

Dark opalescence in near-critical SF_6

Kamran Behnia



The scheduled talk:

Article

<https://doi.org/10.1038/s41467-024-46079-0>

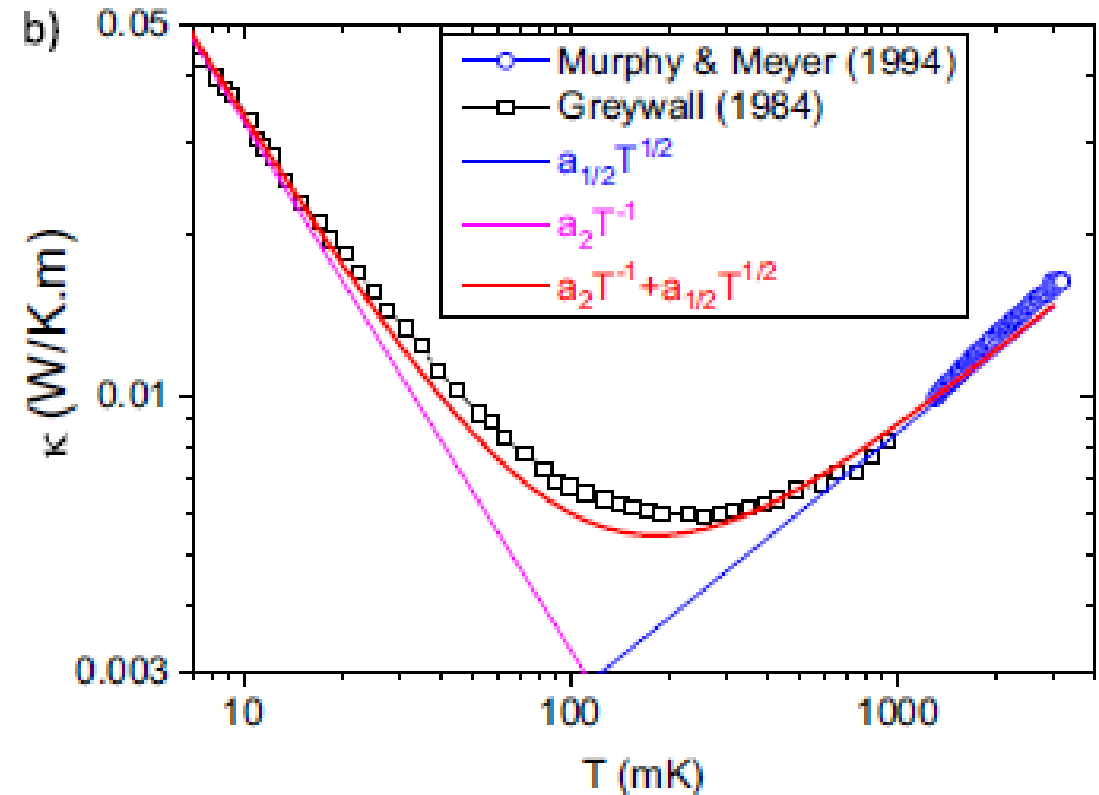
How heat propagates in liquid ^3He

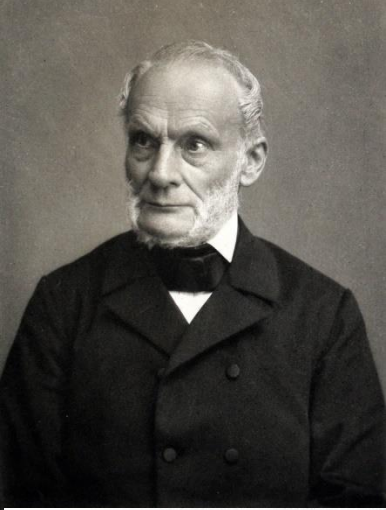
Received: 29 August 2023

Kamran Behnia ¹ & Kostya Trachenko ²

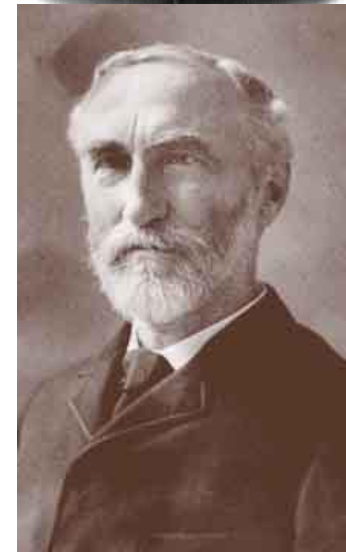
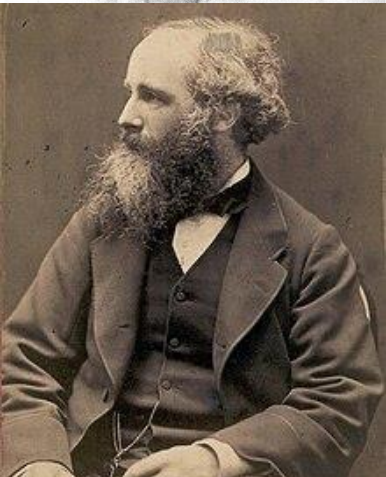
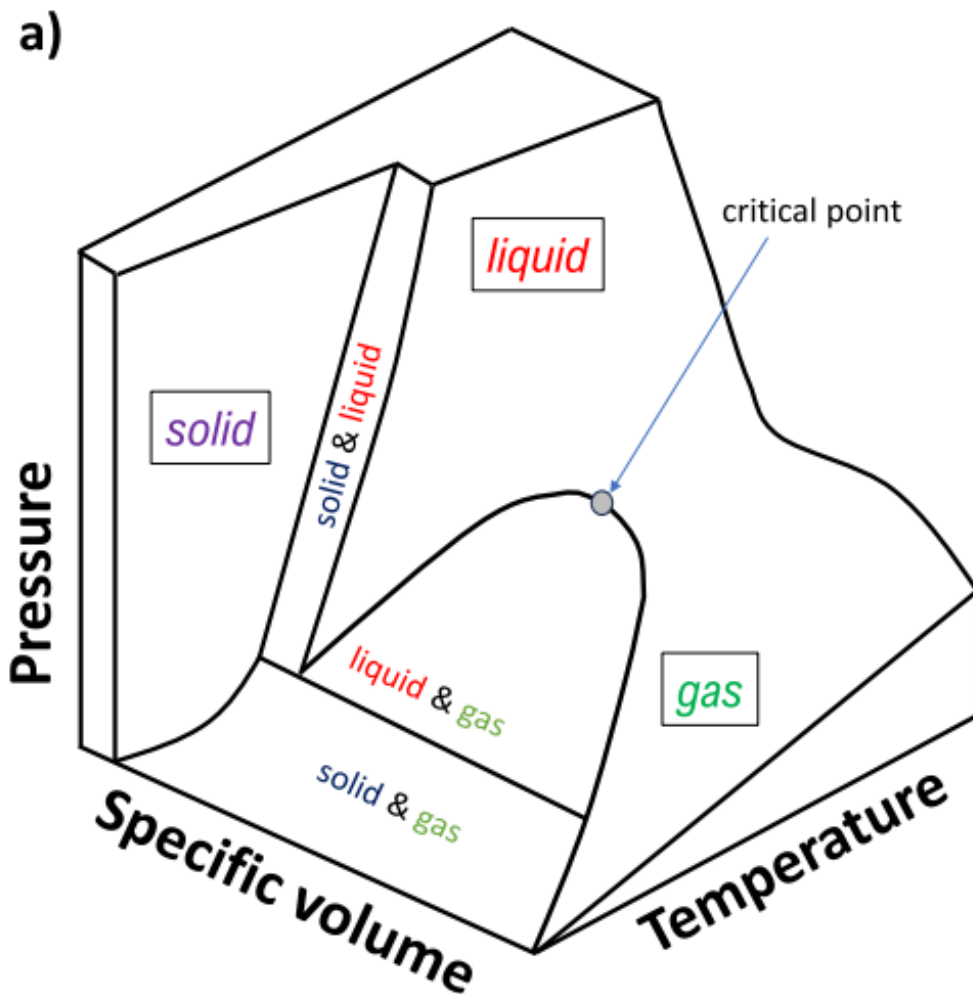
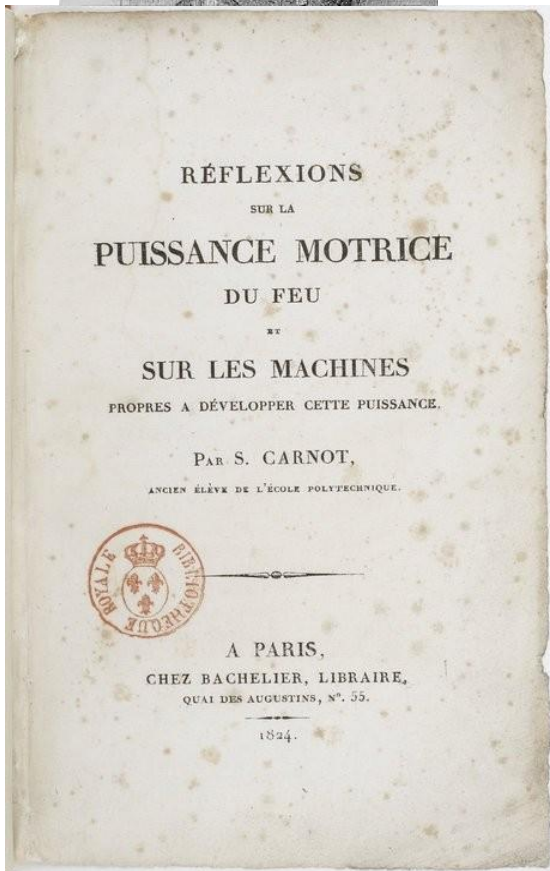
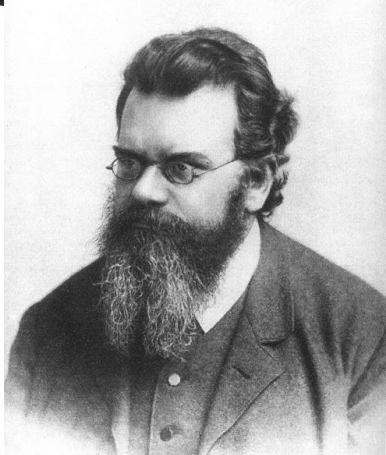
Accepted: 12 February 2024

A quantum version of the Brigman formula (1923) for thermal conductivity of liquids describes thermal conductivity of ^3He .

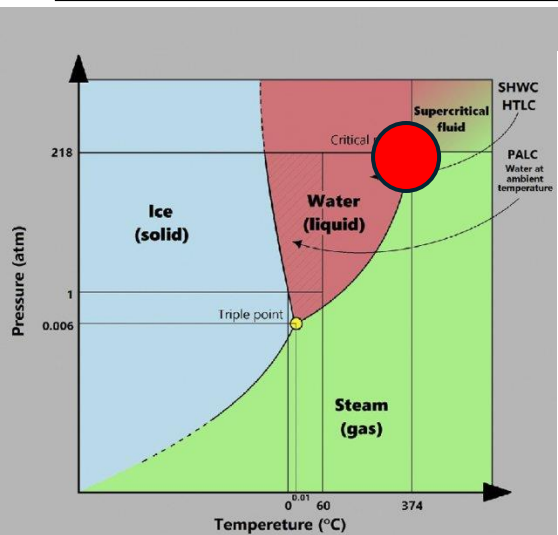
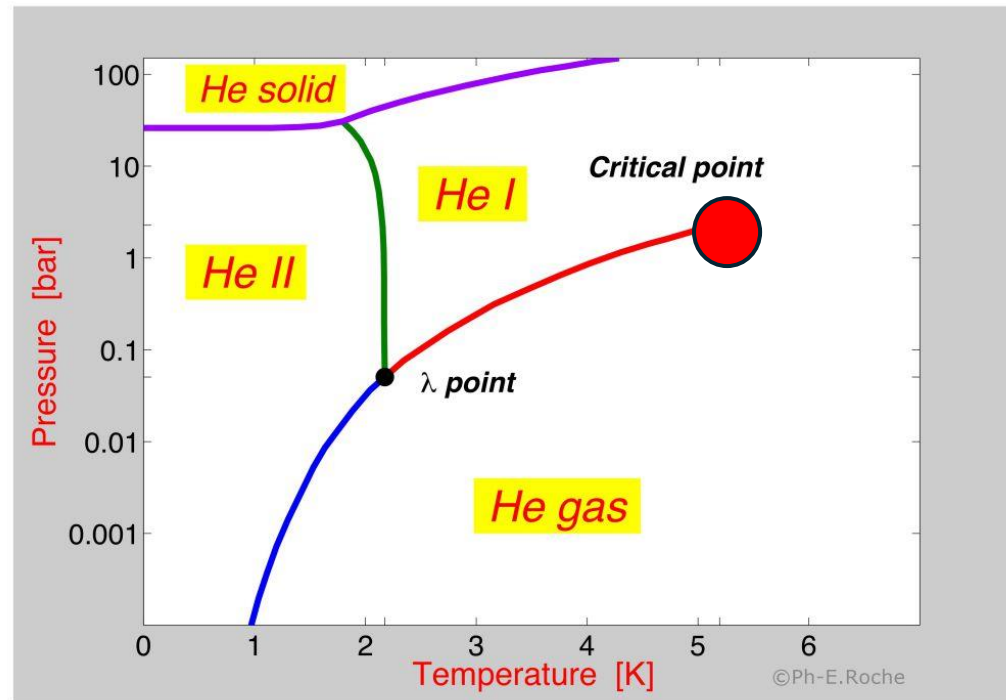
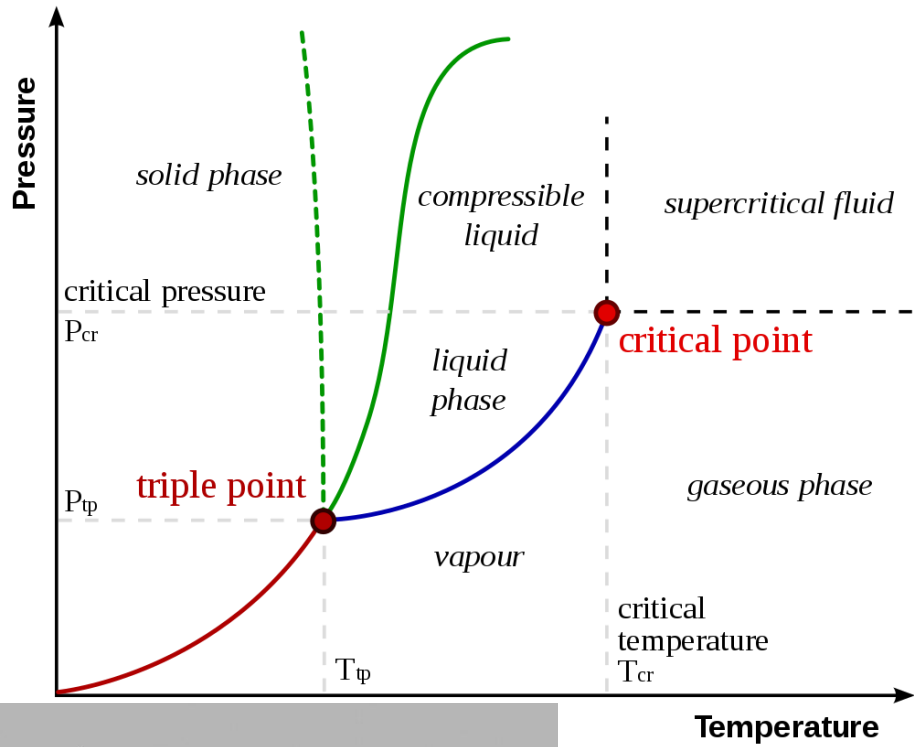




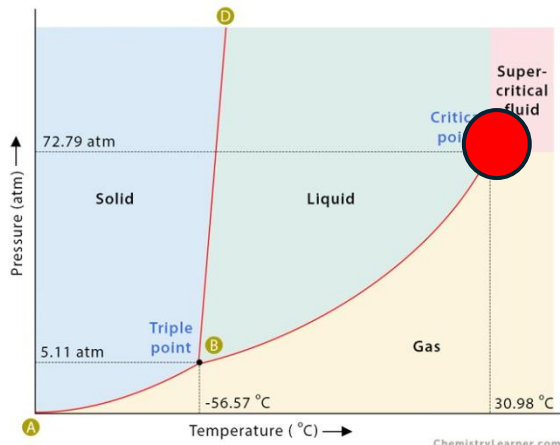
This year is a bicentennial



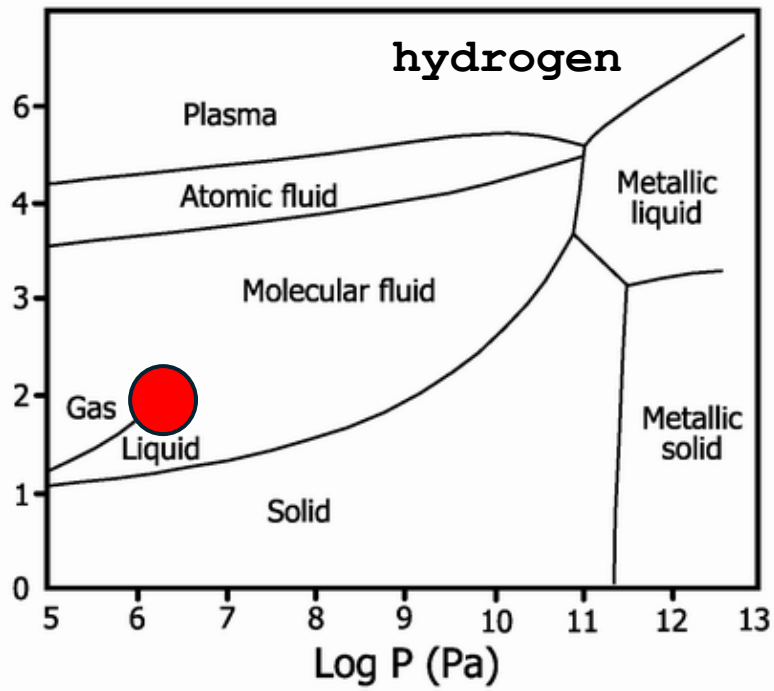
The critical point



Phase Diagram of Carbon Dioxide (CO₂)



Log T (K)



Critical Opalescence

Annales de chimie et de physique. 1822.

EXPOSÉ de quelques résultats obtenus par l'action combinée de la chaleur et de la compression sur certains liquides, tels que l'eau, l'alcool, l'éther sulfurique et l'essence de pétrole rectifiée.

Par M. le Baron CAGNIARD DE LA TOUR.

paru complètement, et s'est converti en une vapeur tellement transparente que le tube semblait être tout-à-fait vide; mais en le laissant refroidir un moment, il s'y est formé un nuage très-épais, après lequel la liqueur a reparu dans son premier état.



Charles Cagniard de La Tour discovers a thick cloud!

Turbidity near the critical point

Early theories of critical opalescence

- Smoluchowski (1908)
- Einstein (1910)

Compressibility diverges at the critical point: $\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T$

Density fluctuations are proportional to compressibility: $\frac{\langle \Delta \rho^2 \rangle}{\rho^2} = \frac{k_B T}{V} \kappa_T$

Density is linked to the refractive index. $\frac{\epsilon - 1}{\epsilon + 2} = \frac{\alpha}{3\epsilon_0} \rho$

Clausius-Mossotti
Lorentz-Lorenz

Fluctuations of the refractive index generate turbidity:

$$\frac{I_{\text{scattered}}}{I_0} = \frac{8\pi^3}{27\lambda^4} (\epsilon - 1)^2 (\epsilon + 2)^2 \kappa_T$$

(See H. B. Callen, Thermodynamics 1960)

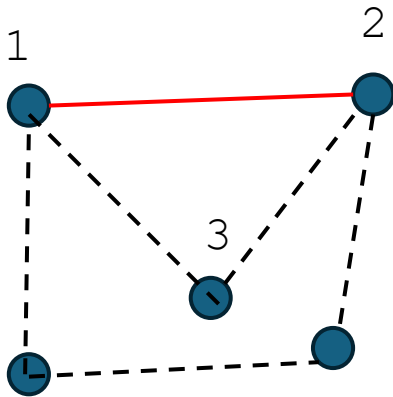
What drives critical opalescence?

Early theories neglected **indirect** correlations between particles.
The Ornstein-Zernike theory integrated them.

Physics. — “Accidental deviations of density and opalescence at the critical point of a single substance.” By DR. L. S. ORNSTEIN and F. ZERNIKE. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of September 26, 1914).

$h(r)$: pair correlation function



$$h(r_{12}) = c(r_{12}) + \int c(r_{13})c(r_{32})\rho dr_3 + \int \int c(r_{13})c(r_{34})c(r_{42})\rho^2 dr_3 dr_4 + \dots$$

$$= c(r_{12}) + \rho \int c(r_{13})h(r_{32})dr_3$$

$$h(r) = c(r) + \rho \int c(R-r)h(R)dR$$

$$h(r) = \frac{1}{r} \exp(-r/\xi)$$

$$T \rightarrow T_c \Rightarrow \xi \rightarrow \infty \Rightarrow h(r) = \frac{1}{r} \quad \text{Correlations become long range!}$$

The expected scattering in Ornstein-Zernike theory

$$I(k) = \frac{\pi^2}{\lambda^4} \frac{\sin^2 \Phi}{1 + (K\xi)^2} \left(\frac{\rho \partial \epsilon}{\partial \rho} \right)^2 k_B T \kappa_T$$

Rayleigh scattering

Brillouin scattering

Diverging compressibility

Refinement by Mathieu Fisher (1964) →

$$h(r) = \frac{1}{r} \exp(-r/\xi) \rightarrow h(r) = \frac{1}{r^\eta} \exp(-r/\xi)$$

$$\eta \simeq 0.9$$

Experimental verification

TURBIDITY MEASUREMENTS IN SF₆ NEAR ITS CRITICAL POINT*

V. G. Puglielli and N. C. Ford, Jr.,

Department of Physics and Astronomy, University of Massachusetts, Amherst, Massachusetts 01002

(Received 13 February 1970)

We have made precision measurements of the turbidity of SF₆ near its critical point using an optical analog of the Wheatstone bridge. From the measurements we obtain values for the compressibility of $\kappa_T = (1.39 \pm 0.19)(T - T_c)^{-1.225 \pm 0.02} = (1.18 \pm 0.16) \times 10^{-3} \times \epsilon^{-1.225 \pm 0.02}/\text{atm}$, and for the correlation length of $\xi = (72 \pm 11)(T - T_c)^{-0.67 \pm 0.07} = (1.5 \pm 0.23)\epsilon^{-0.67 \pm 0.07} \text{ \AA}$.

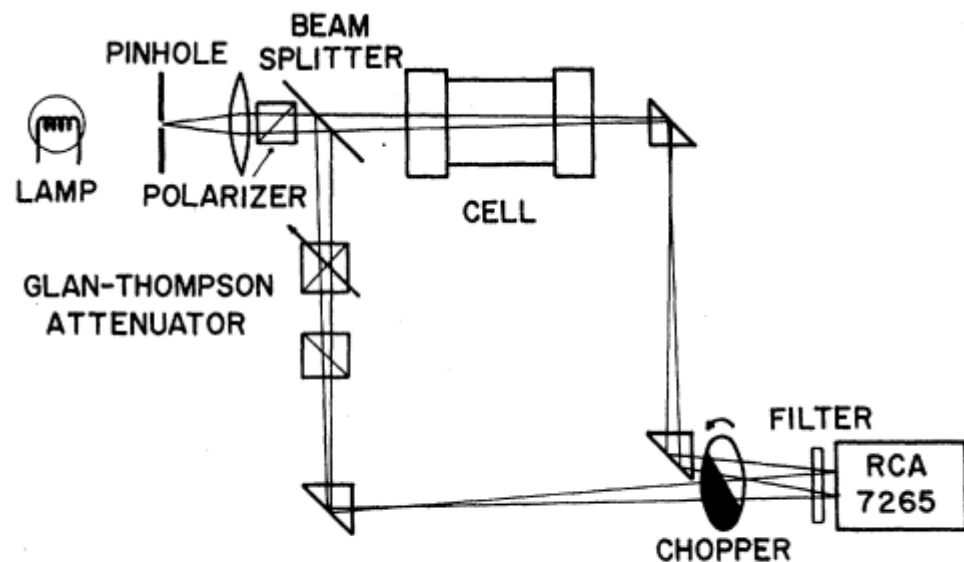
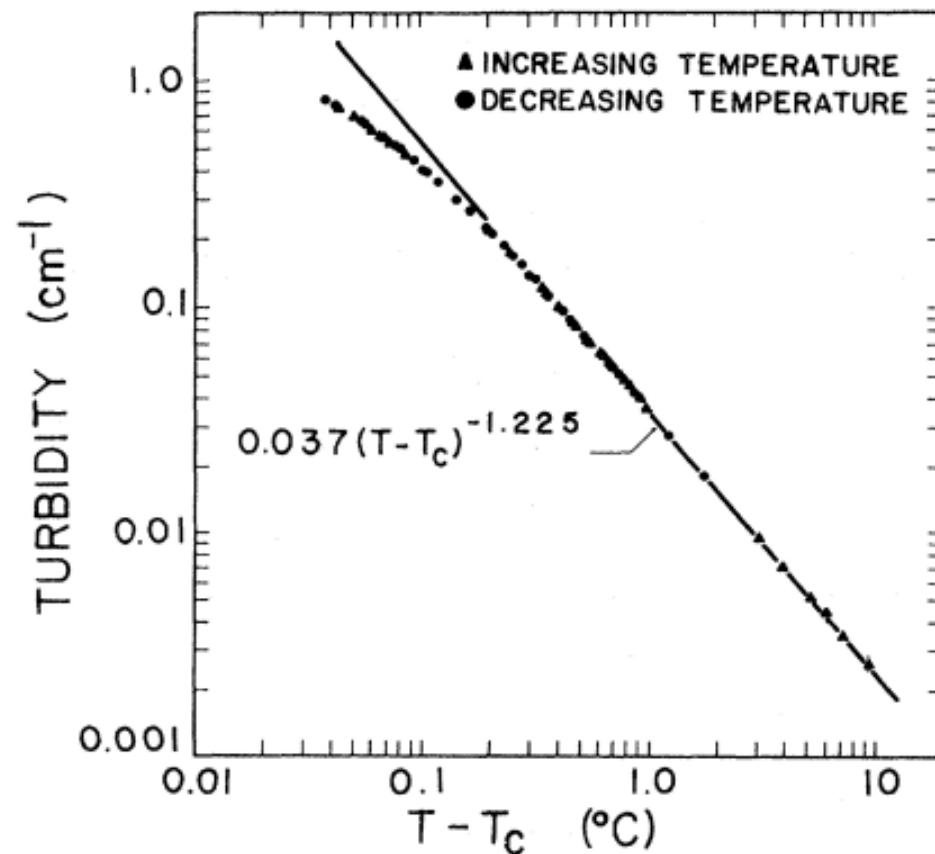


FIG. 1. Schematic of the "optical Wheatstone bridge" apparatus.



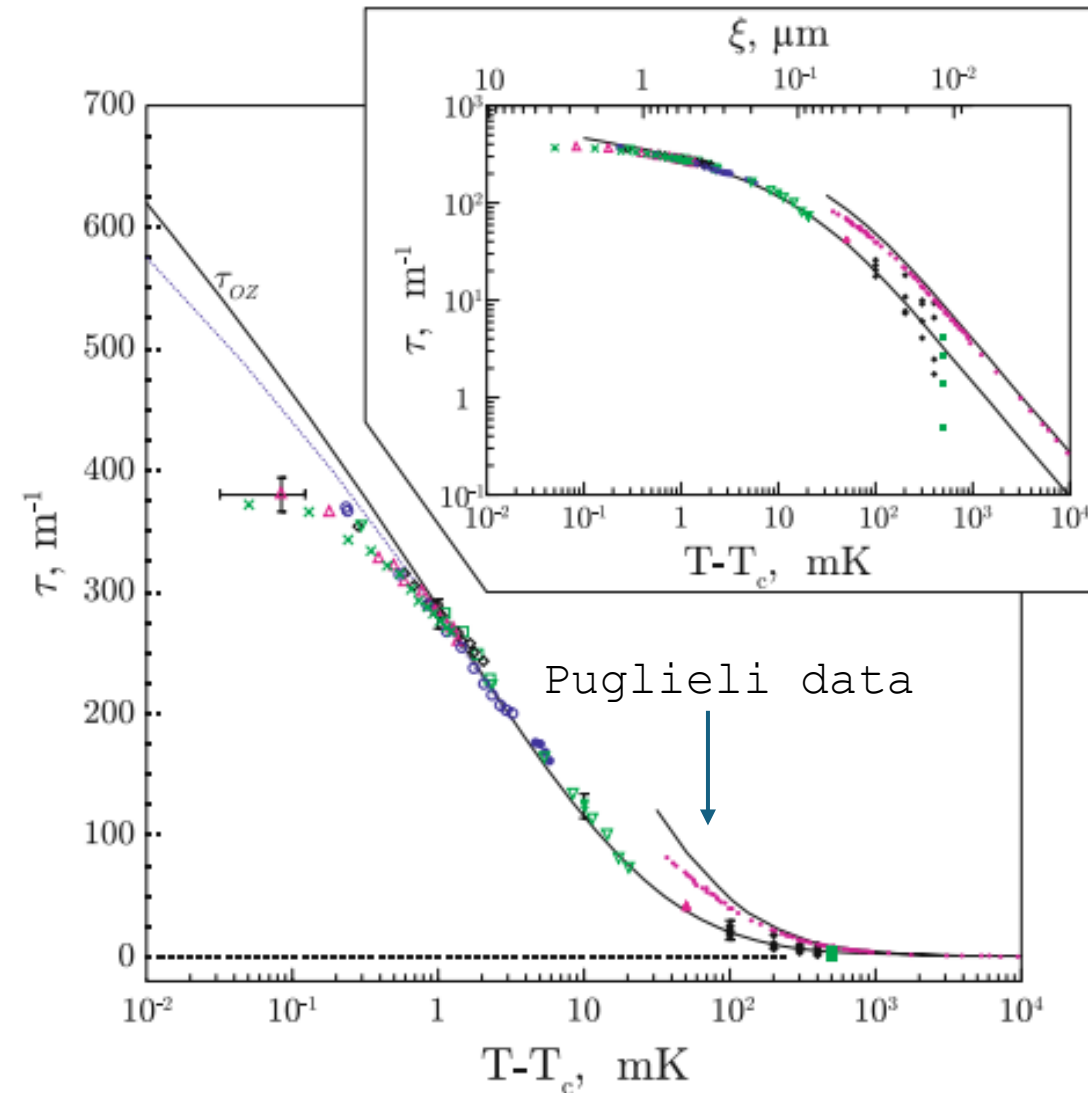
Experimental verification in space

Int J Thermophys (2009) 30:810–832
DOI 10.1007/s10765-009-0582-6

Turbidity Data of Weightless SF₆ Near its Liquid–Gas Critical Point

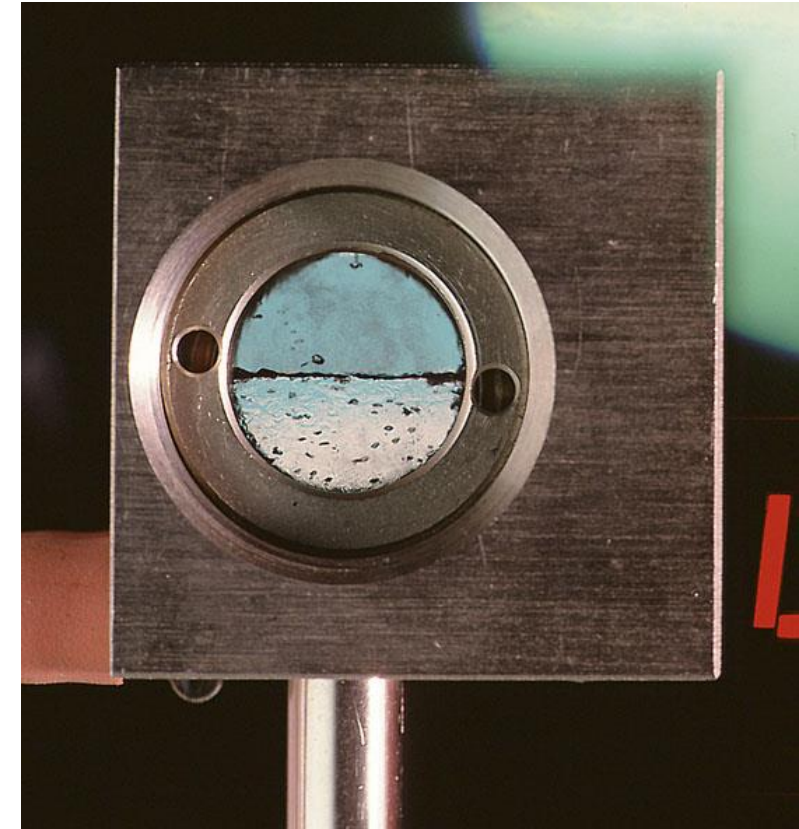
C. Lecoutre · Y. Garrabos · E. Georgin ·
F. Palencia · D. Beysens

Fig. 3 Lin–log plot of turbidity τ (expressed in m^{-1}) as a function of $T - T_c$ (expressed in mK) obtained from light transmission measurements in SF₆ and compared to Eq. 8 with $\lambda_0 = 632.8 \text{ nm}$ (left solid curve) [see Fig. 2 for detail of colored symbols]. Dotted curve represents a correction to Eq. 8 considering the influence close to T_c of the exponent $\eta = 0.0336$ [see Eq. 16]. The horizontal error bar indicates the uncertainty of $\pm 50 \mu\text{K}$ on T_{coex} . The vertical error bars come from experimental uncertainty. Other turbidity data from Ref. [23] (pink disk symbol) are shown together with the corresponding formulation of Eq. 8, with $\lambda_0 = 466 \text{ nm}$. Insert is the same in a log–log plot



2021

An undergrad project during the
pandemic



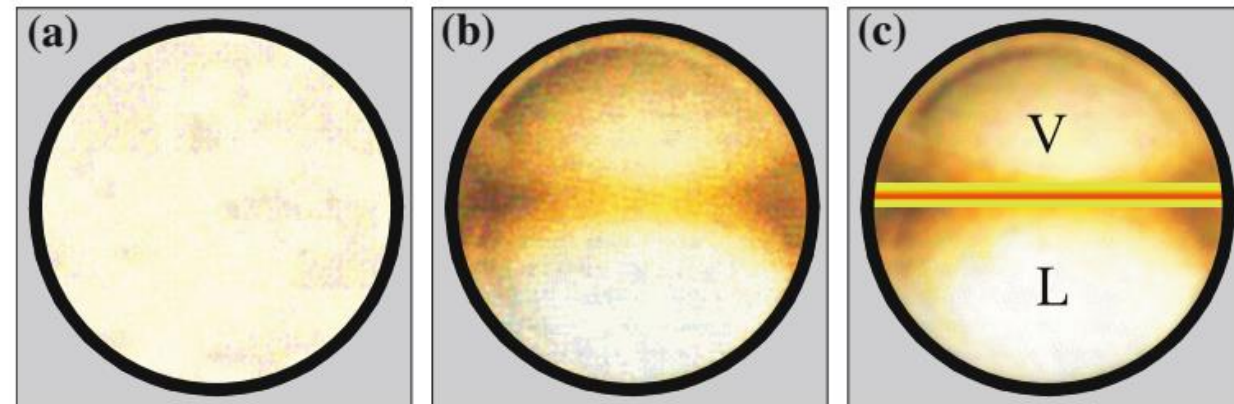
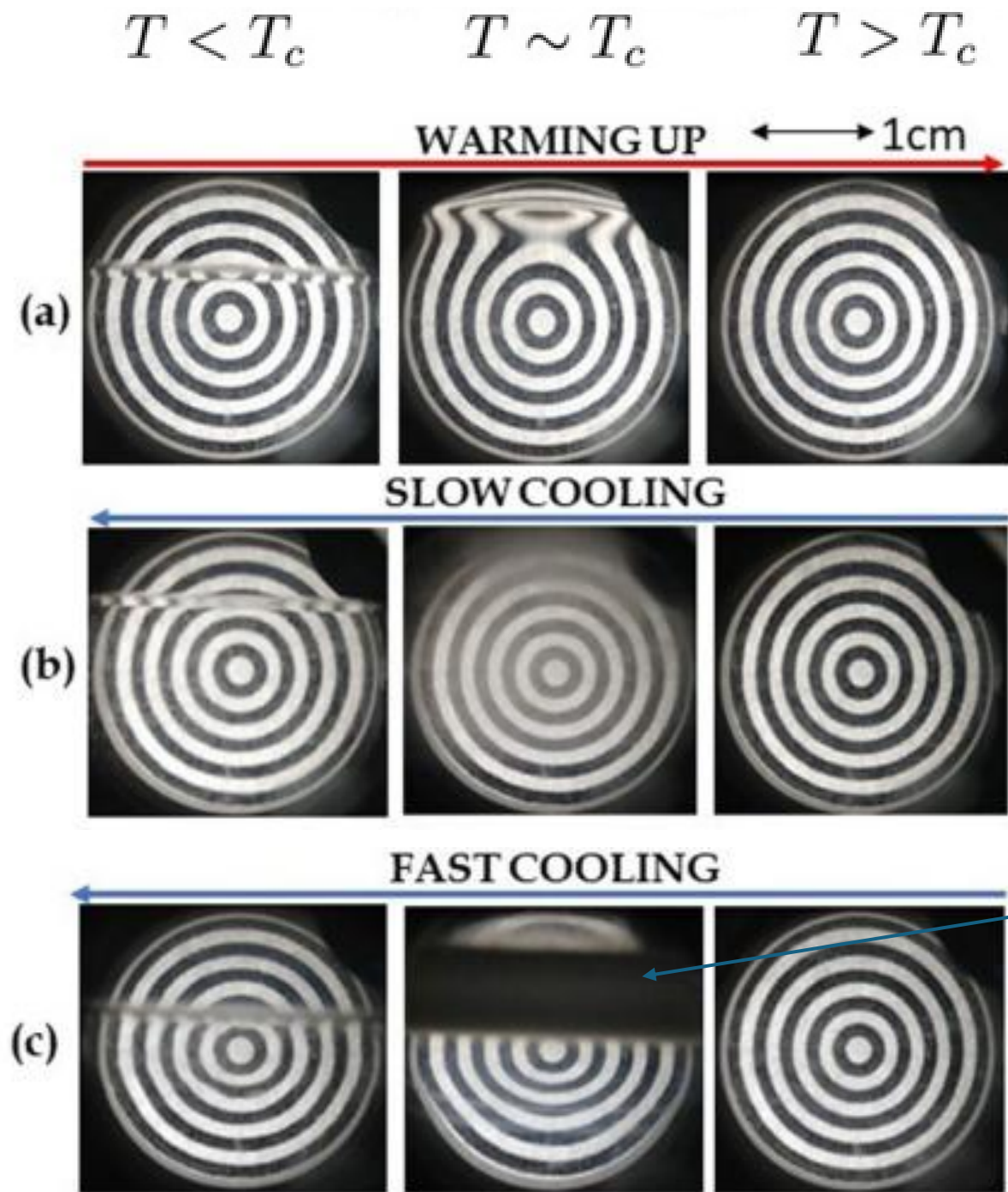
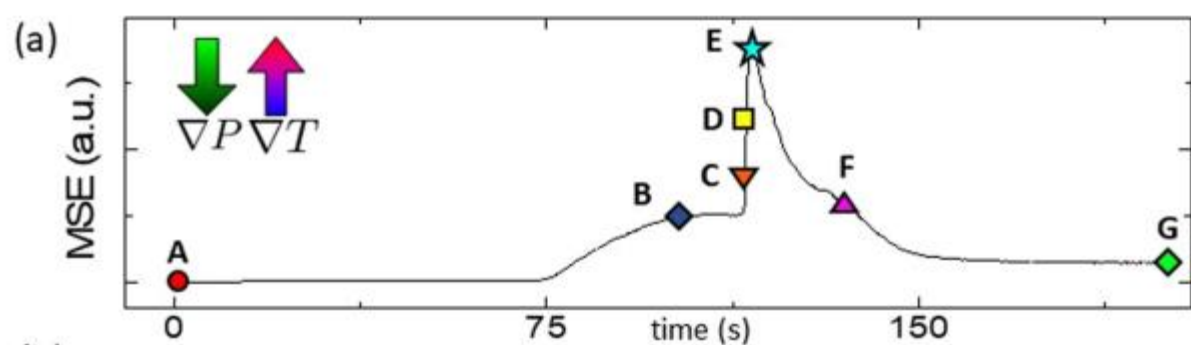
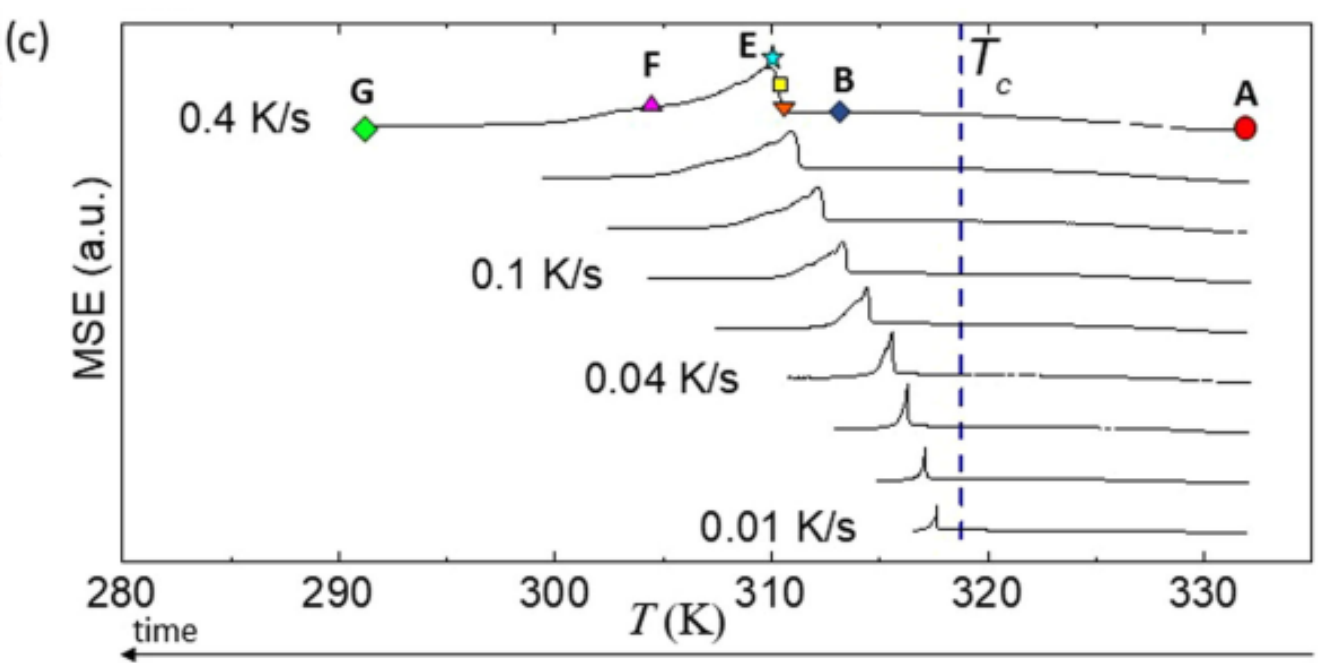
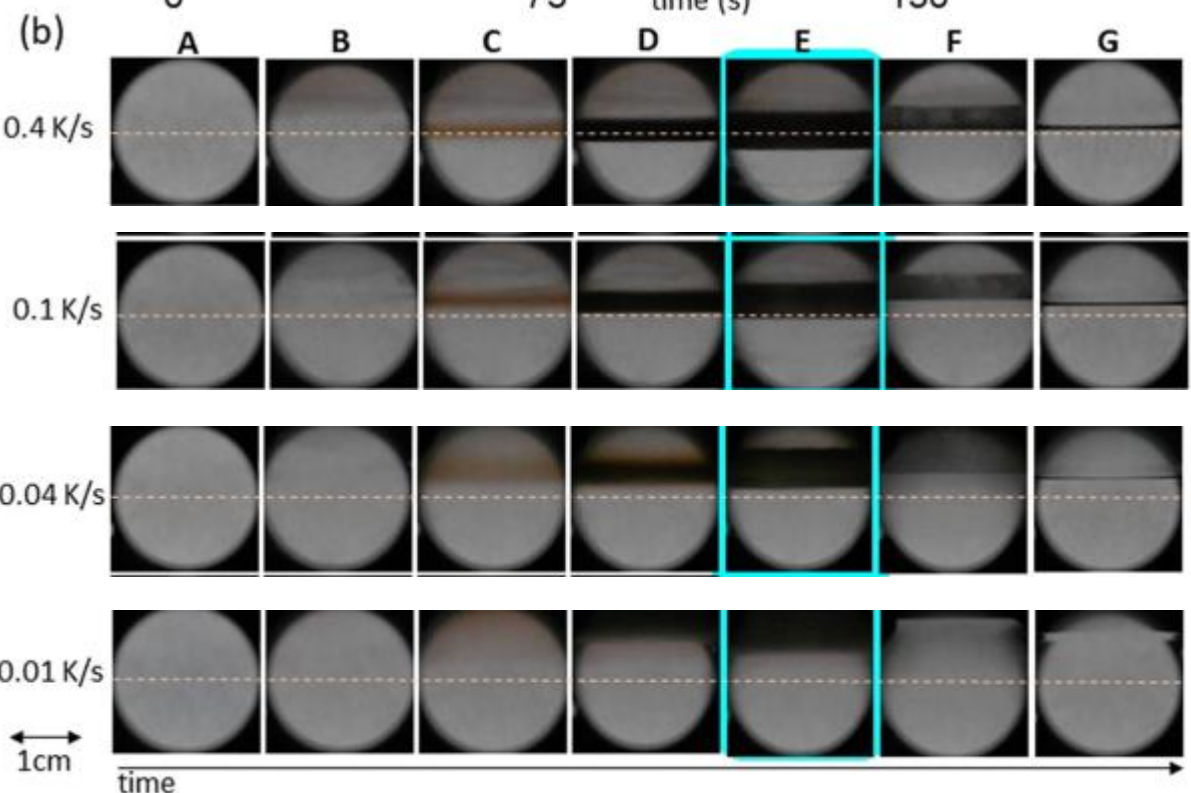


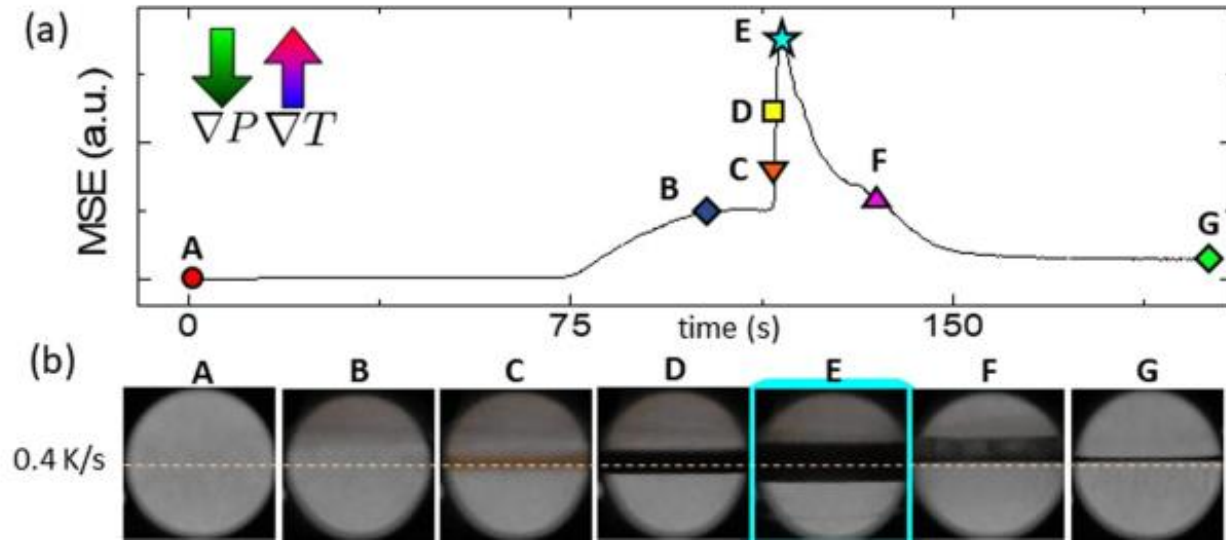
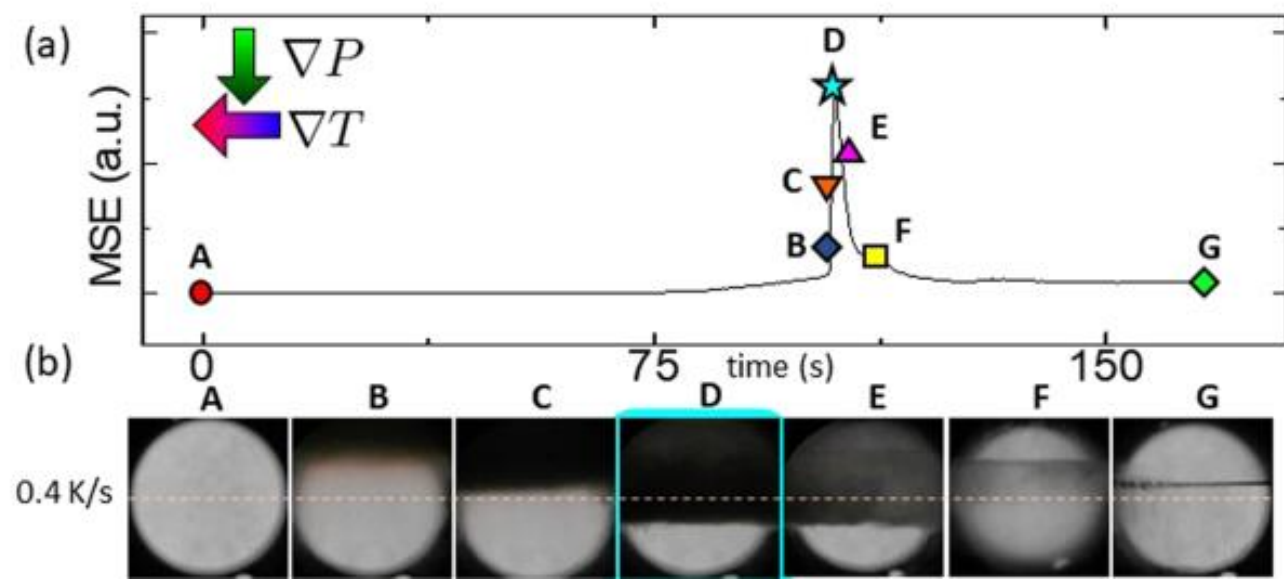
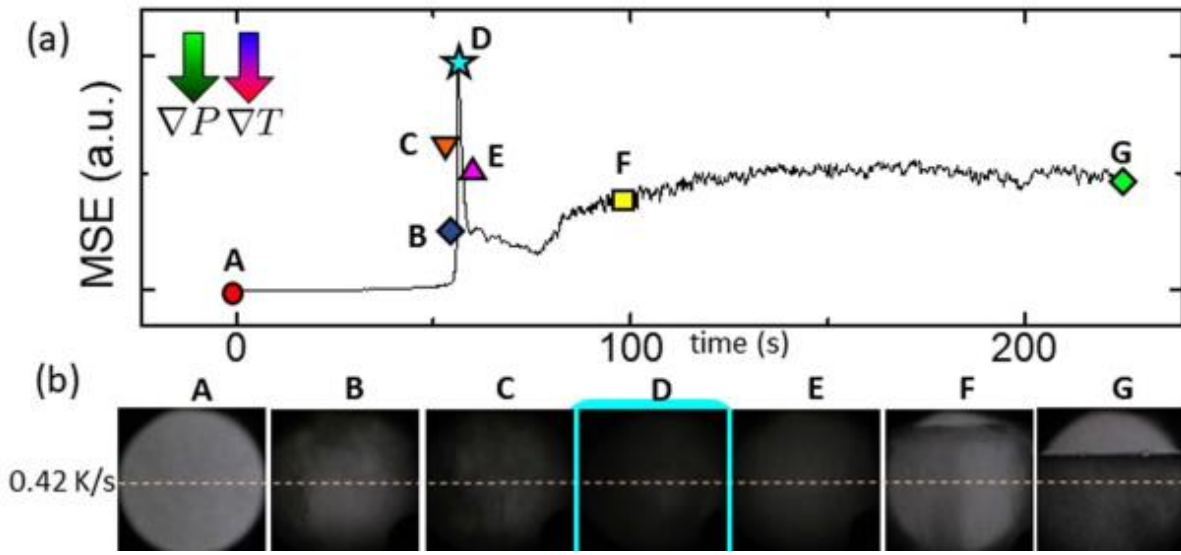
Fig. 1.1 A sample of SF_6 at critical density observed in transmission on Earth (i.e., with gravity directed downwards). **a** 10 K above the critical point (45.5°C ; 3.76 MPa ; 742 kg m^{-3}). **b** 1 mK above the critical point; the sample is compressed under its own weight. Critical density can only be

What is this?



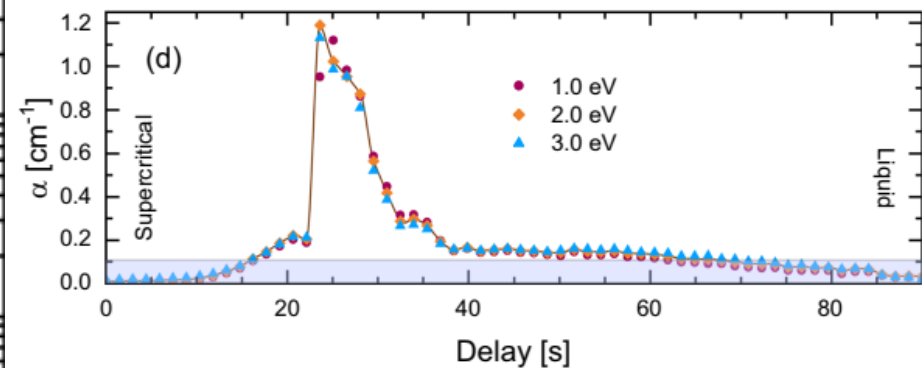
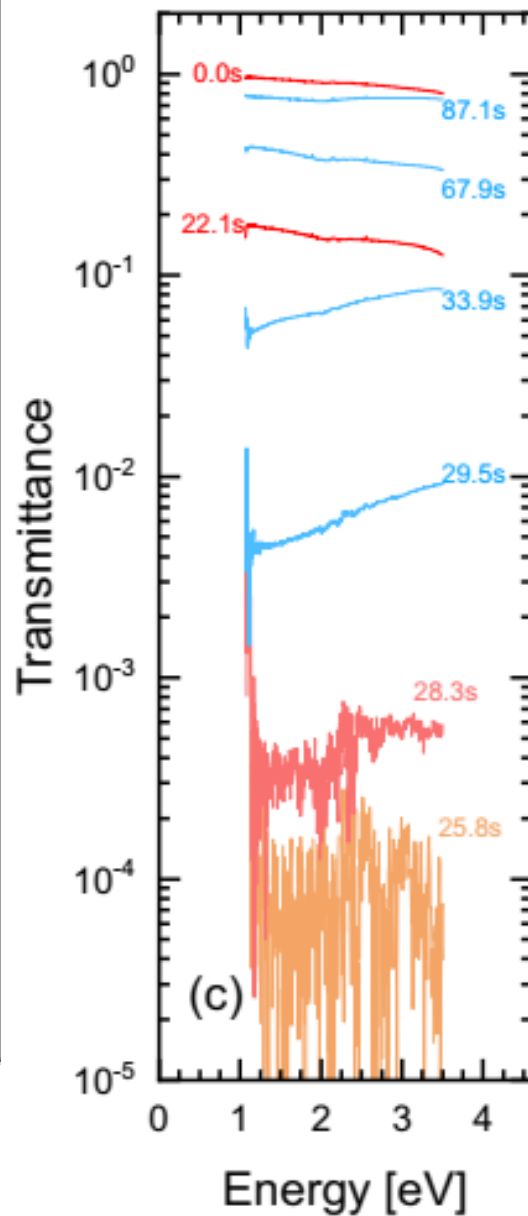
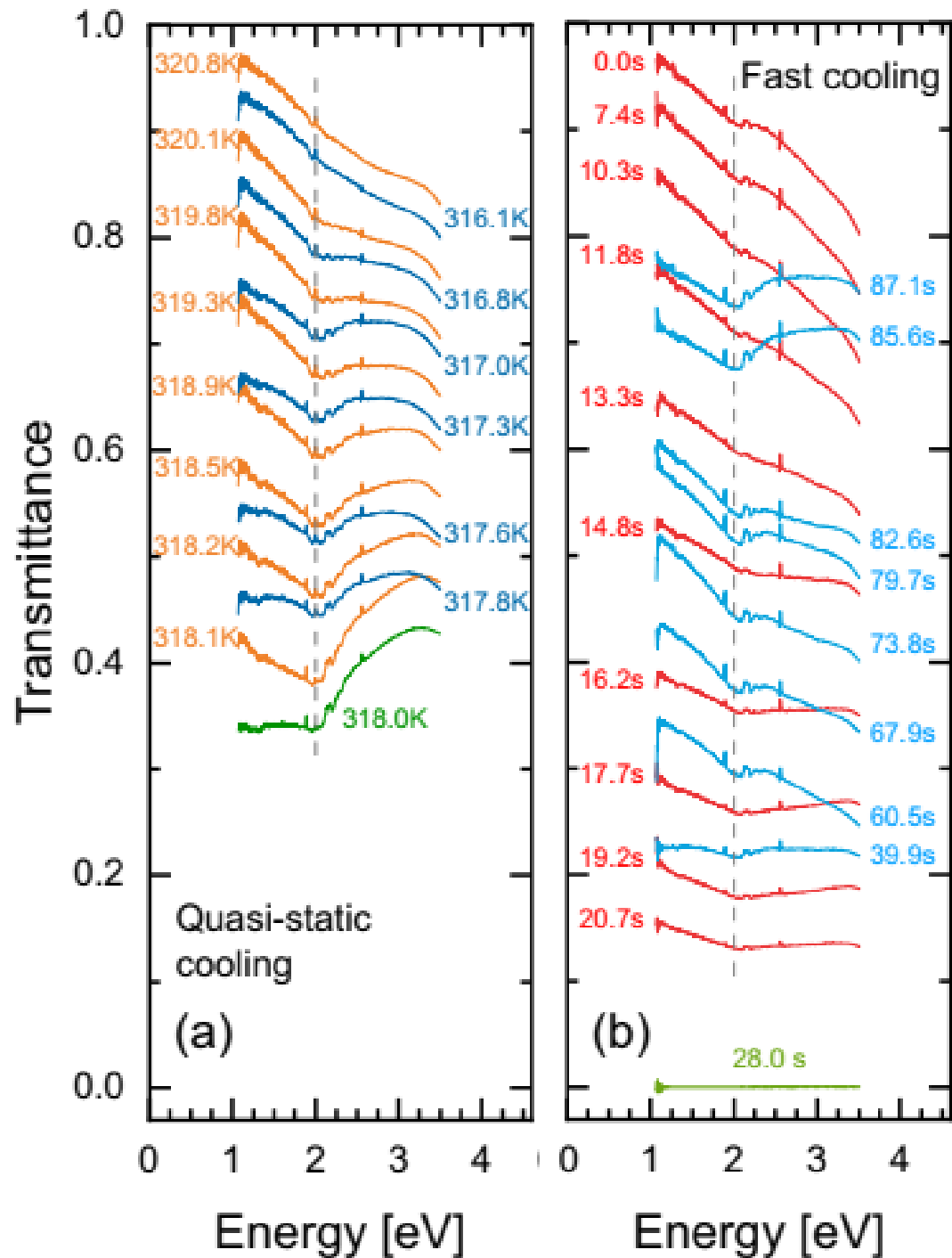
Evolution with cooling rate!





- Three configurations of pressure and temperature gradients .
- Three different patterns at high cooling rate.

Infrared transmittance



New questions

- Why the cooling speed matters?

Ornstein-Zernike and other theories were conceived for thermodynamic equilibrium.

- Can photons be absorbed by the near-critical cooling?

Such a possibility was not considered before.

- If yes, why this is favored by a quench?

Spinodal decomposition may play a role.

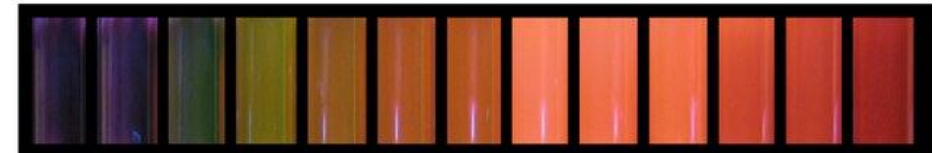
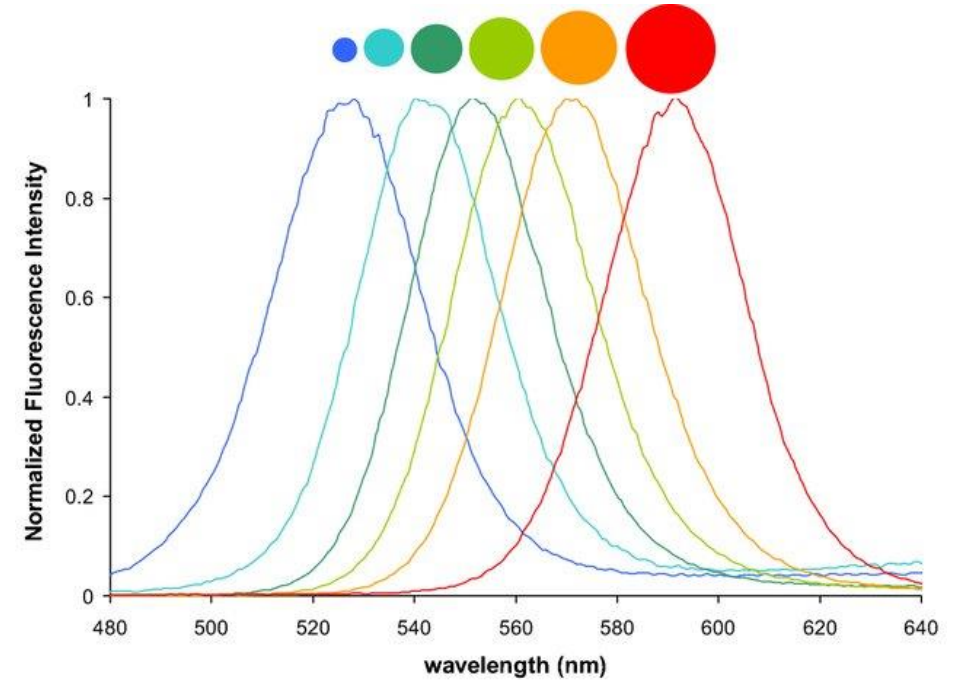
Quantum confinement?

Energy



Bulk

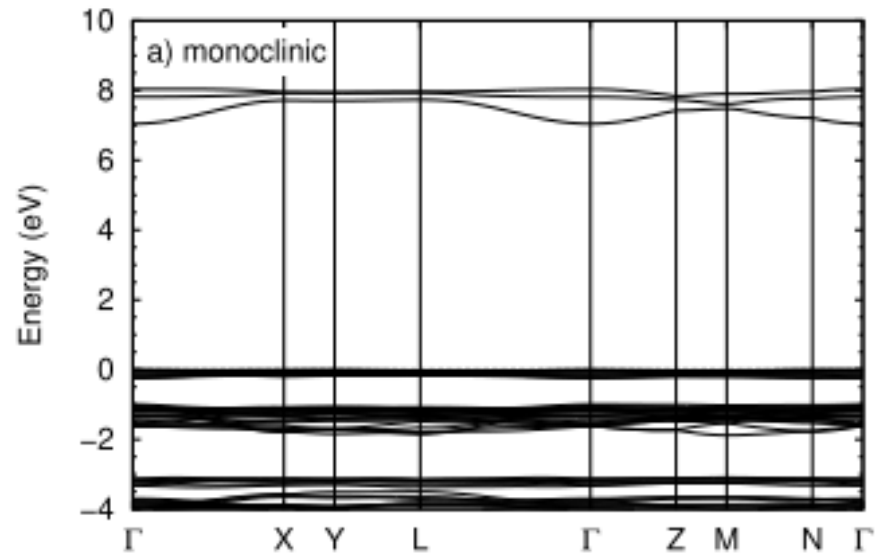
Confined



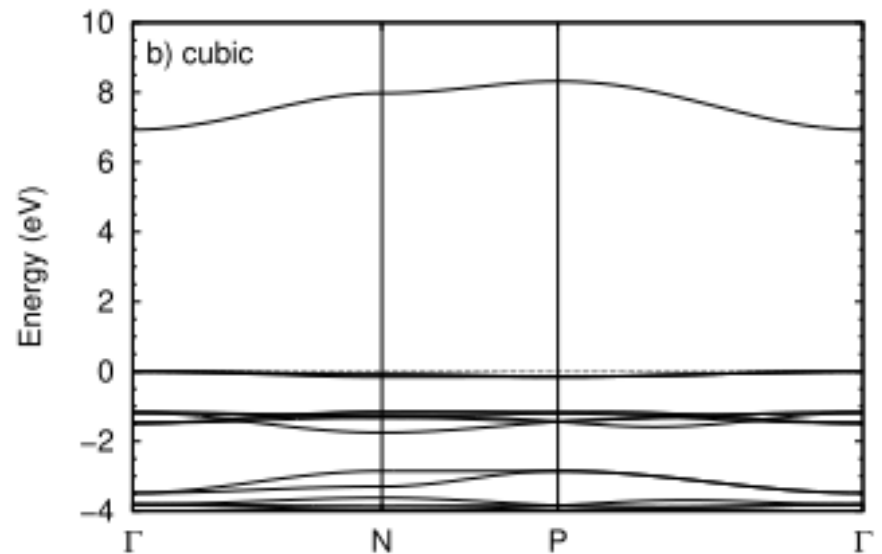
Díaz-González et al. Topics in Current Chemistry (2020)

Can it work in our case?

SF₆: transparent as a solid, a liquid or a gas!

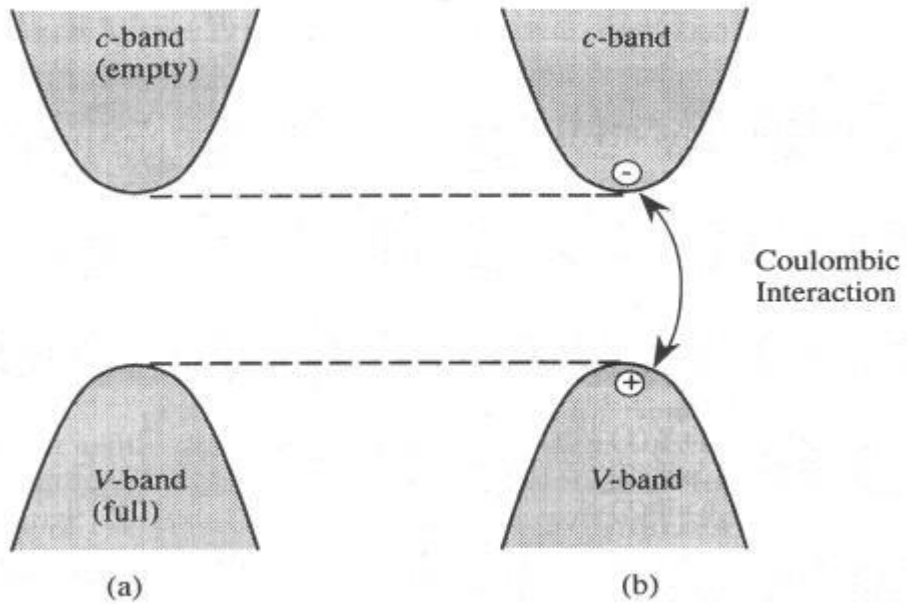


- The band gap of the solid is as large as 7 eV!



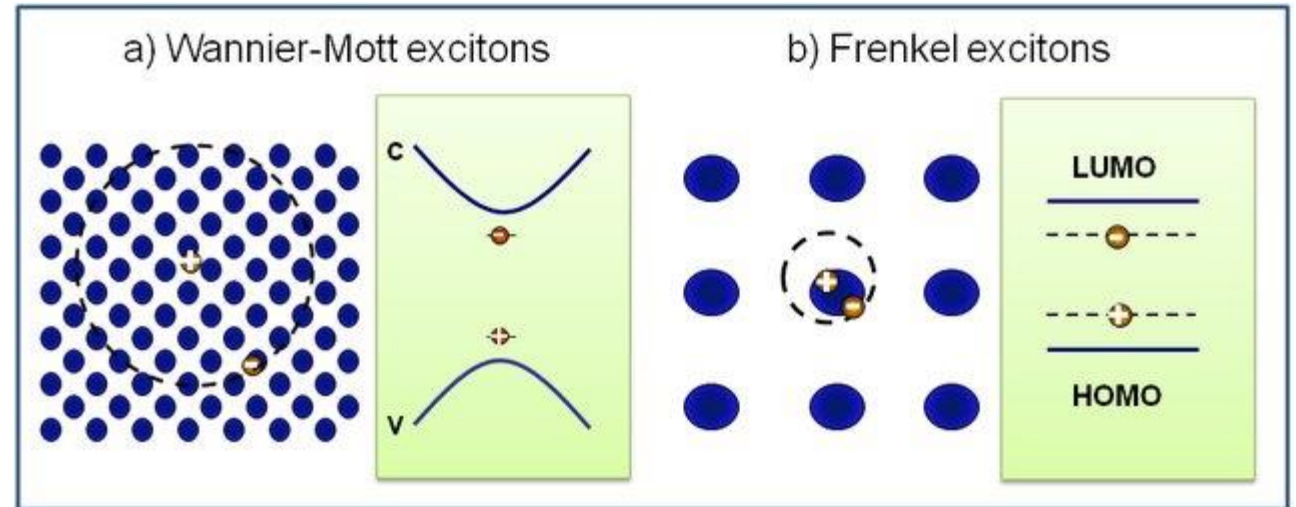
This wide gap insulator is very different from the small-gap semiconductors used for quantum dots.

Excitons

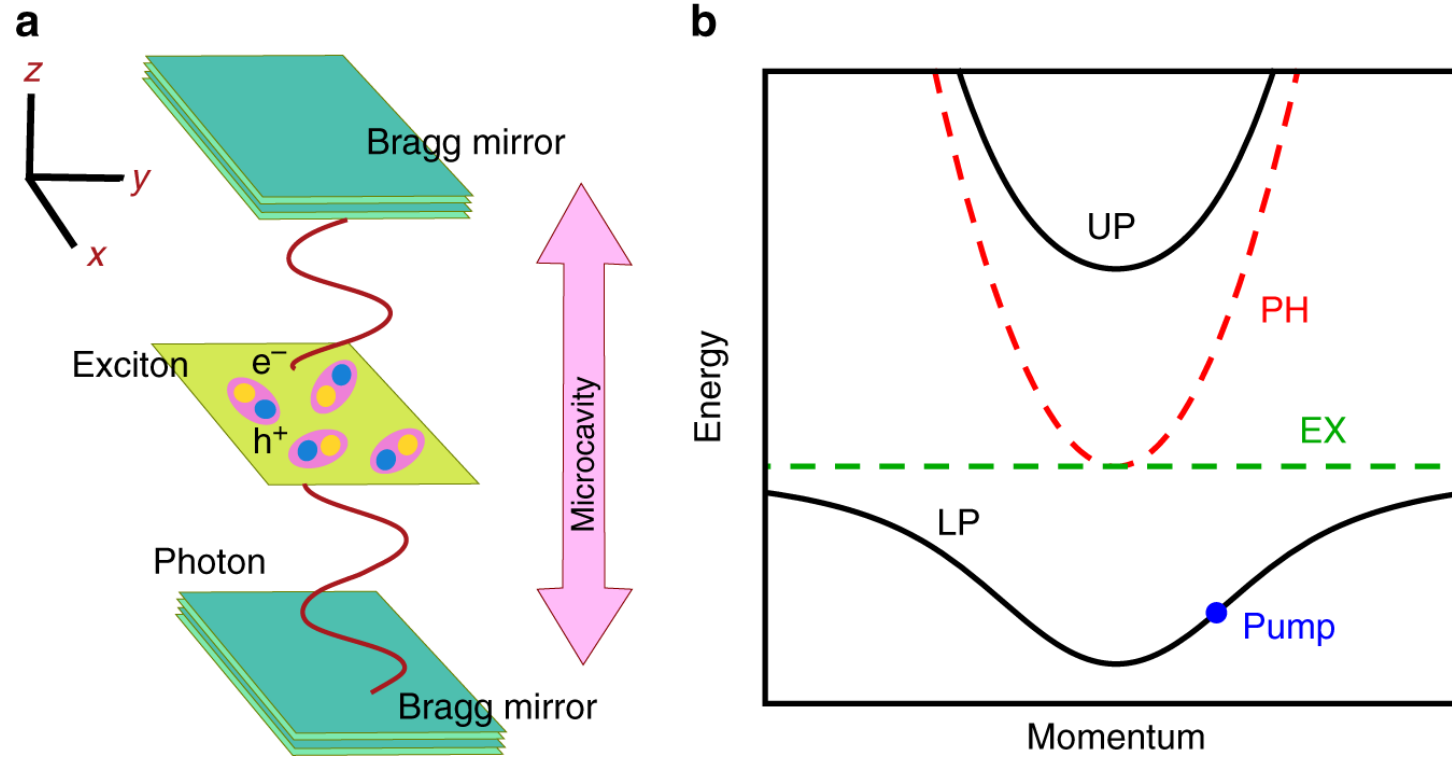


They are bound pairs of electrons and holes. Their formation depends on three energy scales:

- The attractive Coulomb interaction
- The band gap
- The energy of an incoming photon



Polaritons







R.T. Juggins¹, J. Keeling² & M.H. Szymańska¹

NATURE COMMUNICATIONS | (2018)9:4062

Excitons can hybridize with photons and form polaritons.



Strong light–matter interactions: a new direction within chemistry

Manuel Hertzog,  † Mao Wang,  † Jürgen Mony  and Karl Börjesson  *

Cite this: *Chem. Soc. Rev.*, 2019, 48, 937

DE GRUYTER

Nanophotonics 2021; 10(1): 549–577

Review

D. N. Basov*, Ana Asenjo-Garcia, P. James Schuck, Xiaoyang Zhu and Angel Rubio

Polariton panorama

<https://doi.org/10.1515/nanoph-2020-0449>

Received August 5, 2020; accepted October 2, 2020;
published online November 11, 2020

(QED) with atomic systems. Here, we attempt to summarize (in alphabetical order) some of the polaritonic nomenclature in the two subfields. We hope this summary will help

Quantum fluids of light

Iacopo Carusotto*

INO-CNR BEC Center and Dipartimento di Fisica, Università di Trento, I-38123 Povo, Italy

Cristiano Ciuti†

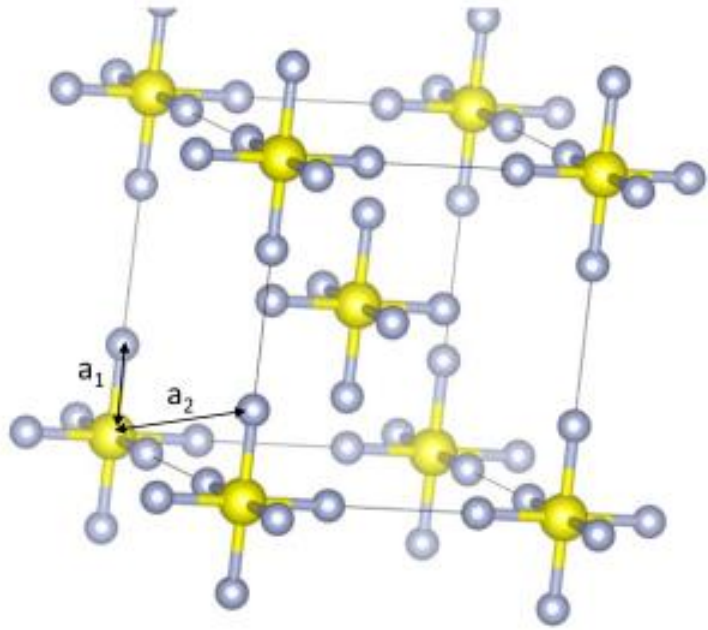
Laboratoire Matériaux et Phénomènes Quantiques, Université Paris Diderot-Paris 7 et CNRS, Bâtiment Condorcet, 10 rue Alice Domon et Léonie Duquet, 75205 Paris Cedex 13, France

(published 21 February 2013)

Abstract: In this brief review, we summarize and elaborate on some of the nomenclature of polaritonic phenomena and systems as they appear in the literature on quantum materials and quantum optics. Our summary includes at least 70 different types of polaritonic light–matter dressing effects. This summary also unravels a broad panorama of the physics and applications of polaritons. A constantly updated version of this review is available at <https://infrared.cni.columbia.edu>.

Phase separation in near-critical SF₆

a)



Clausius-Mossotti

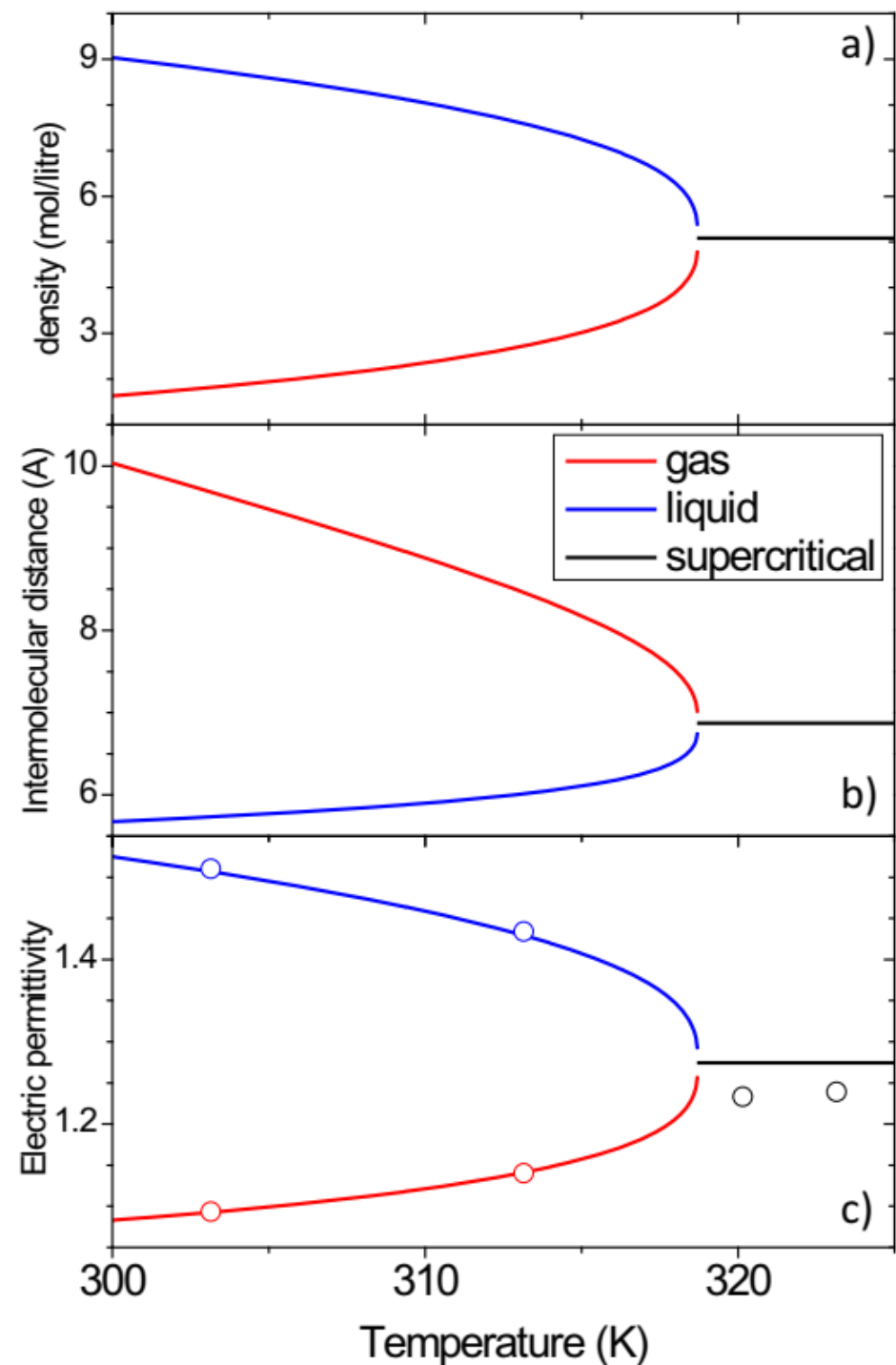
$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\alpha}{3\epsilon_0} \rho$$

Large molecular polarizability

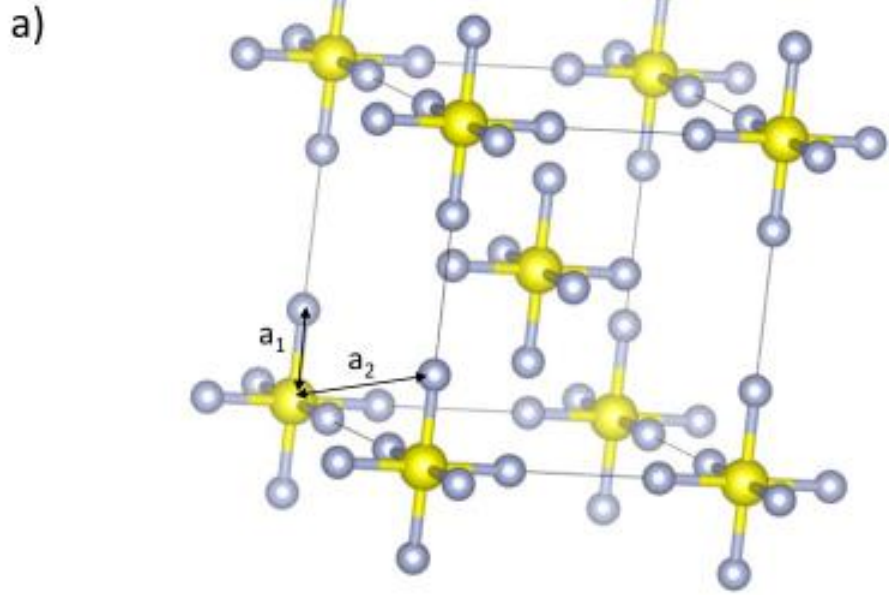


Large dielectric constant

Coulomb attraction is weakly screened.



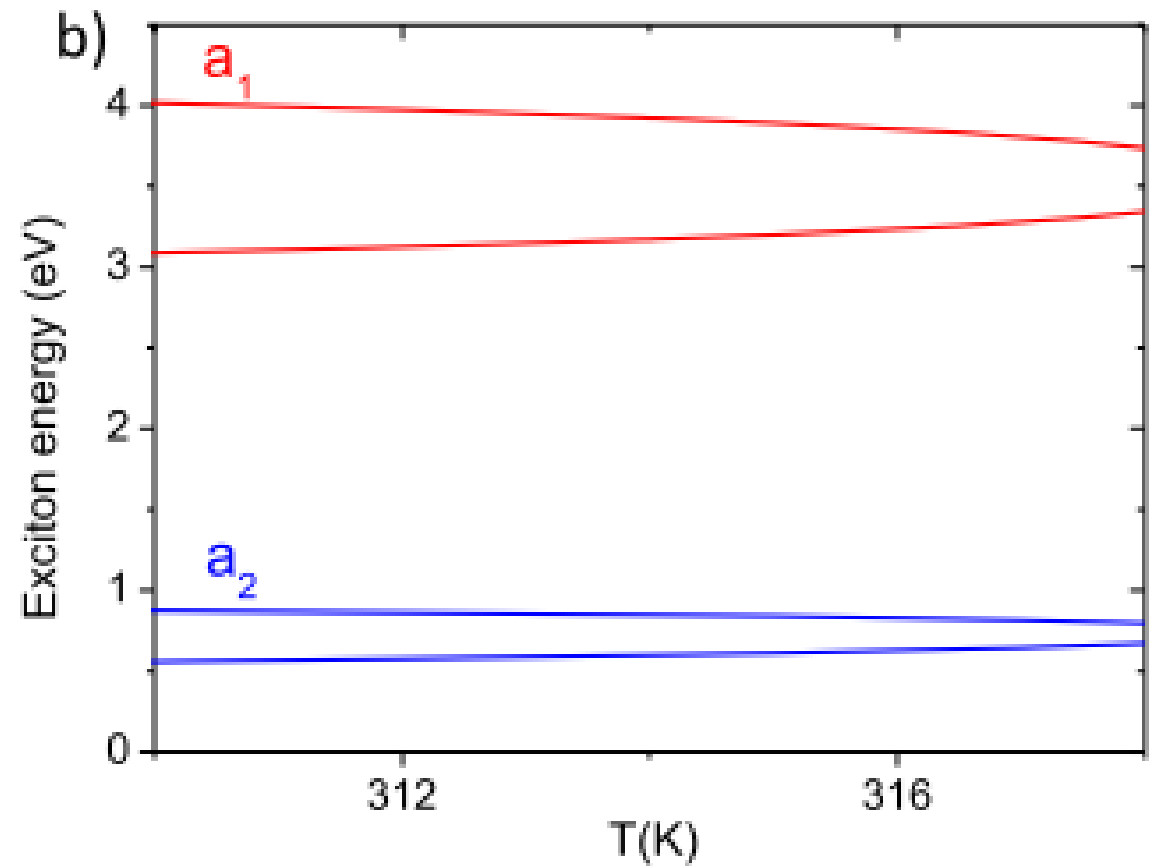
Excitons in near-critical SF₆



Energy of Frenkel excitons: $E_{exc}^F(d_{eh}) = \frac{e^2}{4\pi\epsilon_r\epsilon_0 d_{eh}}$.

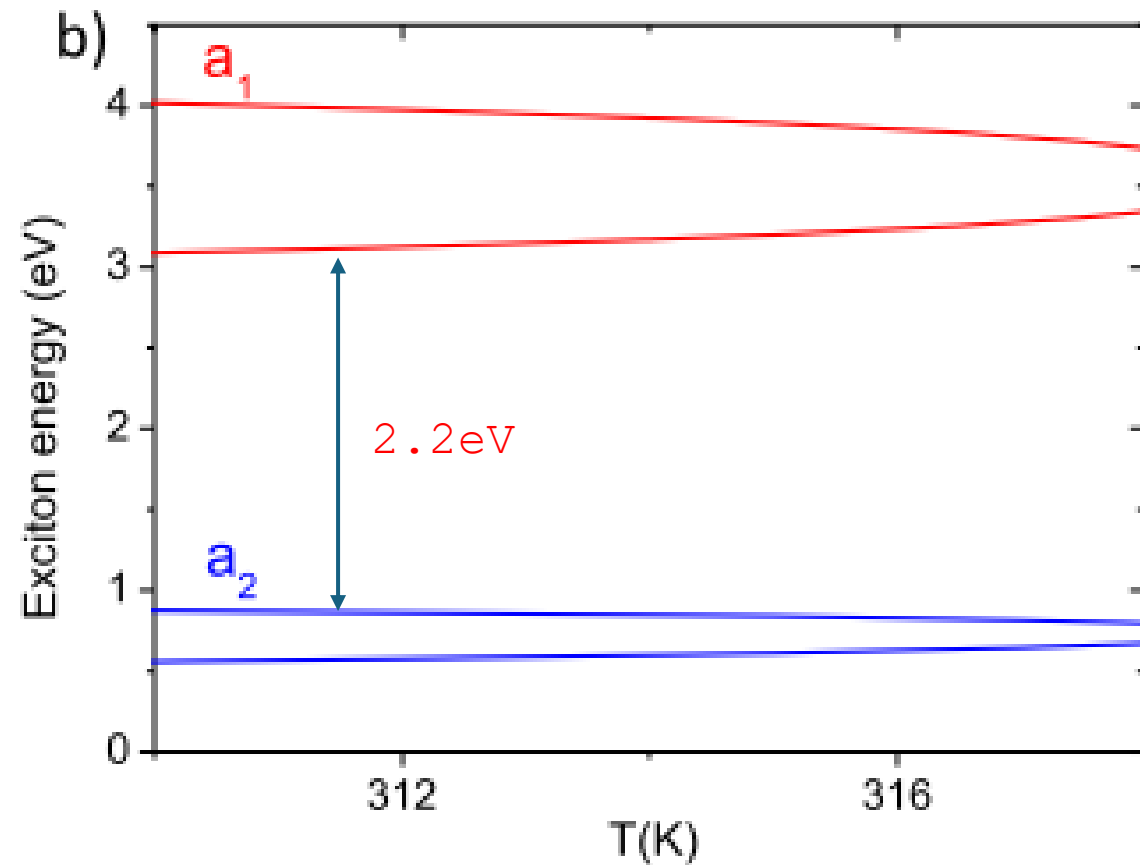
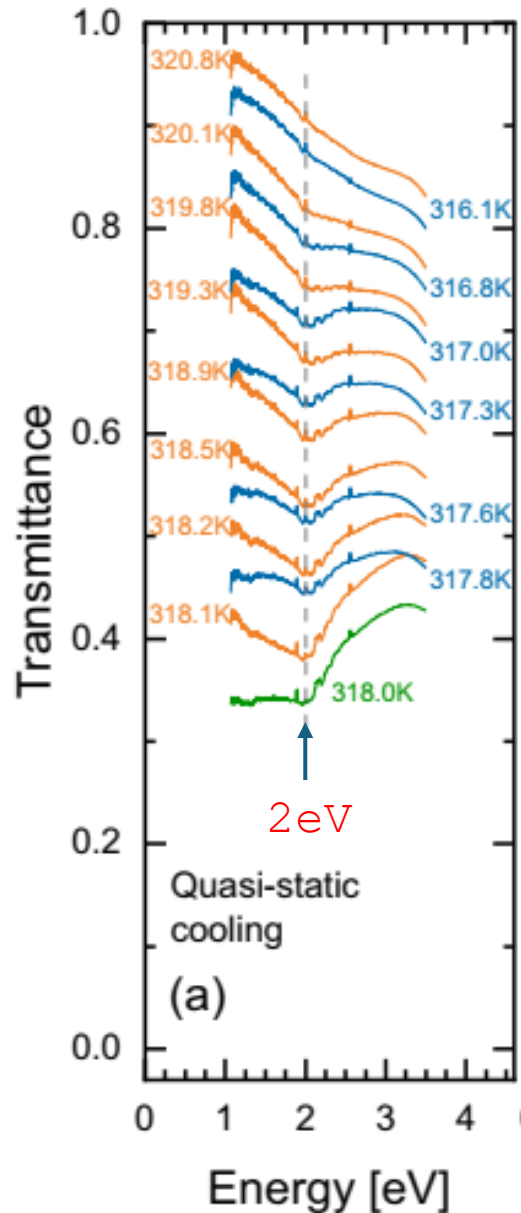
$d_{eh} = a_1$ \longleftrightarrow e^- and h^+ on the same molecule

$d_{eh} = a_2$ \longleftrightarrow e^- and h^+ on adjacent molecules



Excitons in near-critical SF_c

2 eV absorption dip



Is it a coincidence?

Excitons in liquids?

PHYSICAL REVIEW B

VOLUME 8, NUMBER 2

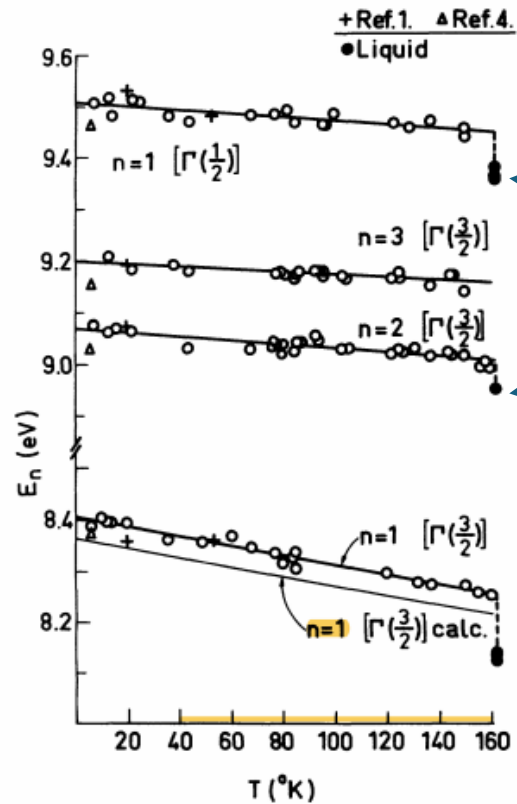
15 JULY 1973

Band-Structure Parameters of Solid and Liquid Xenon

I. T. Steinberger and U. Asaf

The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

Not the first case!



Exciton peaks survive above the melting temperature.

FIG. 2. Exciton peak positions in condensed xenon as a function of temperature.

Unanswered questions

- **What causes darkness (photon absorption&scattering in a wide spectral range) ?**
- **Why one needs rapid cooling ?**

A clue from metallurgy!

ACTA METALLURGICA, VOL. 9, SEPTEMBER 1961

ON SPINODAL DECOMPOSITION*

JOHN W. CAHN †

The stability of a solid solution to all infinitesimal composition fluctuations is considered, taking surface tension and elastic energy into account. It is found that for infinite isotropic solids, free from imperfections the spinodal marks the limit of metastability to such fluctuations only if there is no change in molar volume with composition. Otherwise the elastic energy due to a fluctuation stabilizes the solution and alters the criterion for the limit of metastability. For an unstable solution the kinetics of decomposition are discussed and the expected mean particle size or wavelength of the most rapidly growing fluctuation is derived.

Cahn-Hilliard equation: 'uphill' diffusion

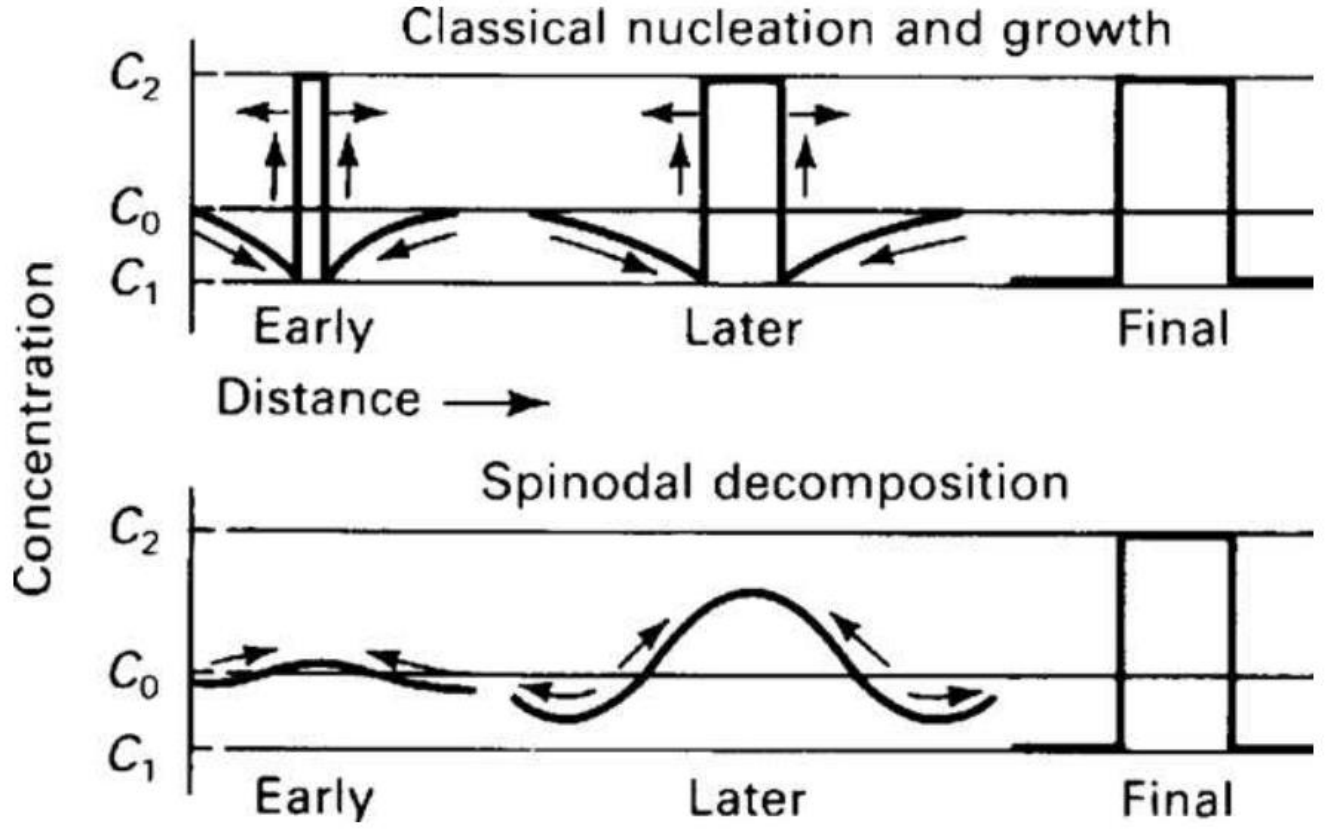
Start homogenous and finish inhomogeneous

Cahn-Hilliard equation

$$\frac{\partial \phi}{\partial t} = D \nabla^2 [-\phi + \phi^3 - \gamma \nabla^2 \phi]$$

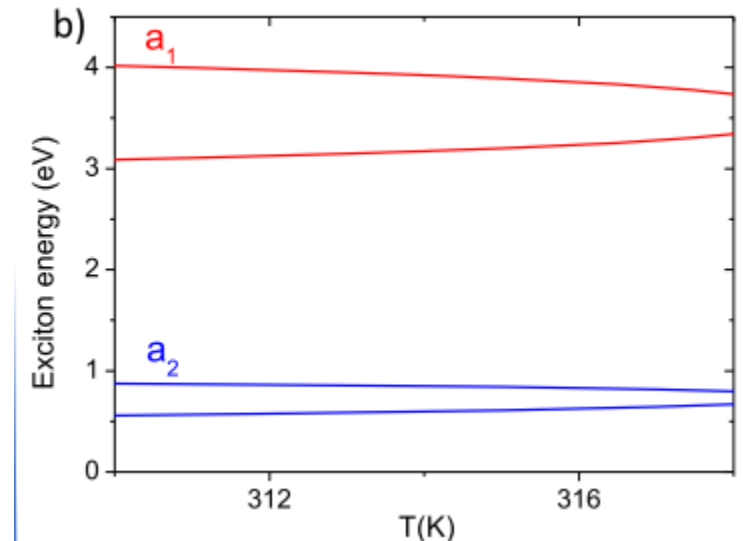
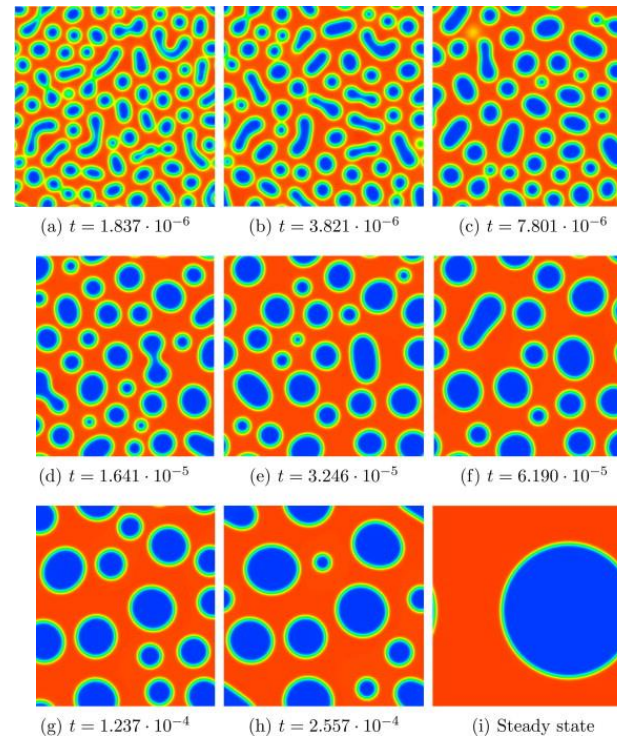
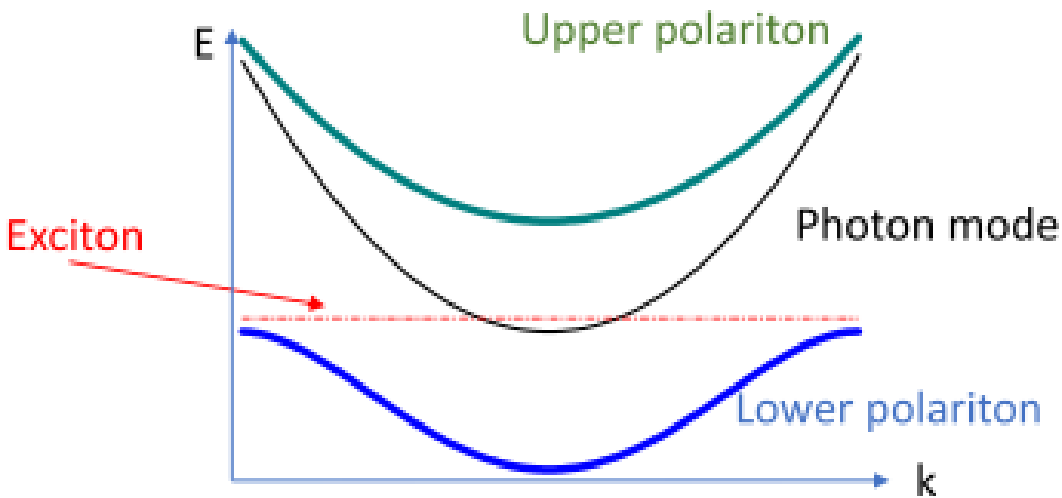
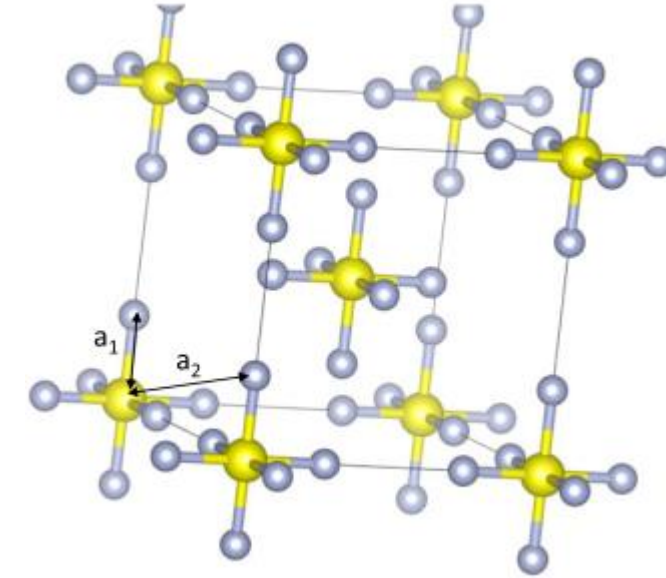
This parameter has the dimensions of a diffusion coefficient.

Periodic modulation of composition with a diffuse interface!



A challenge to numerical condensed matter

- Can the heterostructural fluid retain photons long enough to allow their hybridization with excitons?
- Can droplets/bubbles play the role of micro-cavities?



Collaborators



**Valentina
Martelli**

USP, Sao Paulo



**Ricardo
Lobo**

ESPCI Paris



**Amaury
Anquetil**

Now in Lille



**Lynn Al
Atic**

*Now in
Atlanta*



**Alaska
Subedi**

*Ecole
Polytechni
que
Palaiseau*



**Ilyas
Benjabbar**

ESPCI Paris



**Arthur
Marguerite**

ESPCI Paris

Summary

- Opalescence across the critical point depends on the cooling rate. During a quench, the fluid becomes black.
- A proper understanding of this experimental observation is missing.
- The binding energy for Frenkel excitons on SF₆ molecules is 2ev.
- Thermal quench triggers spinodal decomposition leading to a heterostructural fluid with diffuse gas-liquid interface.
- Is there boson-boson STIMULATION (think of **S** in **LASER**)?