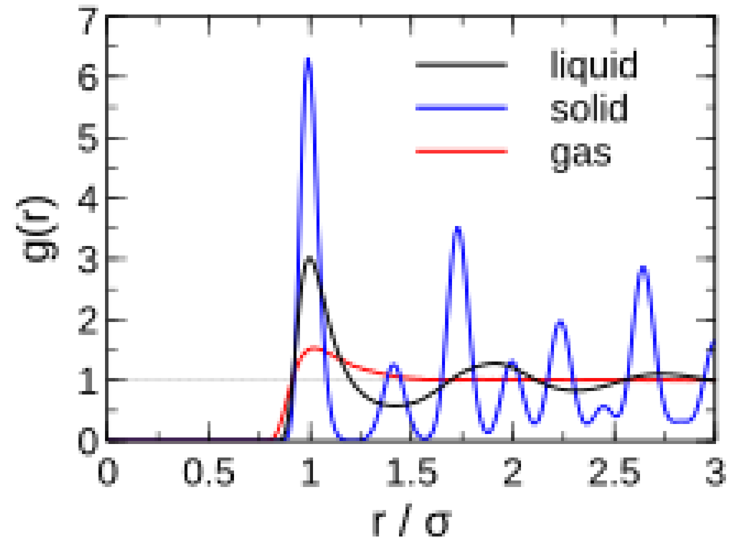


The theoretical framework
looks consistent with
all the experimental
observations

Exploiting Keldysh-Schwinger techniques (and your smart collaborators) and the two-form construction (thanks Saso), one can write a full non-linear action for this ...

[check the paper ☺]


Order parameter
$\oint du_i = -b_i$
Burgers vector
broken phase
(non-affine
dynamics)
b_i non zero !
strong breaking
weak breaking
explicit
breaking
LIQUIDS
GLASSES
SOLIDS
$b_i = 0$
topological
higher-form
generalized
global symmetry



Solids and fluids are not different at the level of spacetime symmetries !

Their distinction is <u>dynamical</u> (related to the system under deformation) and <u>topological</u> (cf. relation with generalized global symmetries)

Order parameter : **BURGERS VECTOR** !

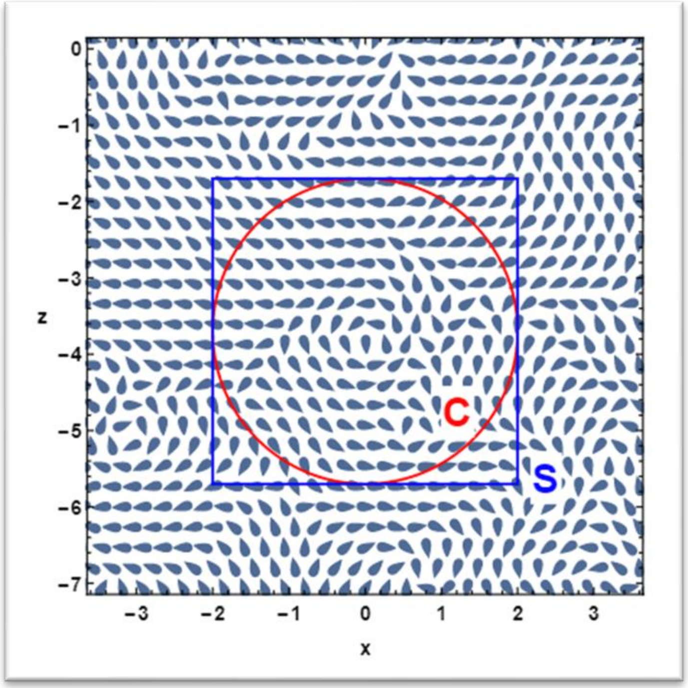
$$\oint du_i = -b_i$$

Zero in solids (without defects)

Finite in liquids and glasses

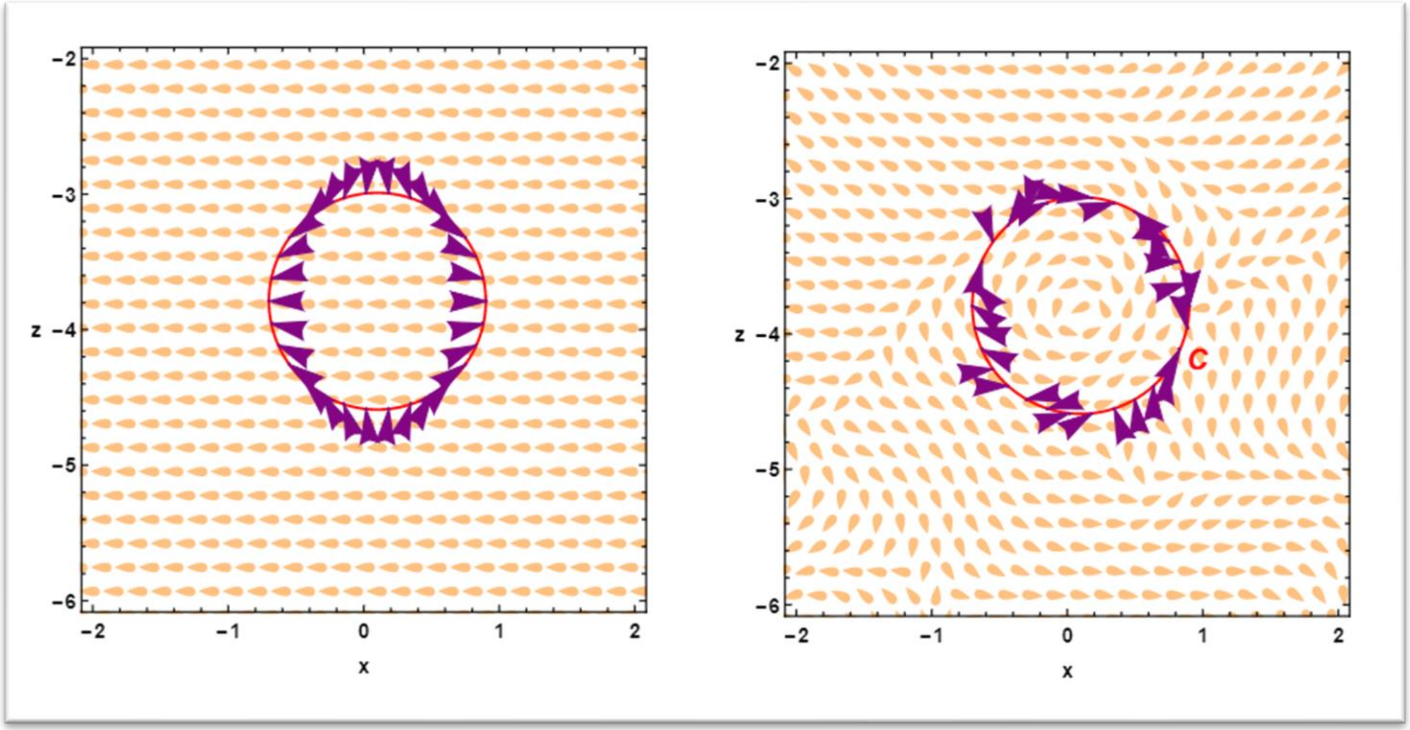
Let us compute it !

Baggioli, Kriuchevskyi,
Sirk, Zaccone
2021
[Arxiv tomorrow]

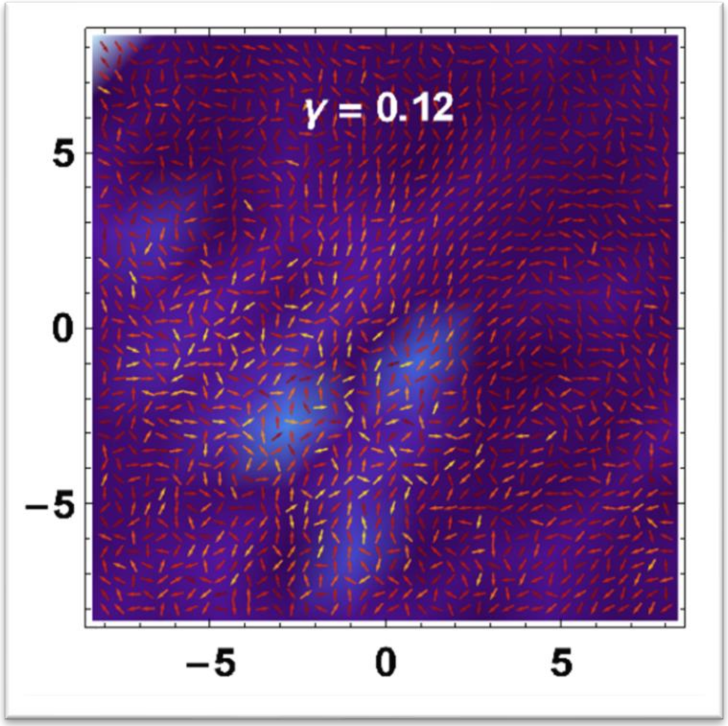


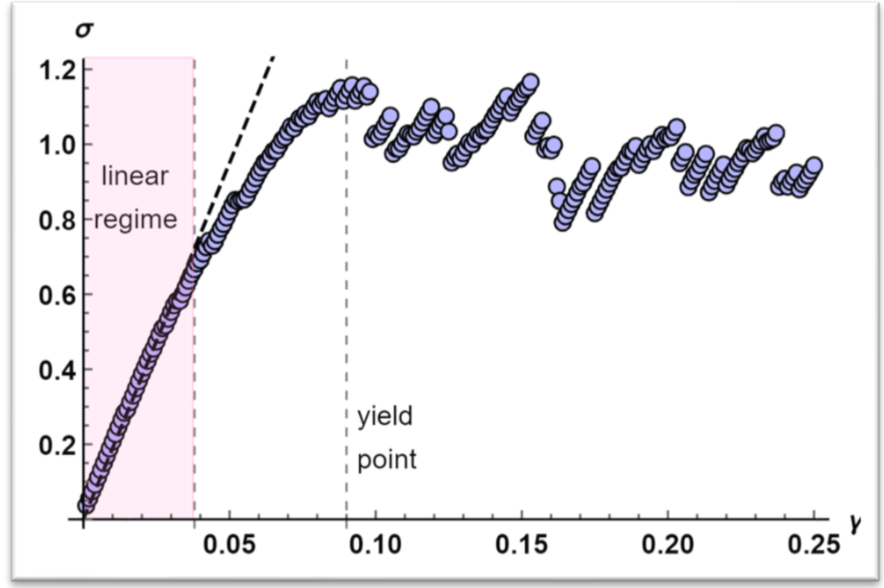
From MD simulations in solids and glasses

“solid”
Only affine
dynamics



glass
non - affine
dynamics

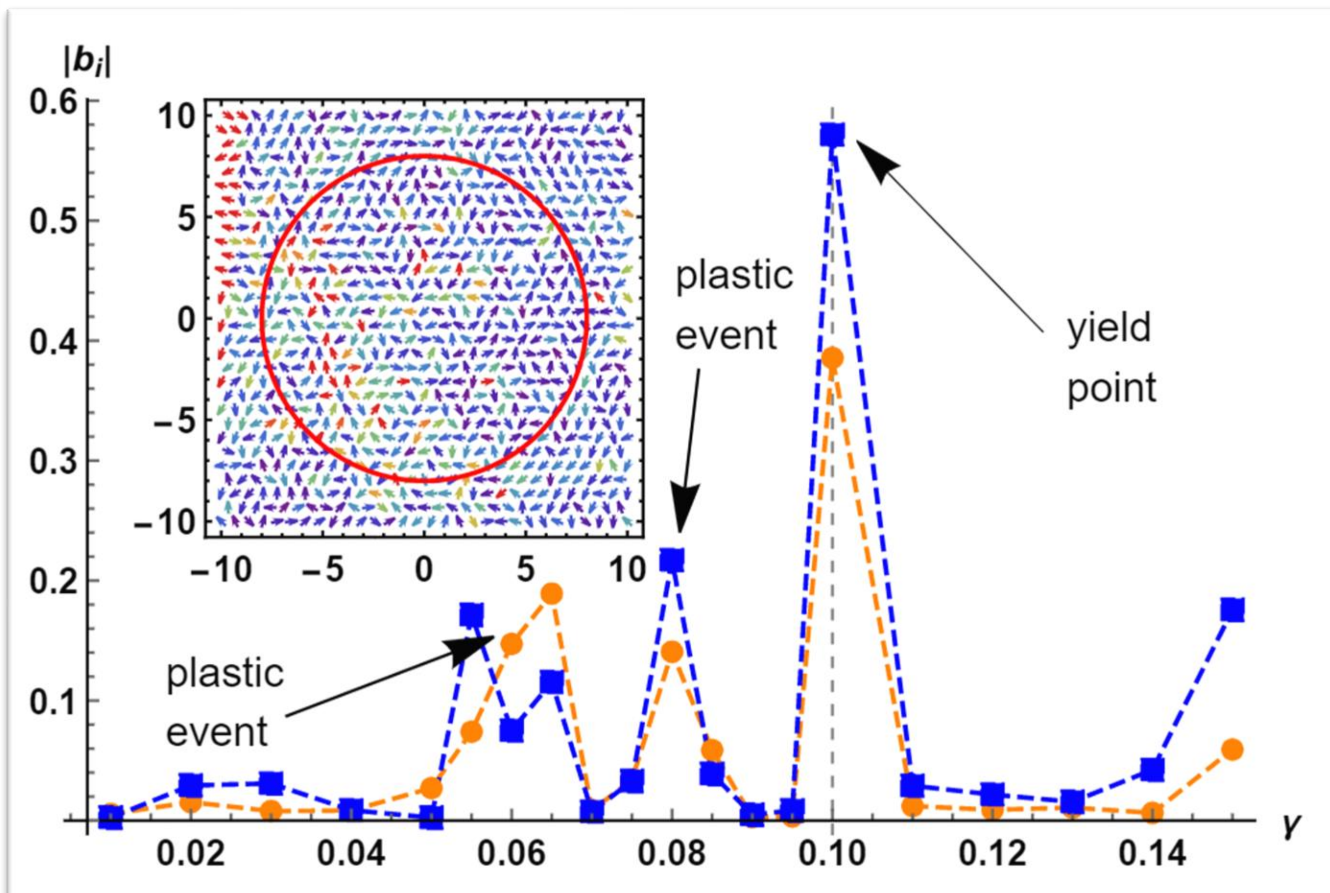




Topological defects in glass deformations

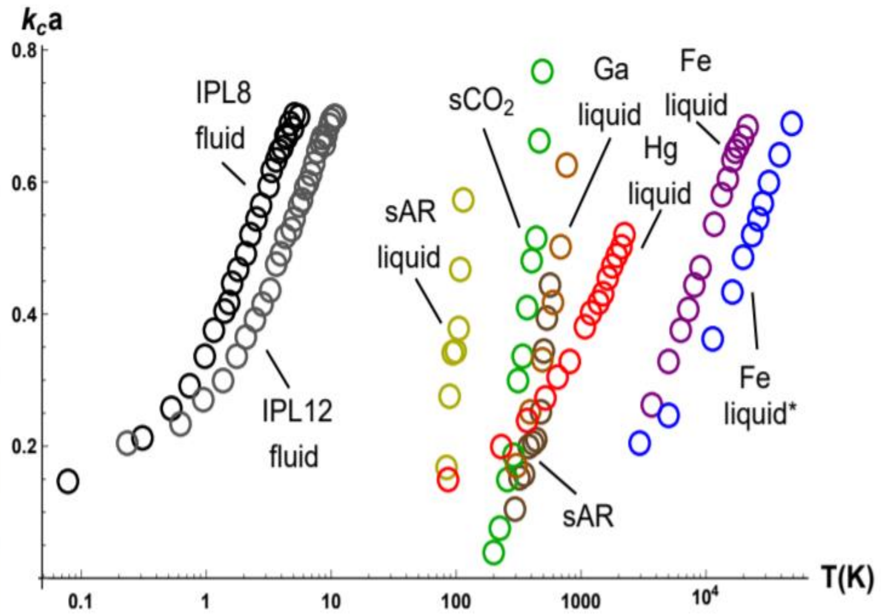
$$b_i \equiv -\oint_{\mathcal{L}} du_i = \oint_{\mathcal{L}} \frac{du_i}{dx^k}\, dx^k$$

Important correlations with plasticity and yielding




"perdersi in un bicchere d'acqua"
Maybe they were serious ….

Baggioli 2020 [Submitted]



Hydrodynamics

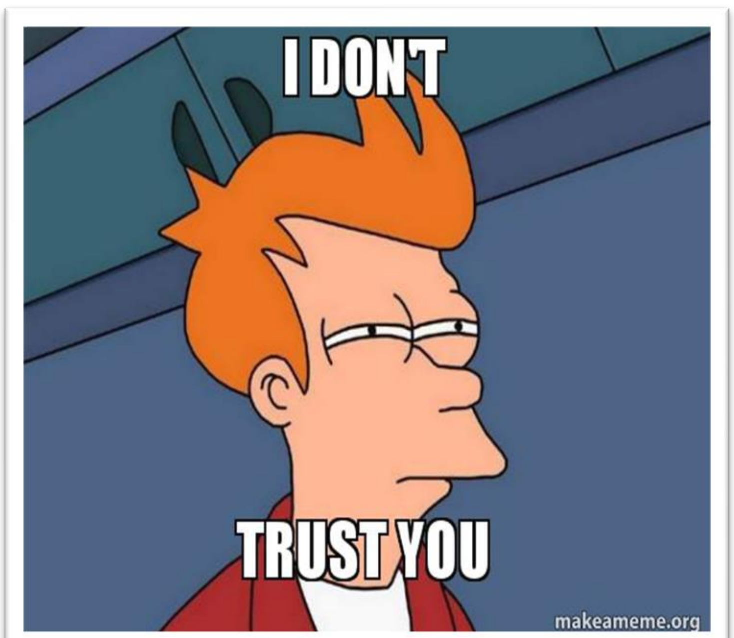
Effective field theories are effective !

Linearized hydrodynamics

$$\omega_{\rm diff}(z \equiv \mathbf{q}^2) = -i \sum_{n=1}^{\infty} c_n z^n,$$

$$\omega_{\rm sound}^{\pm}(z \equiv \sqrt{\mathbf{q}^2}) = -i \sum_{n=1}^{\infty} a_n e^{\pm \frac{i\pi n}{2}} z^n,$$

As every effective theory, it is a perturbative (asymptotic) series



1) Is it convergent ?
2) If not, what is the radius of convergence ?

Linearized hydrodynamic modes : $$F(\omega, k^2) = 0$$

Critical points $$F(\omega_c, k_c^2) = 0\,, \qquad \frac{\partial F(\omega_c, k_c^2)}{\partial \omega} = 0\,,$$

for both $\omega_c, k_c^2 \in \mathbb{C}$.

$$\mathcal{R} \equiv |k_c|\,.$$

The radius of convergence is determined by the distance from the nearest critical point !

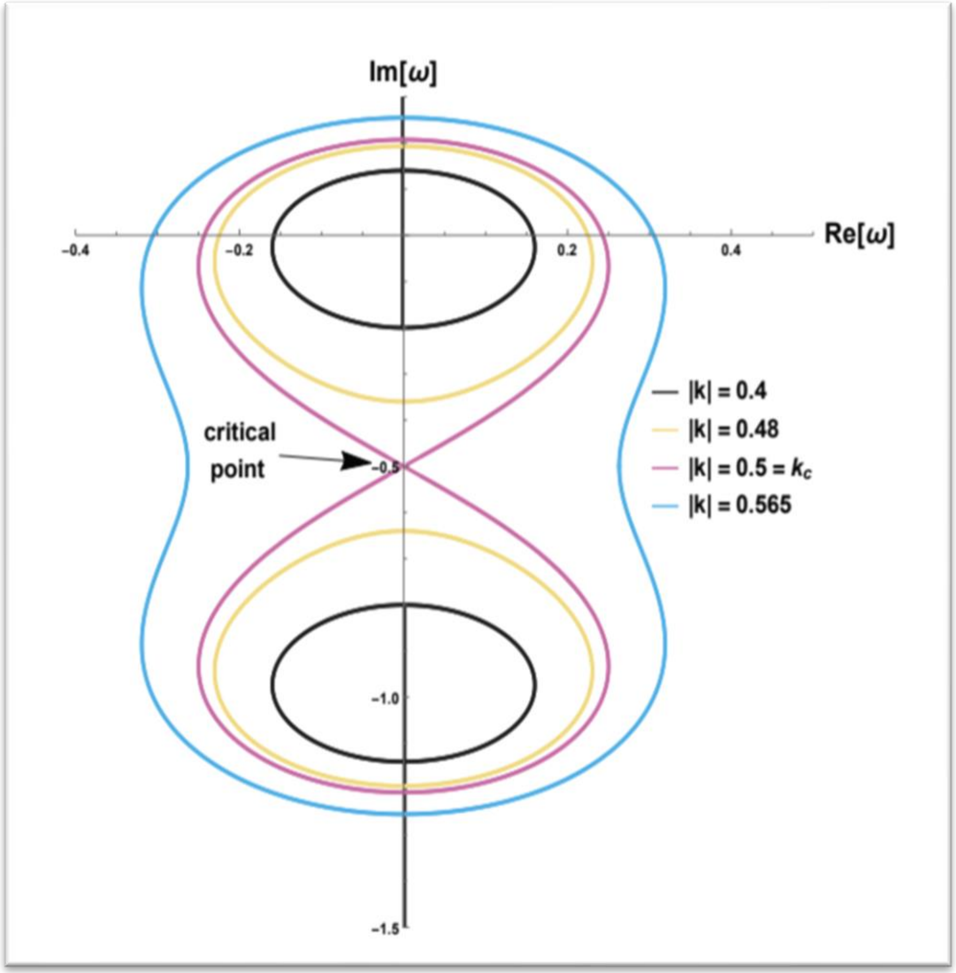
TELEGRAPHER EQUATION
(Heaviside)

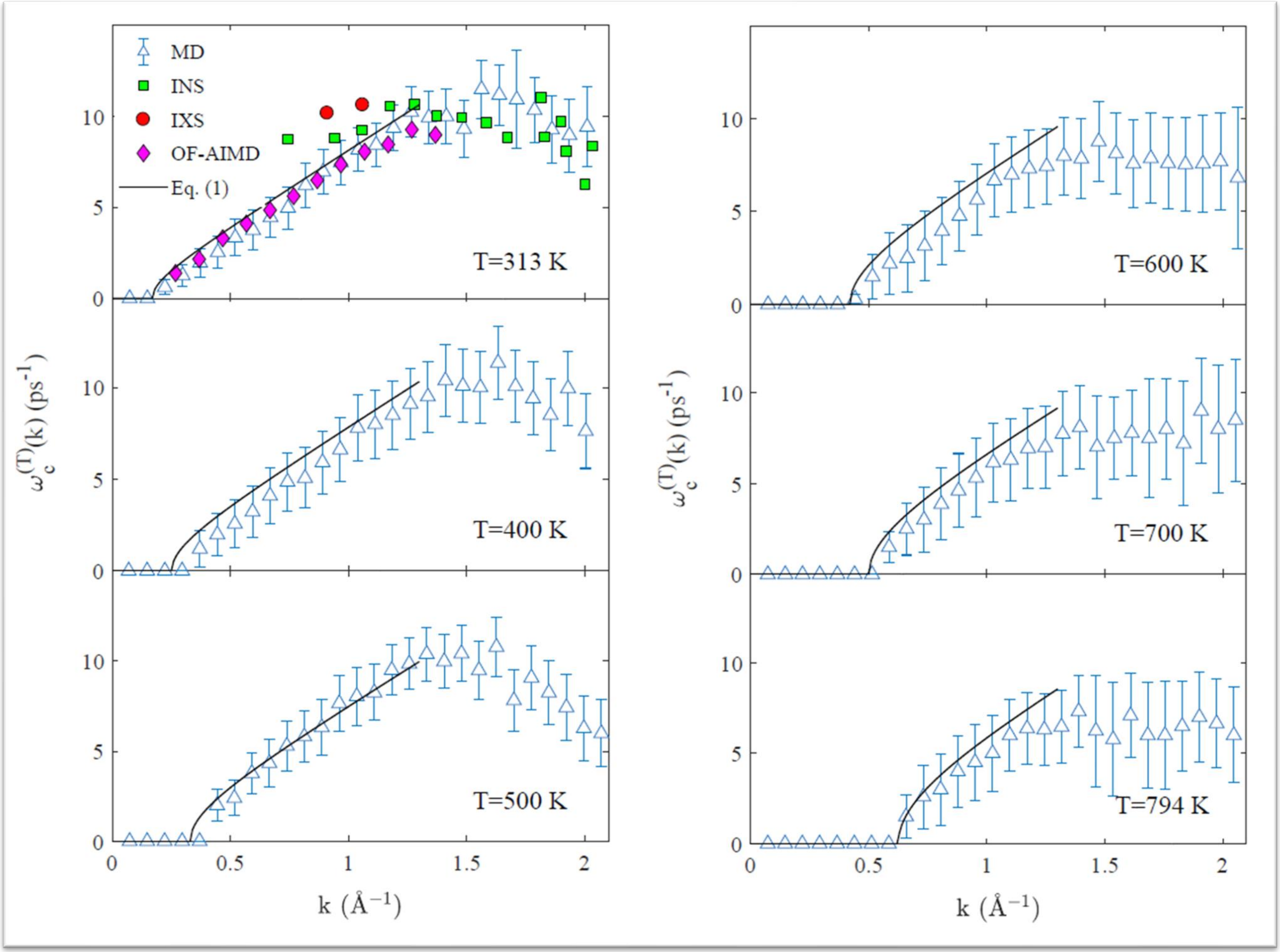
$$\omega^2 + i\,\omega/\tau - v^2\,k^2 = 0\,,$$

Several simulations and (few) experiments confirm this is a good description for shear waves in liquids

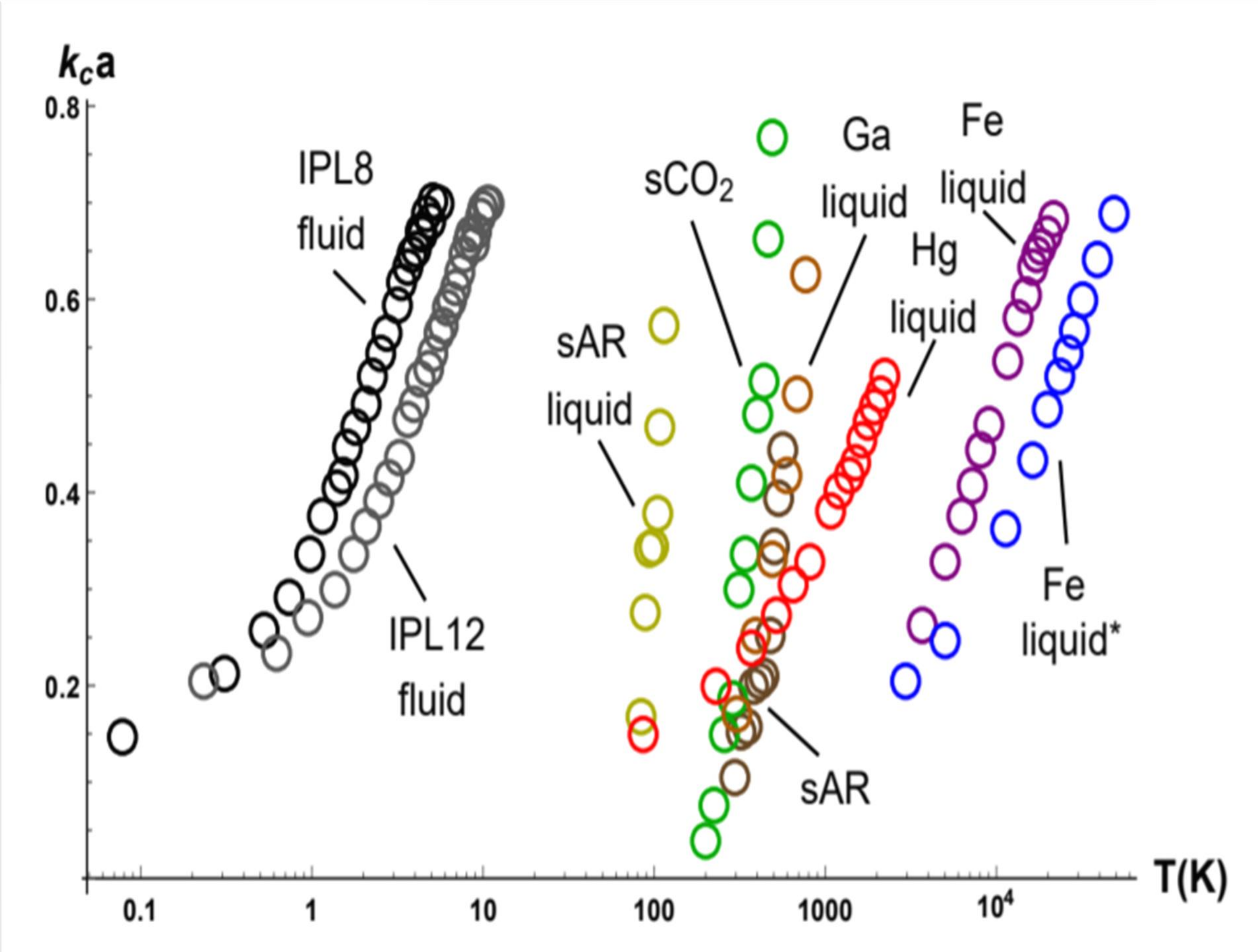
$$\omega = -\frac{i}{2\,\tau} \pm \sqrt{v^2\,k^2 - \frac{1}{4\,\tau^2}}\,,$$

$$\mathcal{R} \equiv |k_c| = \frac{1}{2\,v\,\tau} = k_g\,.$$





MD
INS
IXS
OF-AIMD
Eq. (1)
T=313 K
T=400 K
T=500 K
T=600 K
T=700 K
T=794 K
$\omega_c^{(T)}(k)$ (ps^{-1})
k (Å^{-1})

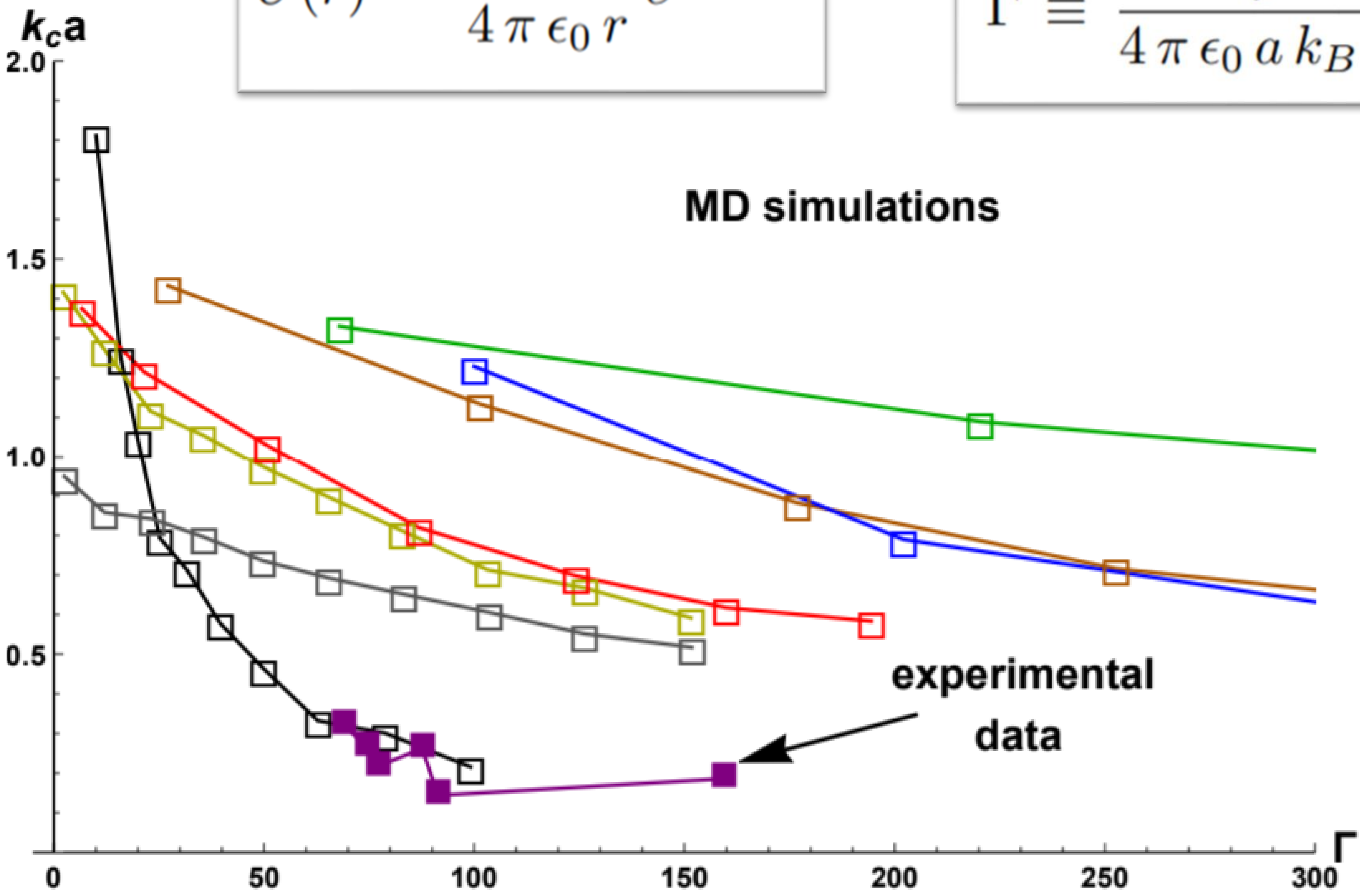


$k_c a$
0.8
0.6
0.4
0.2
IPL8
fluid
IPL12
fluid
sAR
liquid
sCO$_2$
Ga
liquid
Fe
liquid
Hg
liquid
sAR
Fe
liquid*
T(K)
0.1
1
10
100
1000
10^4

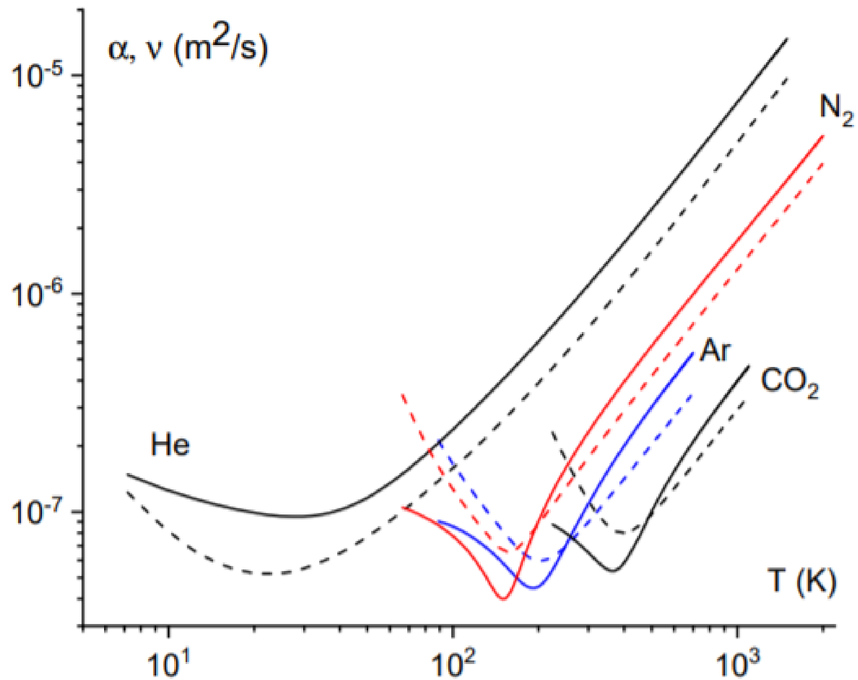
COULOMB LIQUIDS

$$U(r) = \frac{Q}{4\,\pi\,\epsilon_0\,r}\,e^{-r/\lambda_D}$$

$$\Gamma \equiv \frac{Q^2}{4\,\pi\,\epsilon_0\,a\,k_B\,T}$$



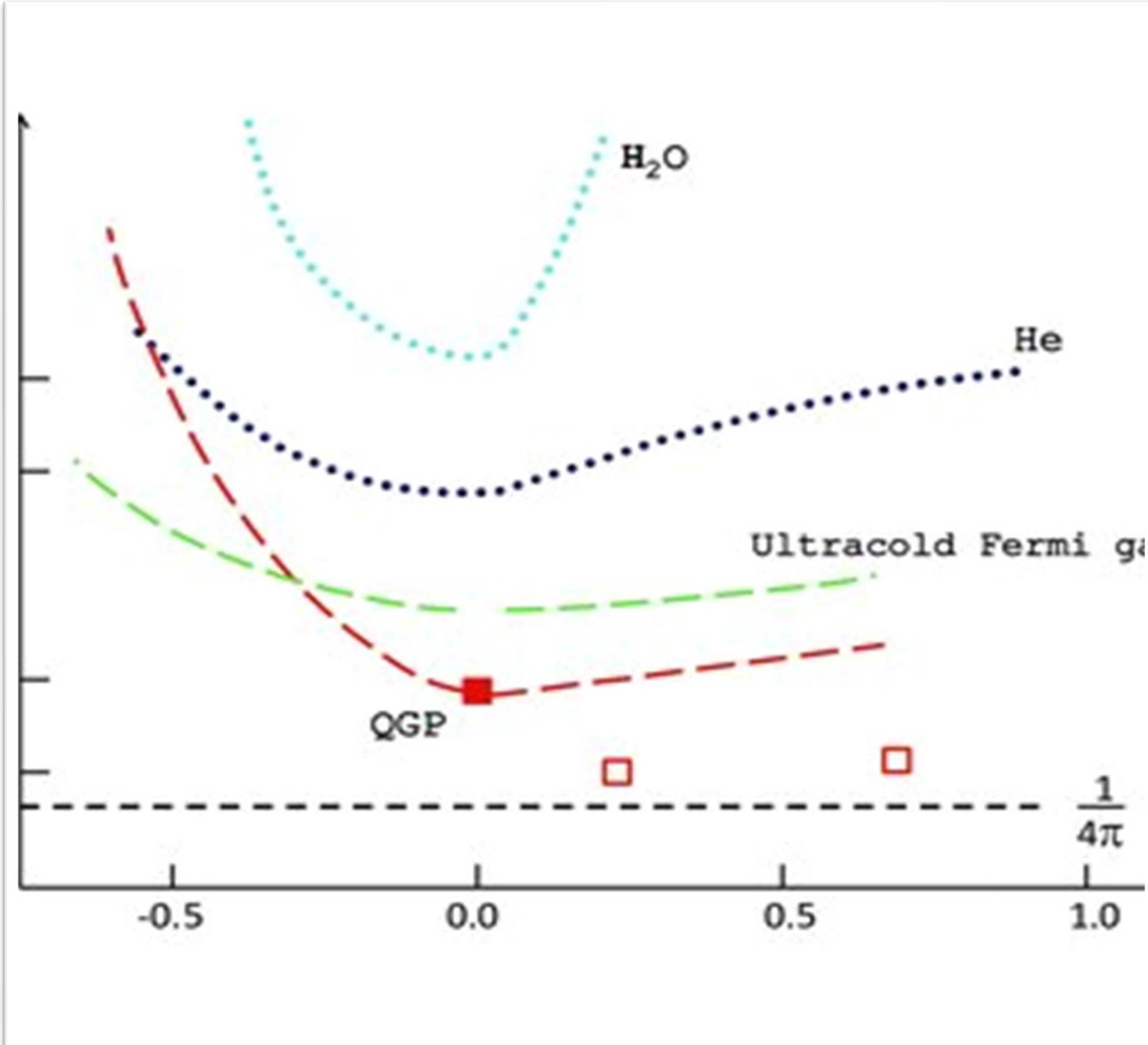
Baggioli, Trachenko, Benhia, 2020 [Submitted]



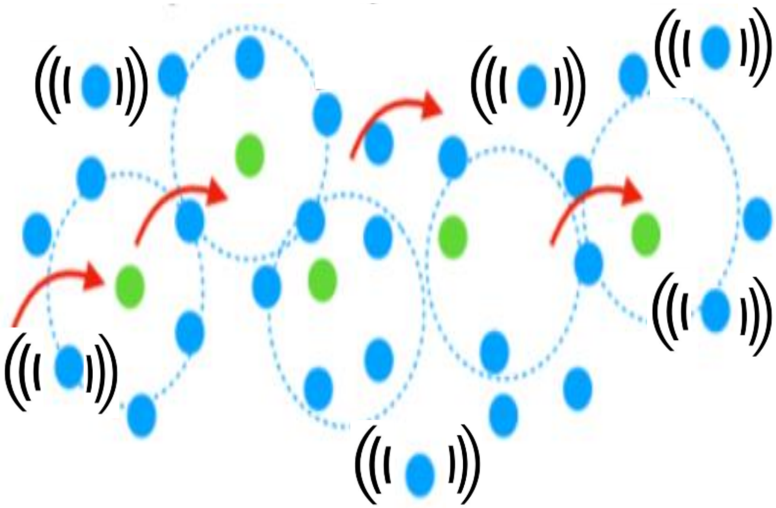
Diffusivities

Are some liquids more equal than others?

Viscosity/entropy ratio



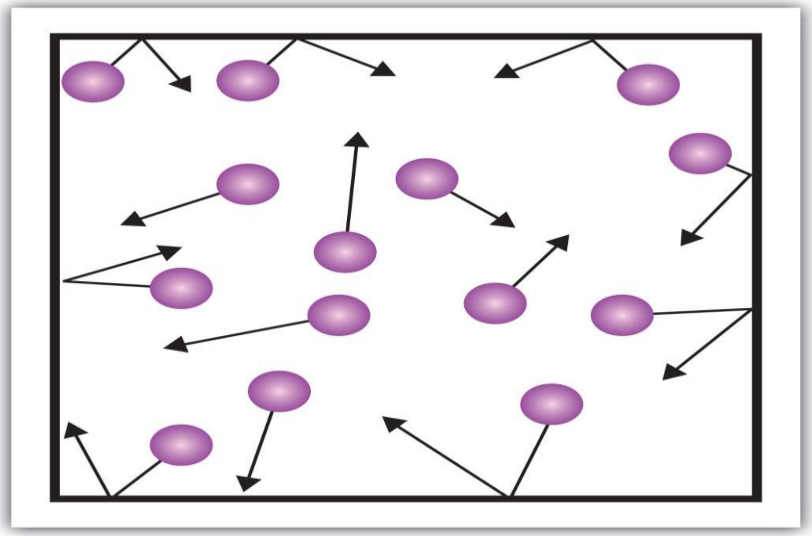
Why a minimum ?



Oscillatory motion
+
Diffusive jumps

$$\eta = \eta_0 \exp\left(\frac{U}{T}\right)$$

$$D \sim \tau^{-1} \sim \eta^{-1}$$



Ballistic motion
Viscosity comes from collisions

$$\eta = \frac{1}{3}\rho v L$$

$$D \sim \eta \sim l_{mfp}$$

LIQUID DYNAMICS **Tc** **GAS DYNAMICS**

A universal minimum

[Trachenko, Brazhkin, Sci.Advances 2020]

$$\nu_m = \frac{1}{4\pi}\frac{\hbar}{\sqrt{m_e m}}$$

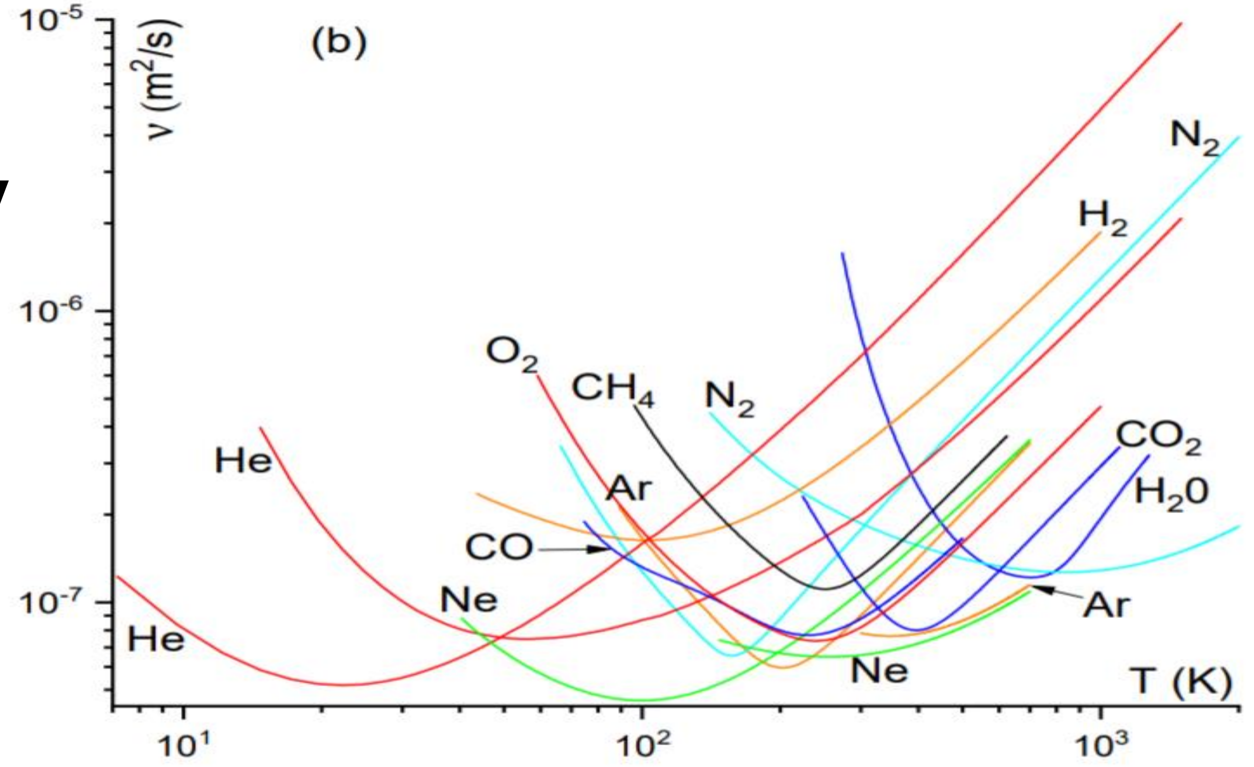
$$\nu_m^{exp} = (0.5-2)\cdot 10^{-7}\ \frac{\mathrm{m}^2}{\mathrm{s}}$$

[See derivation therein]

Kinematic viscosity

= momentum diffusion constant

[cf.Hartnoll's ideas]



What about QGP ?

E/V	$1\ \mathrm{GeV/fm^3}$ [23]
η	$5 \cdot 10^{11}\ \mathrm{Pa \cdot s}$ [7]
m_p	$1.67 \cdot 10^{-27}\ \mathrm{kg}$
a_p	$0.84 \cdot 10^{-15}\ \mathrm{m}$
a	$0.5 \cdot 10^{-15}\ \mathrm{m}$ [24]
T_{QGP}	$2 \cdot 10^{12}\ \mathrm{K}$ [7]

THE SHEAR VISCOSITY IS HUGE
(COMPARABLE TO LIQUIDS
AT THE GLASS TRANSITION)

But the density is also huge !

$$D = \frac{a_p^2}{\hbar} k_{\mathrm{B}} T_{\mathrm{QGP}}$$

Compatible with the standard liquid formula and using the Planckian relaxation time !

It can be derived in several ways :
(check the paper 😉)

$$\nu_{\mathrm{QGP}}^{exp} \approx 10^{-7} \frac{\mathrm{m}^2}{\mathrm{s}}$$

I naturally want to be provocative.

$$\boxed{\frac{\eta}{s}}$$

Is it a good universal quantity ??

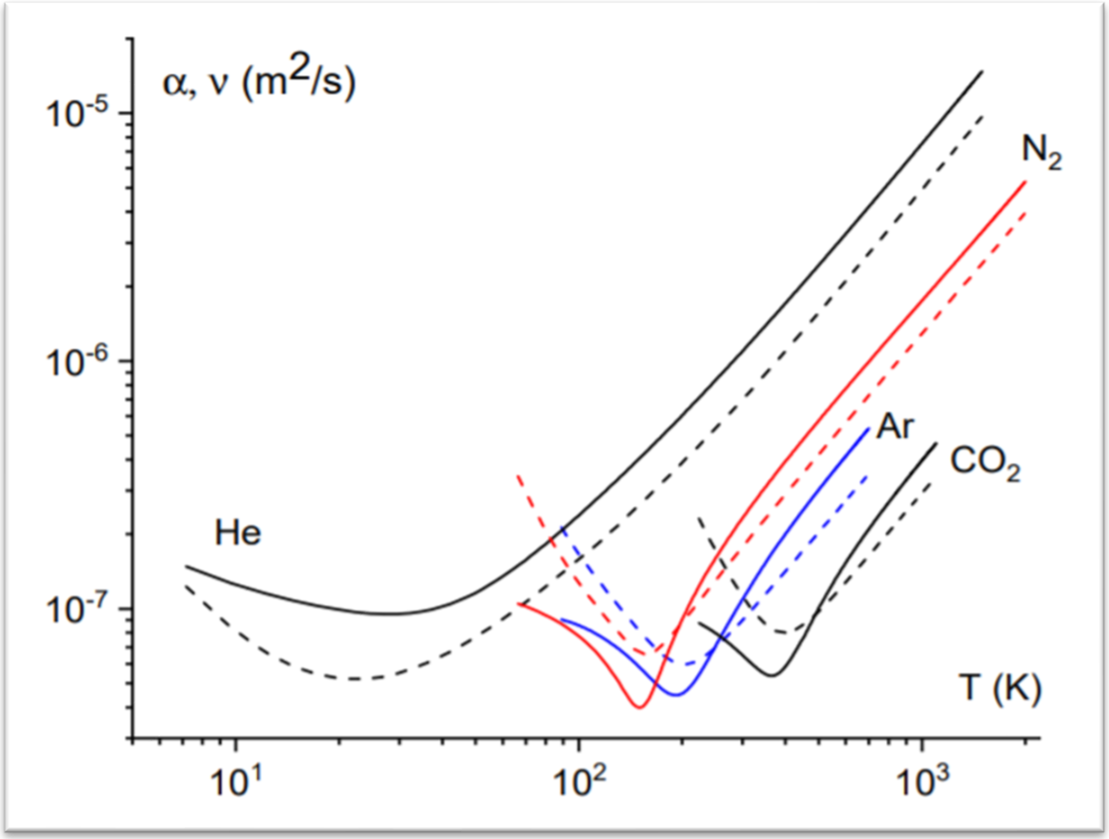
[One objection: away from neutral relativistic hydrodynamics It does not control anything]

[Reply-to-comment: it controls entropy production]

[Reply-to-Reply-to-comment: but only for a very specific external deformation]

Is it D (diffusion constant) better ??

What about thermal diffusion?



1) *also a minimum*
2) *also value of the minimum universal*
3) *approximately same value of diffusion of momentum (from theory we get exactly the same result)*

Super-universality ??

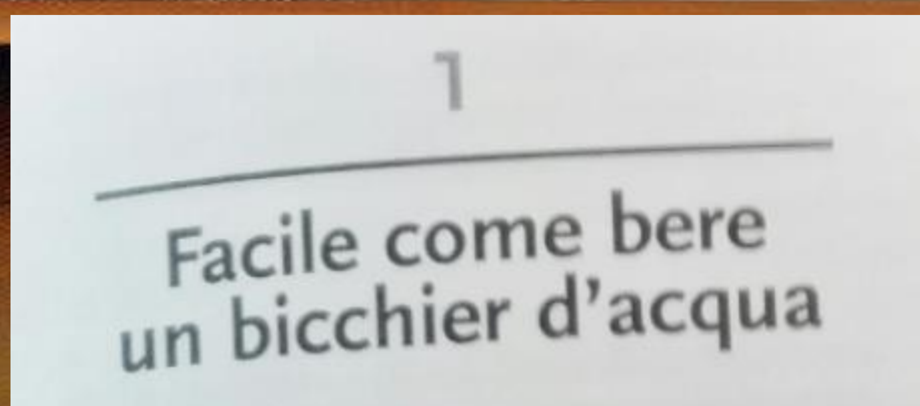
For the Holographers in the audience

1) the specific heat of the holographic models grows with T

2) the viscosity grows with T

IS THIS A LIQUID?

CONCLUSIONS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Facile come bere
un bicchier d'acqua

Thanks To my collaborators

Thanks for listening !

Matteo Baggioli (SJTU Shanghai)