

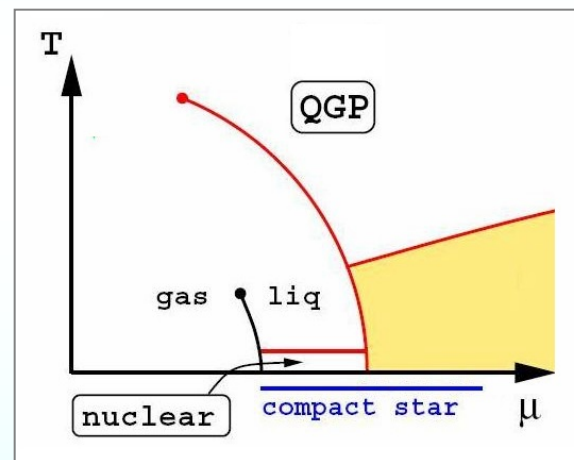
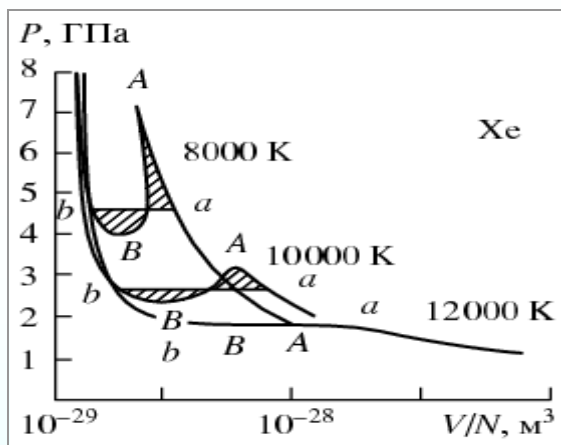


Helmholtz International Summer School
Nuclear Theory and Astrophysical Applications
 Dubna, Russia, July 2017



Enhalpic *and* Entropic Phase Transitions

& anomalous thermodynamics of high energy density matter



Igor Iosilevskiy

Joint Institute for High Temperature (Russian Academy of Science)
 Moscow Institute of Physics and Technology (State University)

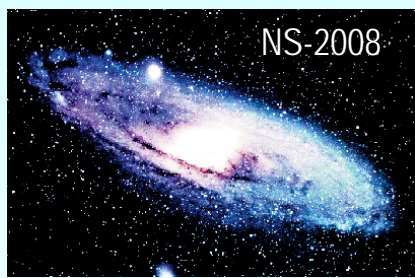
[arXiv:1005.4186v1](https://arxiv.org/abs/1005.4186v1)

[arXiv:1401.5481](https://arxiv.org/abs/1401.5481)

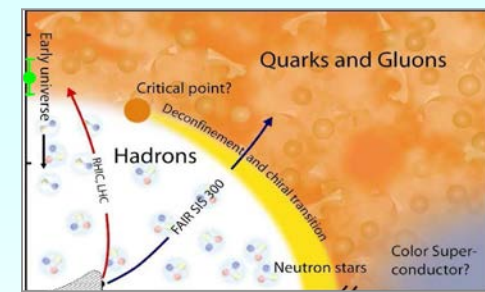


[arXiv:1504.0585](https://arxiv.org/abs/1504.0585)

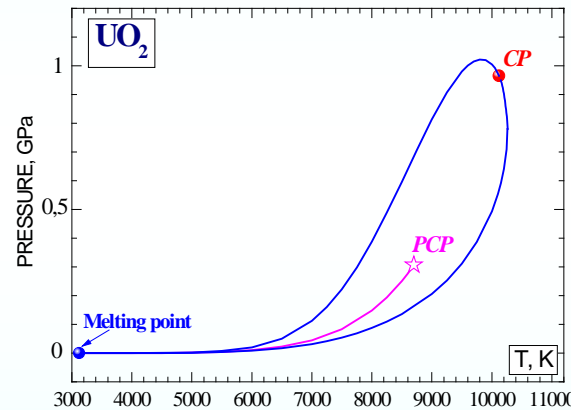




2008



Non-Congruent Phase Transitions in High Energy Density Matter



Igor Iosilevskiy

*Moscow Institute of Physics and Technology
(State University)*



Content *(PT – phase transition)*

- Motivation
 - Enthalpic and Entropic PTs. Terminology.
 - Historical comments
 - Entropic PT – what does it mean ?
 - Pressure delocalization of bound complexes – key driving mechanism.
 - Entropic PTs via 1st principle approaches
 - Anomalous thermodynamics within and nearby the boundaries of entropic phase transitions
- Illustrations: Entropic phase transitions in hydrogen and nitrogen plasmas
- Summary and outlook

The main point

Proposal:

Additional subdivision (*classification*) of all 1st-order phase transitions (PT) into two subclasses – **enthalpic** and **entropic** PTs

The term **enthalpic** PT – does not exist !

The term **entropic** PT – is used already for rather delicate structural PTs (*Daan Frenkel et al*)

NB!

I propose to use these terms in general context

Entropic Phase Transitions



Entropic Phase Separation in Polymer-Microemulsion Networks

A. Zilman, J. Kieffer, F. Molino, G. Porte, and S. A. Safran

Phys. Rev. Lett. **91**, (2003)

We study theoretically a model system of a transient network of **microemulsion droplets connected** by telechelic **polymers** and explain recent experimental findings. Despite the absence of any specific interactions between either the droplets or polymer chains, we predict that as the number of polymers per drop is increased, the system undergoes a first-order phase separation into a dense, highly connected phase, in equilibrium with dilute droplets, decorated by polymer loops. The phase transition is purely entropic and is driven by the interplay between the translational entropy of the drops and the configurational entropy of the polymer connections between them. Because it is dominated by entropic effects, the phase behavior of the system is extremely and is independent of the detailed properties of either polymers or drops.

Entropic Phase Transitions

?

Entropy-driven phase transitions in Hard-body systems

Daan Frenkel

Physica A, 263, (1999)

We study theoretically a model system of hard-body particles

$$F = U - TS$$

$$U \equiv 0$$

$$F = -TS$$

Freezing in the Hard-sphere system is *enthalpy-driven* transition !

$$G = H - TS$$

$$\Delta V < 0$$

$$\Delta H = -T\Delta S \leq 0$$

Journal of Modern Physics, 7 (2016)

Entropic and Enthalpic First-Order Phase Transitions in Strongly Interacting Matter

F. Wunderlich, R. Yaresko, B. Kämpfer

Helmholtz-Zentrum, Institut für Strahlenphysik, Dresden, Germany

Institut für Theoretische Physik, TU Dresden, Germany

Published 29 April 2016

FAIR, NICA, LHC...

Physical Review D, 94 (2016)

A Hot Third Family of Compact Stars and the Possibility of Core-collapse Supernova Explosions

**Hempel M., Heinemann O., Yudin A., Iosilevskiy I., Liebendoerfer M.,
Thielemann F-K.,**

Basel University, Switzerland; Joint Institute for High Temperature, Russia;

Institute for Experimental and Theoretical Physics, Russia

Published, December 2016

Astrophysics

Motivation - I

The wide world *of* phase transitions
in high energy density matter

**There are many phase transitions
which differ significantly from
the well-known gas-liquid PT of VdW-type**

What should we classify when we meet unexplored phase transition -?

1st *or* 2nd order ?

Isostructural *or* non-isostructural ?

Congruent *or* non-congruent ?

Enthalpic *or* entropic ?

Do we use **Coulomb-less approximation** *or* we take into account all consequences *of* long-range nature *of* **Coulomb** interaction ?

Scenario *of* phase transformation *in* two-phase region –
– Macro- *or* Mesoscopic ?

Phase transitions *in* high energy density matter

Enthalpic *vs* Entropic
?

The main subject of our interest

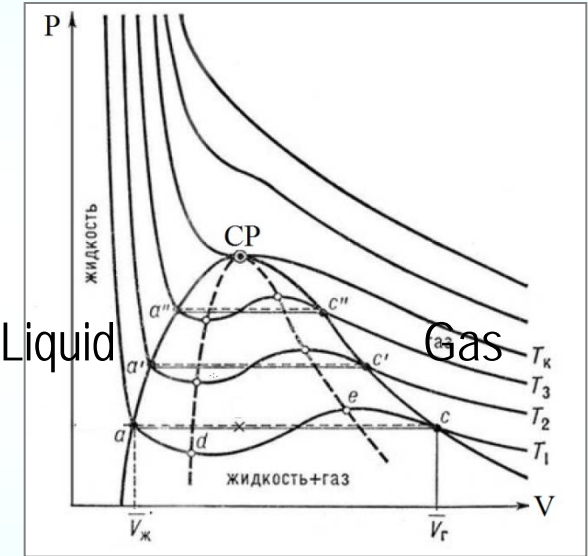
Isostructural 1st-order entropic
fluid-fluid phase transitions

Entropic iso-structural phase transitions with critical point

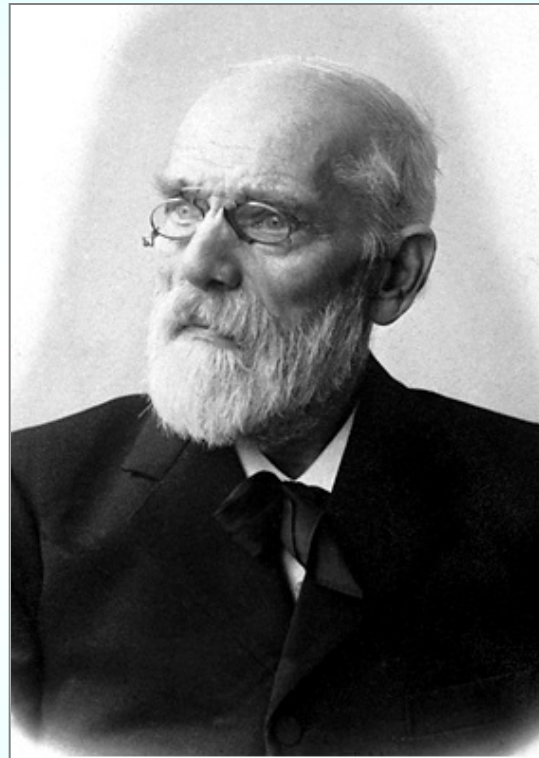
Historical comments

Van der Waals model of gas-liquid phase transition

$$(P + a\rho^2)(1 - \rho b) = \rho T,$$

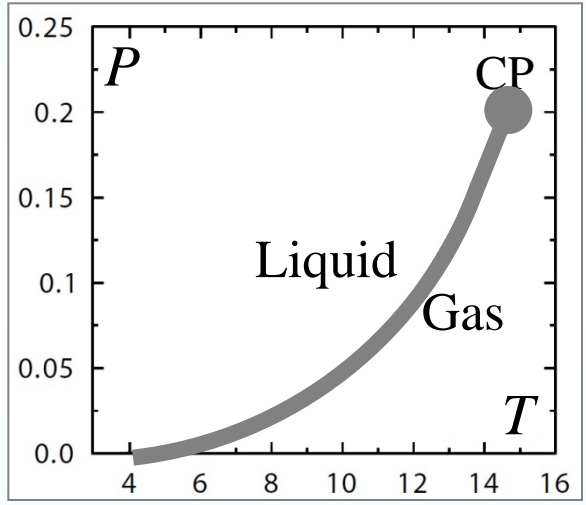


Two-phase region
 Binodals, Spinodals
 Critical Point
 VdW-loops at iso-T
 Two metastable zones
 Unstable state region
 Etc



Ян Дидерик Ван-дер-Ваальс

Johannes D. Van der Waals
 (1837 – 1923)
On the Continuity of the Gaseous and Liquid States,
 Ph.D. Diss. Leiden, **1873**

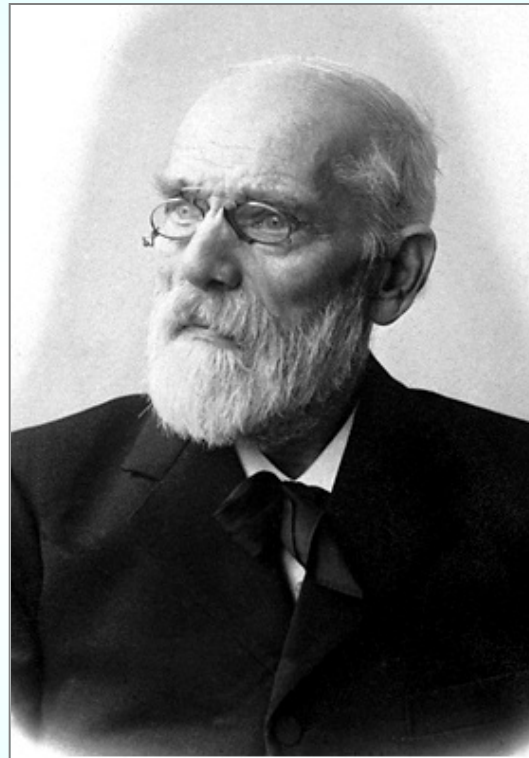
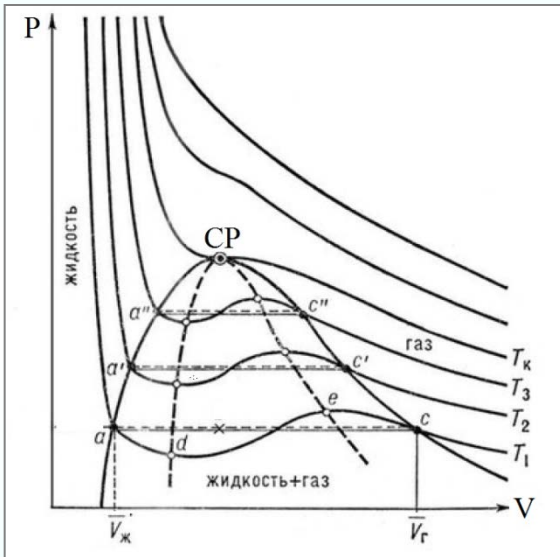


Saturation Curve . . .

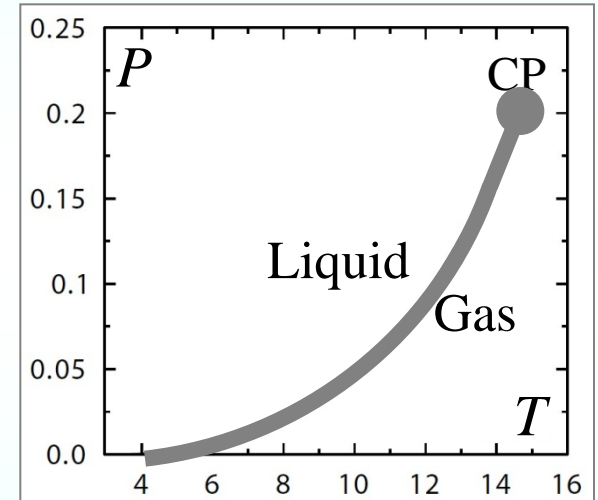
144 years

VdW - typical "enthalpic" phase transition !

$$(P + a\rho^2)(1 - \rho b) = \rho T,$$



Ян Дидерик Ван-дер-Ваальс



Johannes D. Van der Waals

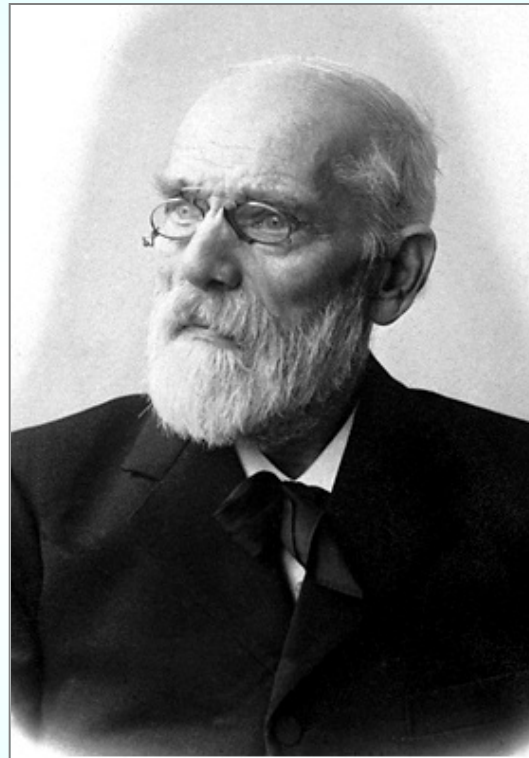
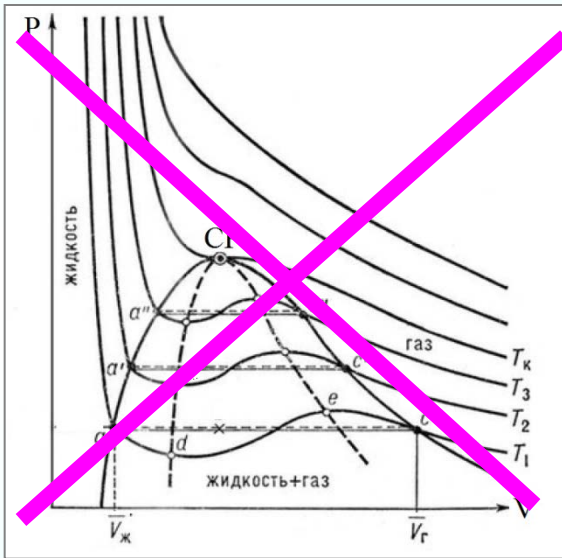
(1837 – 1923)

On the Continuity of the Gaseous and Liquid States,

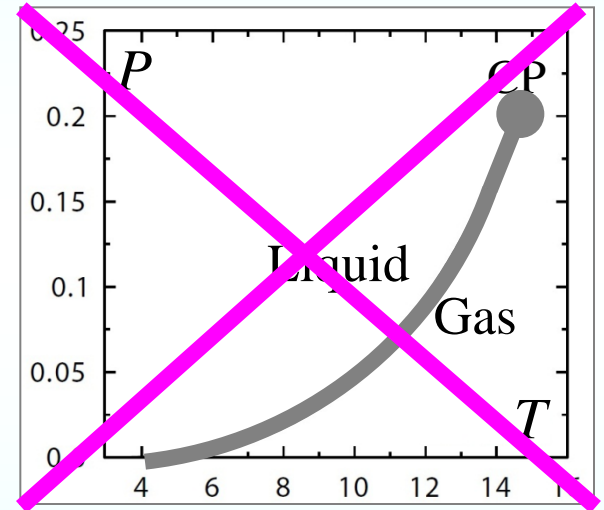
Ph.D. Diss. Leiden, 1873

And what about typical "entropic" phase transition ?

$$(P + a\rho^2)(1 - \rho b) = \rho T,$$



Ян Дидерик Ван-дер-Ваальс



- Two-phase region* - **diff.**
- Binodals, Spinodals* - **diff.**
- Critical Point* - **diff.**
- VdW-loops at iso-T* - **diff.**
- ~~*Two metastable zones* - **diff.**~~
- Unstable state region* - **diff.**
- Etc*

Debye – Hückel non-ideality correction

The simplest model of Coulomb nonideality (DHLL)

Debye and Hückel, *Phys. Zeitschr.*, 24, 8, 1923.



Peter Debye



Erich Hückel

(1923)

94 years

$$\frac{P}{nkT} = 1 - \frac{\Gamma_D}{6} + \dots$$

NB!

$$\Gamma_D = 4$$

$$\left(\frac{\partial P}{\partial V} \right)_T = 0$$

$$\Gamma_D > 6$$

\Leftrightarrow

$$P < 0 !$$

$$\Gamma_D \equiv Z^2 e^2 / k T r_D$$

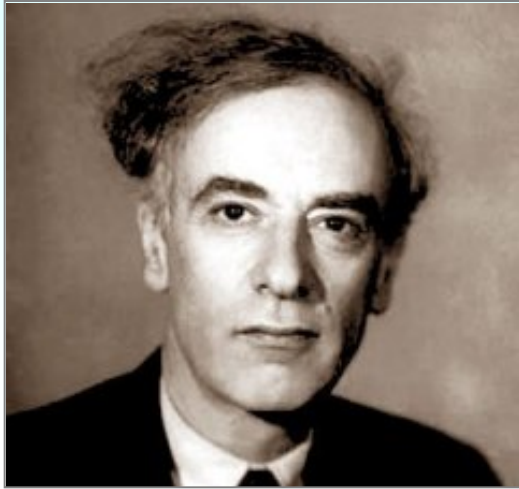
Phase transitions *in* high energy density matter

Ionization-driven (“*plasma*”) phase transition

is it Enthalpic *or* Entropic

?

Hypothetical 1st order phase transition “insulator-conductor” *in* metals



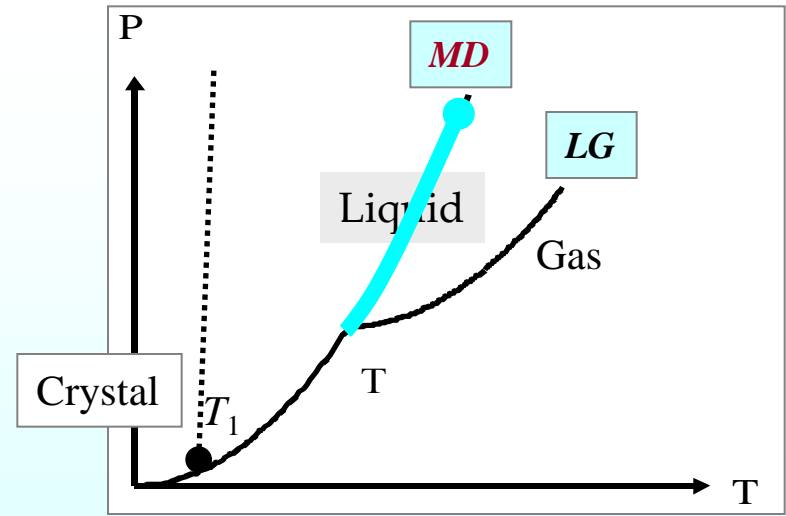
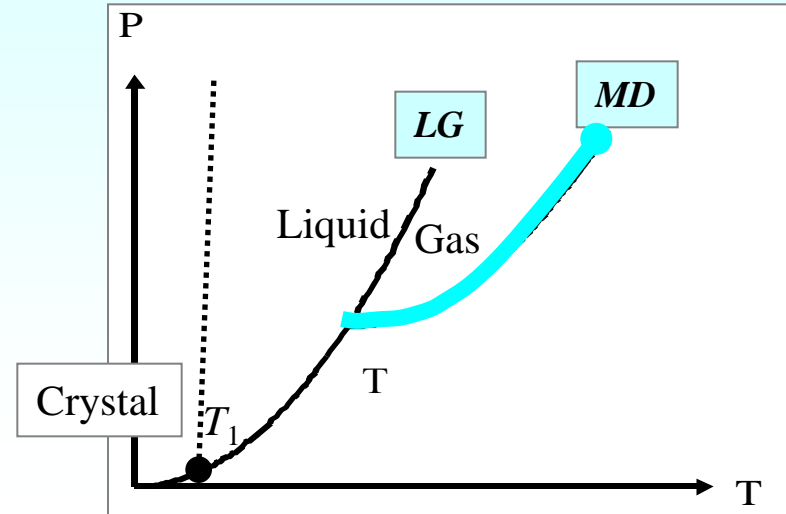
Lev Landau

(1943)



Yakov Zeldovich

74 years



Landau L.D., Zeldovich Ya.B., *Acta Physico-Chimica URSS*, 18, (1943)
On the relation between the liquid and the gaseous states of metals

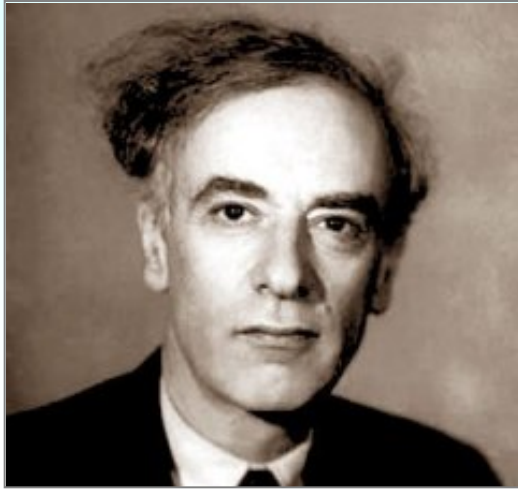
Phase transitions *in* high energy density matter

**“Pressure ionization”-driven phase transition
in compressed metal vapors**

- is it Enthalpic *or* Entropic

?

Hypothetical 1st order phase transition “insulator-conductor” *in* metals

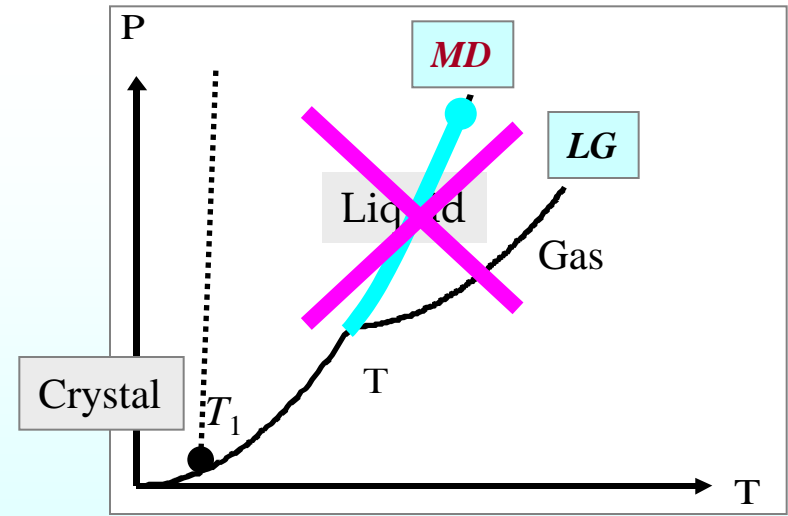
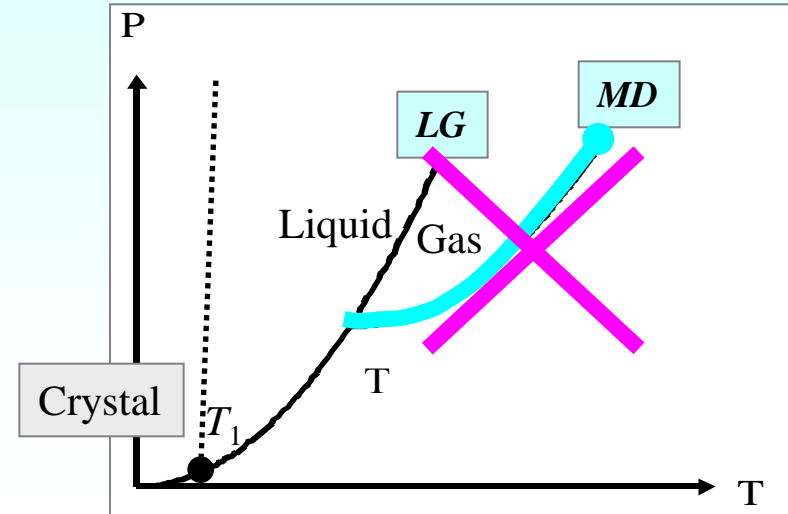


Lev Landau



Yakov Zeldovich

(1943)



Landau L.D., Zeldovich Ya.B., *Acta Physico-Chimica URSS*, 18, (1943)
On the relation between the liquid and the gaseous states of metals

"Plasma" phase transitions theory

(Coulomb attraction + quantum repulsion)

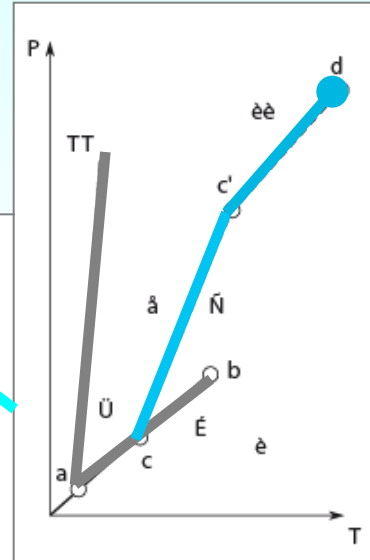
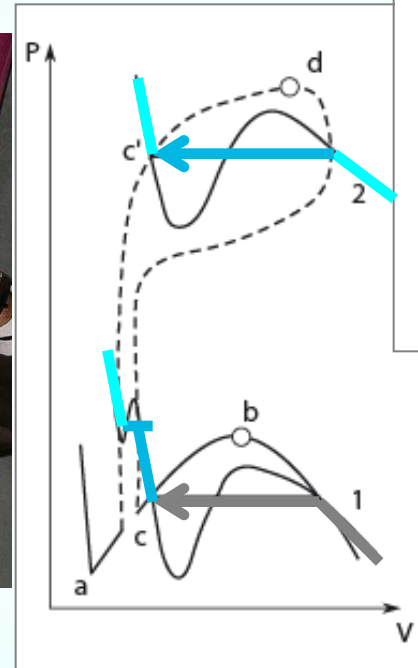
(1968-1970)



Andrew Starostin



Henry Norman



~ 50 years

Norman H., Starostin A. *High Temperature*, 6, (1968)
Plasma phase transitions

See also: Ebeling W., Kraeft W.D., Kremp D. *Theory of Bound States and Ionization Equilibrium in Plasmas*
(Akademic-Verlag, Berlin, 1976 / МИР, Москва, 1979)

Phase transitions *in* high energy density matter

Ionization-driven (“*plasma*”) phase transition

is it Enthalpic *or* Entropic

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"Plasma" phase transitions theory

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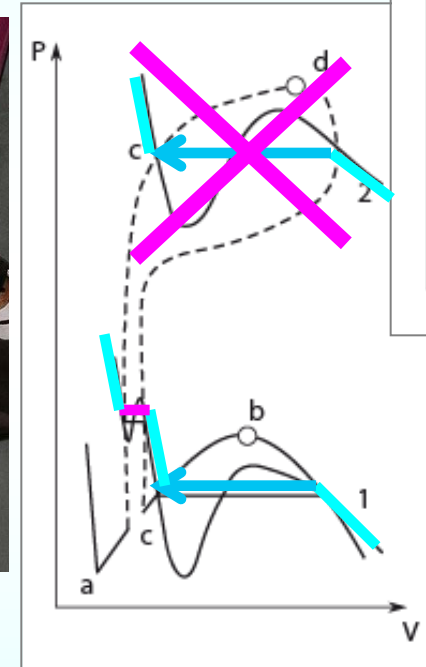
(1968-1970)



Andrew Starostin



Henry Norman



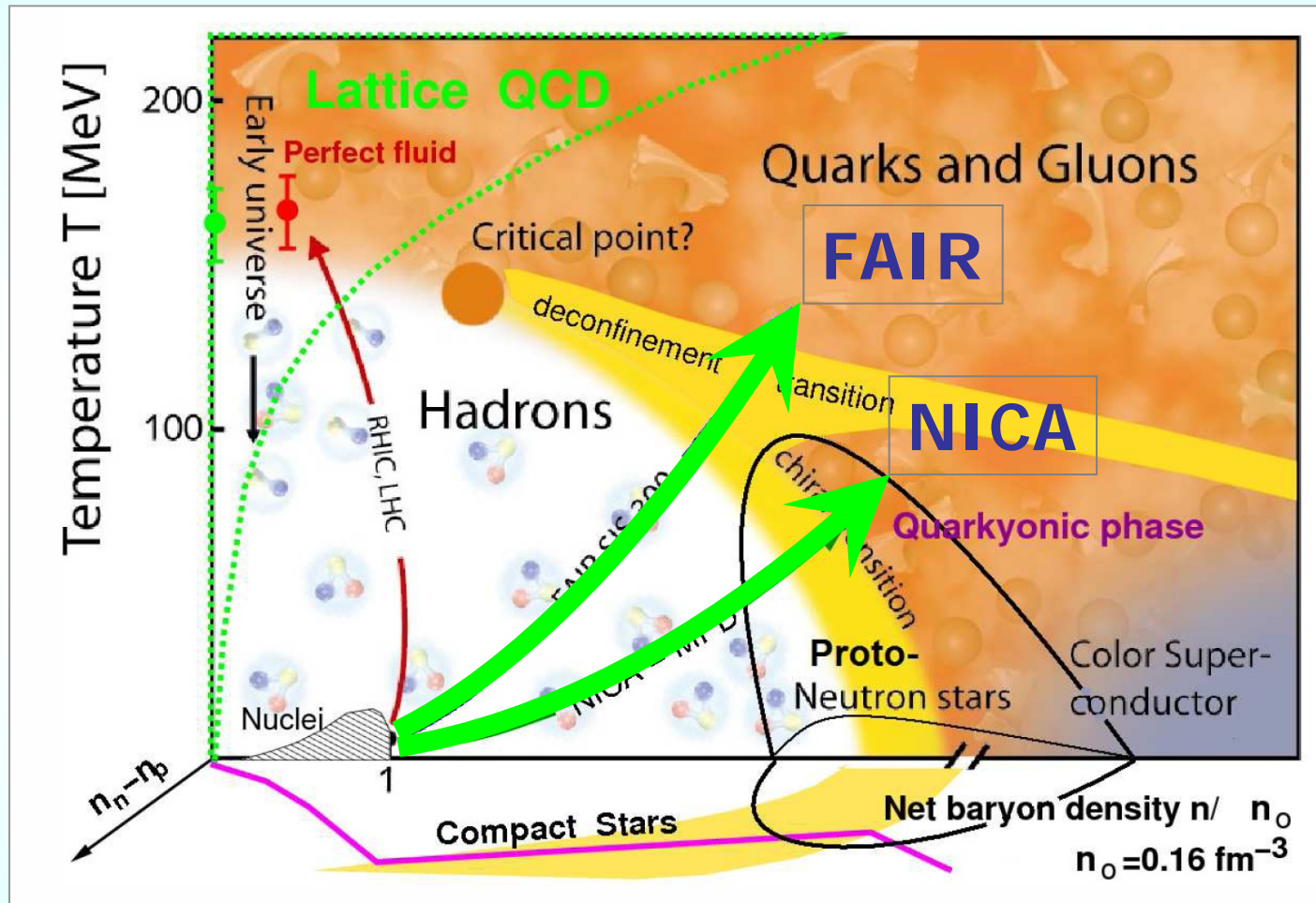
Norman H., Starostin A. *High Temperature*, 6, (1968)
Plasma phase transitions

See also: Ebeling W., Kraeft W.D., Kremp D. *Theory of Bound States and Ionization Equilibrium in Plasmas*
(Akademic-Verlag, Berlin, 1976 / МИР, Москва, 1979)

Motivation - II

Motivation

Phase diagram of matter *in* ultra-high energy *and* density

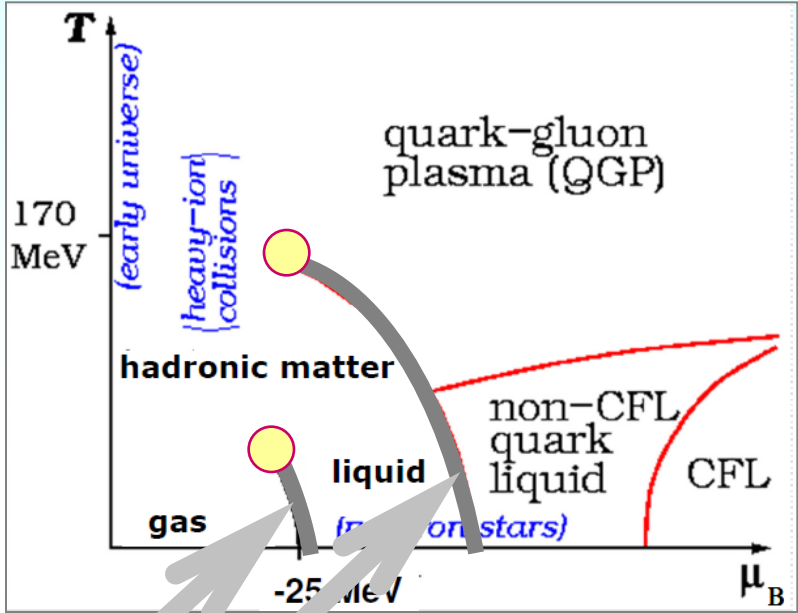
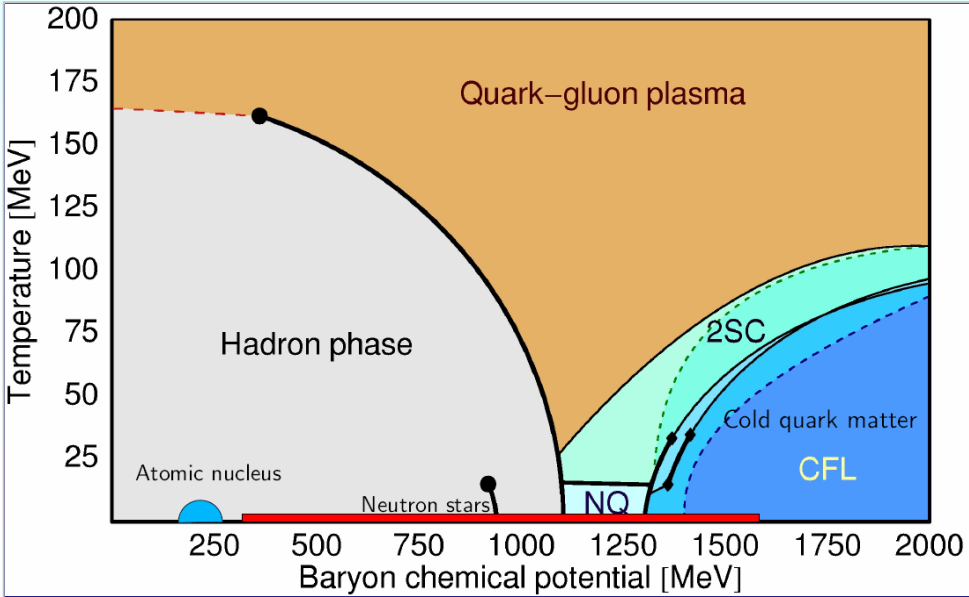


NICA White Book

After David Blaschke, NICA Workshop, Dubna, 2009

Phase diagram of matter in ultra-high energy and density

(schematic)



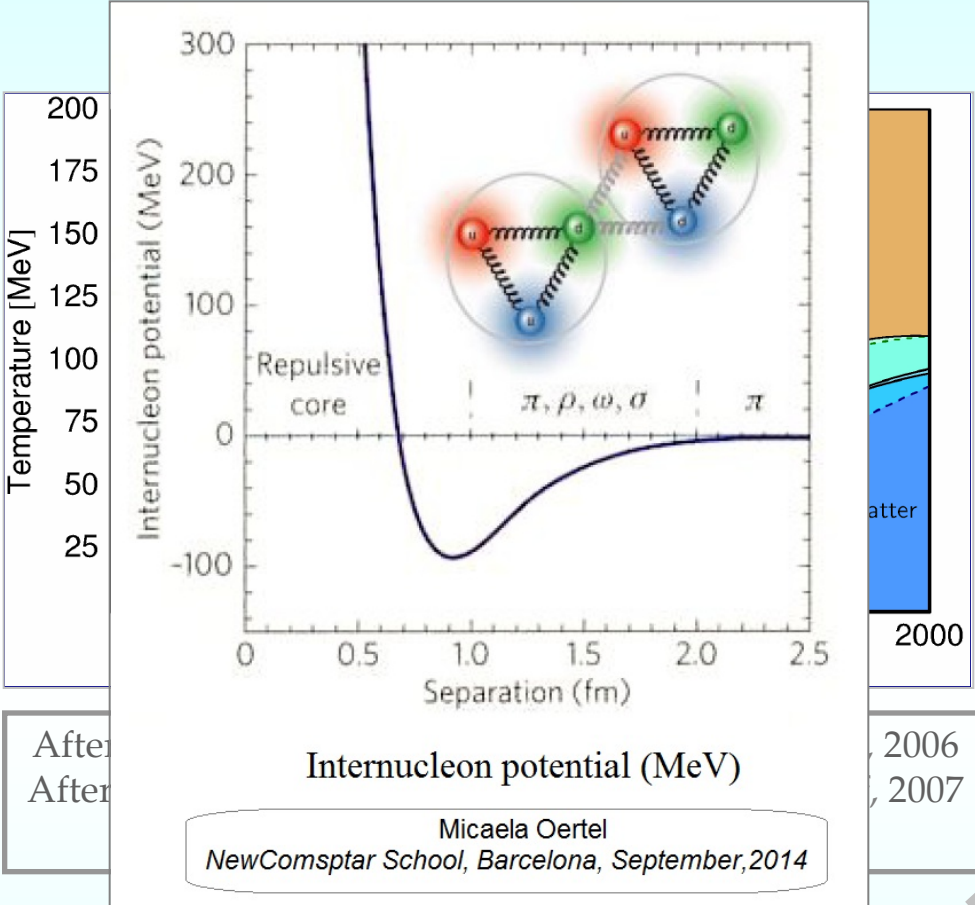
After Fridolin Weber, WEHS Seminar, Bad Honnef, 2006
 After David Blaschke, WEHS Seminar, Bad Honnef, 2007

Source: WIKIPEDIA

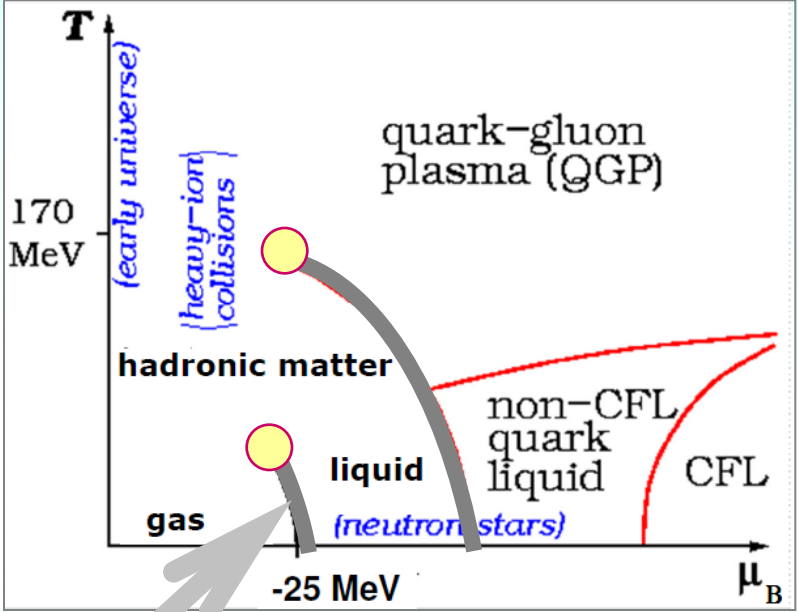
“Gas-liquid” phase transition in Coulombless system $\{p, n, N(A, Z)\}$
 / GLPT /

Quark-Hadron phase transition
 / QHPT /

Phase diagram of matter in ultra-high energy and density



(schematic)



Source: WIKIPEDIA

“Gas-liquid” phase transition in Coulombless system $\{p, n, N(A, Z)\}$
/ GLPT /

Quark-Hadron phase transition
/ QHPT /

Direct numerical simulation in simplified model

Horowitz C., Pérez-García M.A., et al. *Phys. Rev. C*, **69**, (2004)

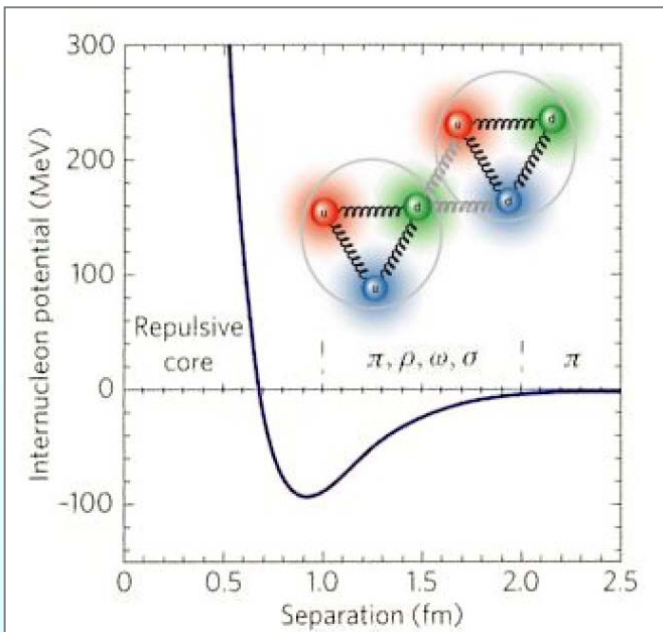
$$V_{tot} = \sum_{i < j} V(i, j) ,$$

$$V(i, j) = ae^{-r_{ij}^2/\Lambda} + \left[b + c\tau_z(i)\tau_z(j) \right] e^{-r_{ij}^2/2\Lambda} + V_c(i, j)$$

$\tau_z(j) = 1$ - protons

$\tau_z(j) = -1$ - neutrons

V_c - Coulomb



"Pasta"

Direct numerical simulation in simplified model

Horowitz C., Pérez-García M.A., et al. *Phys. Rev. C*, **69**, (2004)

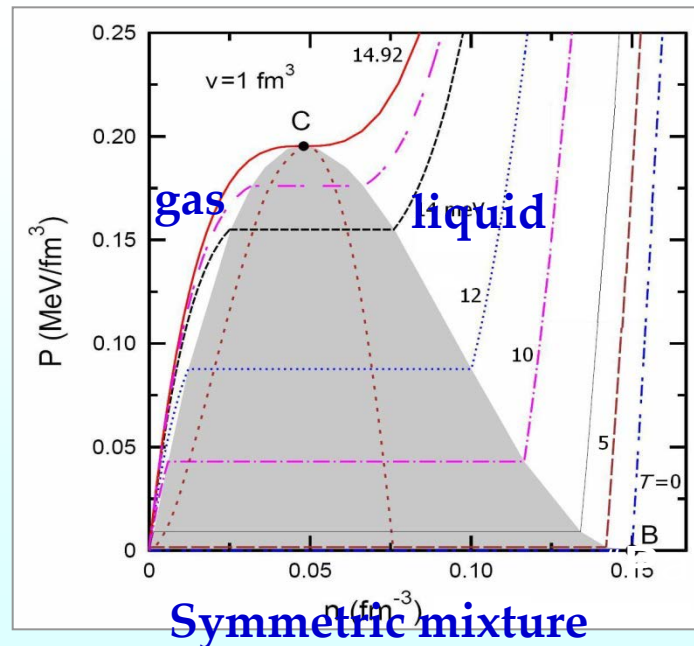
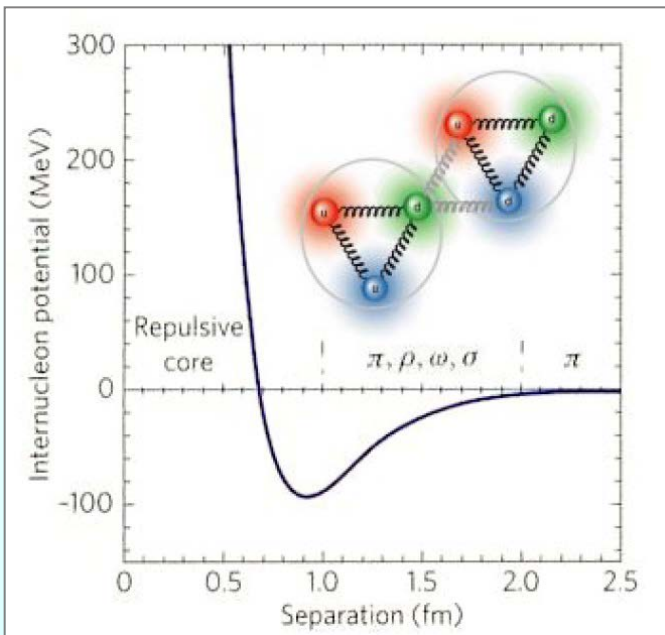
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$\tau_z(j) = 1$ - protons

$\tau_z(j) = -1$ - neutrons

V_c



Asymmetric mix.



Non-congruent phase transition

Symmetric mixture

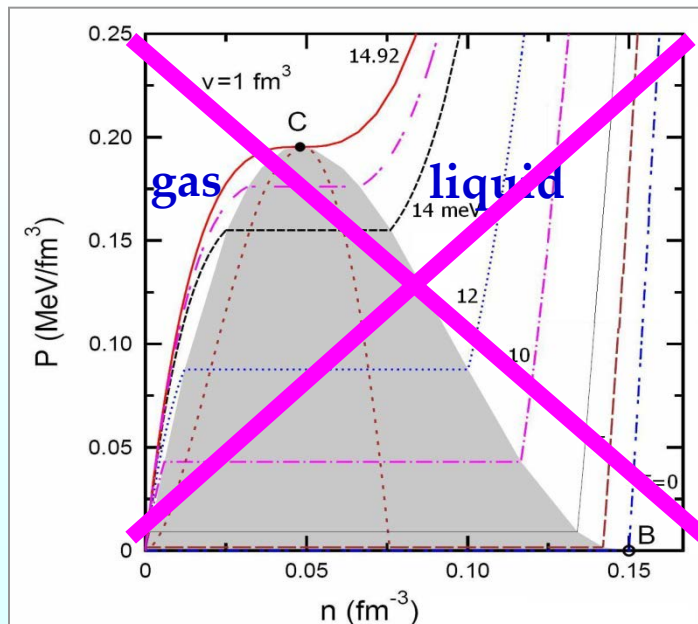
Direct numerical simulation in simplified model

Horowitz C., Pérez-García M.A., et al. *Phys. Rev. C*, **69**, (2004)

$$V_{tot} = \sum_{i < j} V(i, j) ,$$

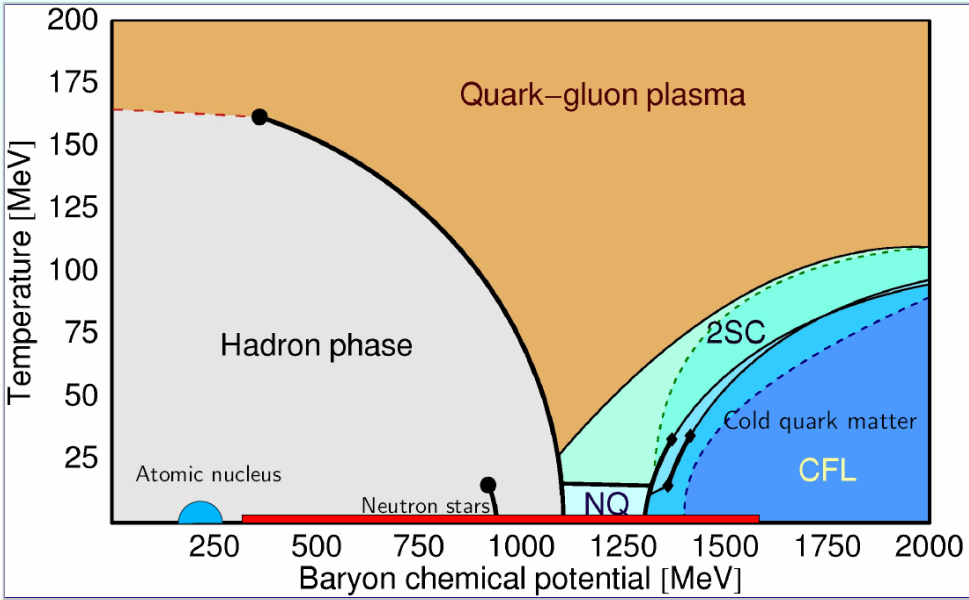
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$\tau_z(j) = 1$ - protons $\tau_z(j) = -1$ - neutrons V_c - Coulomb



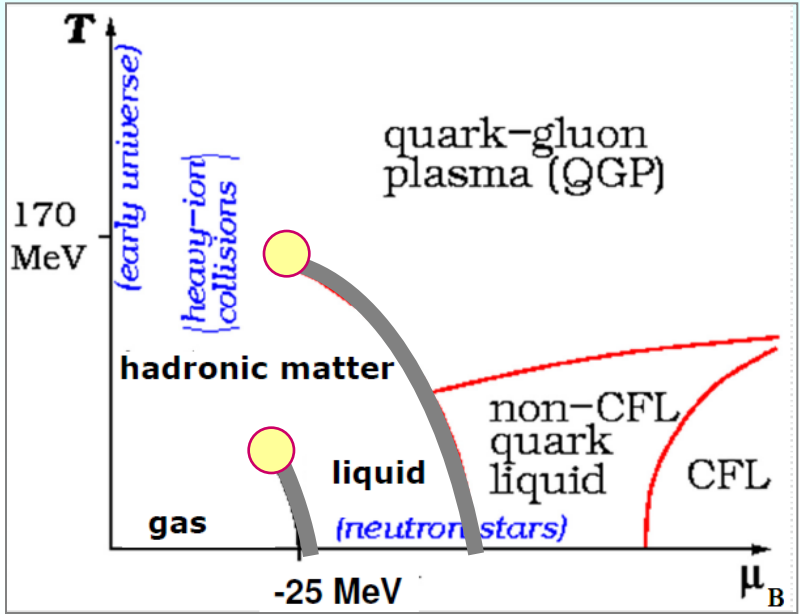
Mesosopic scenario

Phase diagram of matter in ultra-high energy and density



After David Blaschke, WEHS Seminar, Bad Honnef, 2007

(schematic)



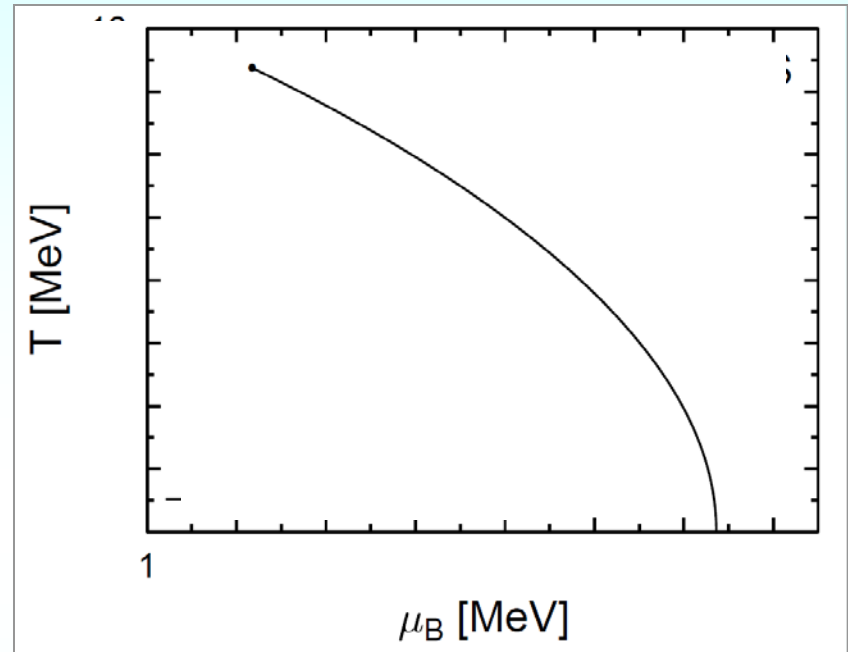
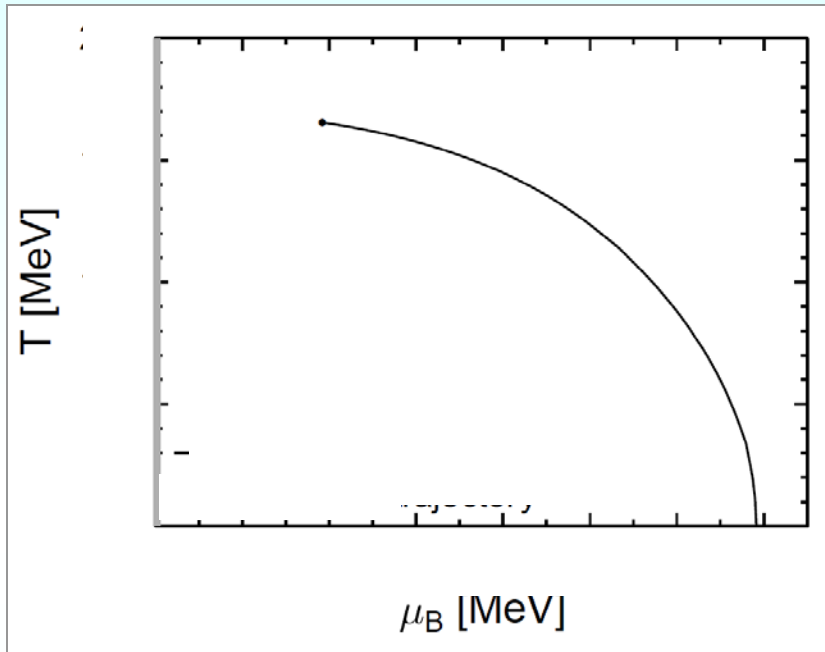
Source: WIKIPEDIA

“Gas-liquid” phase transition in Coulombless system $\{p, n, N(A, Z)\}$
 / GLPT /

Quark-Hadron phase transition
 / QHPT /

T - μ phase diagram *for* symmetric GLPT *and* QHPT

Coulombless approximation



Non-congruence of the nuclear liquid-gas and the deconfinement phase transitions

Matthias Hempel, Veronica Dexheimer, Stefan Schramm, Igor Iosilevskiy
(*Phys. Rev. C*, **88**, 2013)

[arXiv:1504.058050](https://arxiv.org/abs/1504.058050)

NB!

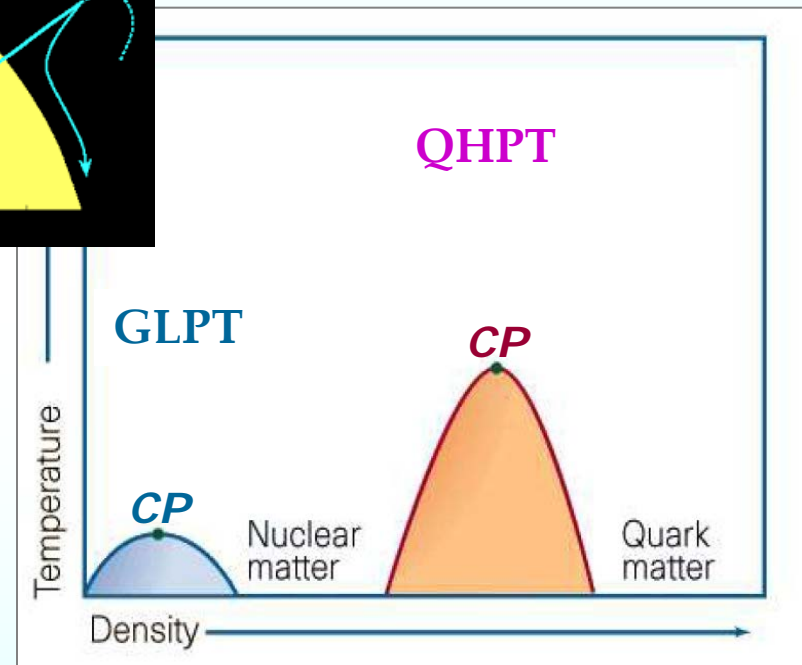
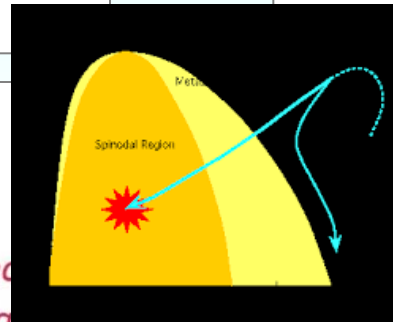
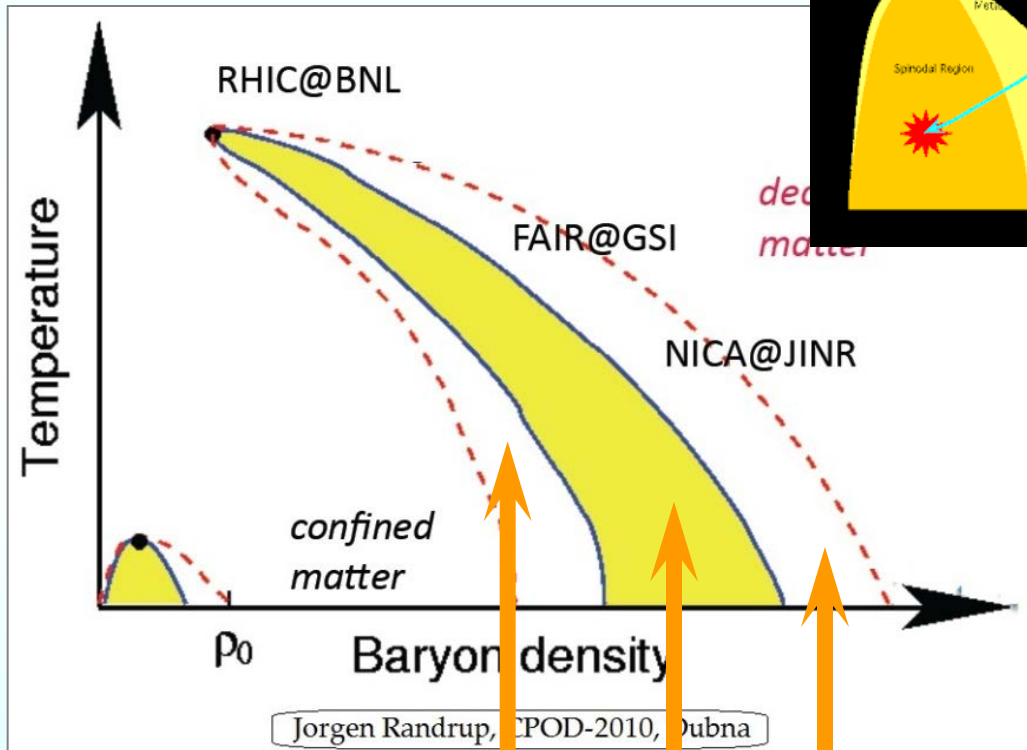
One could not distinguish GLPT vs. QHPT in T - μ plane

Gas-liquid *and* Quark-hadron phase transitions are often considered as similar

Jorgen Randrup

“Critical Point and Onset of Deconfinement”
Dubna, Russia, 2009

“Critical Point and Onset of Deconfinement”
Napa, USA, 2013



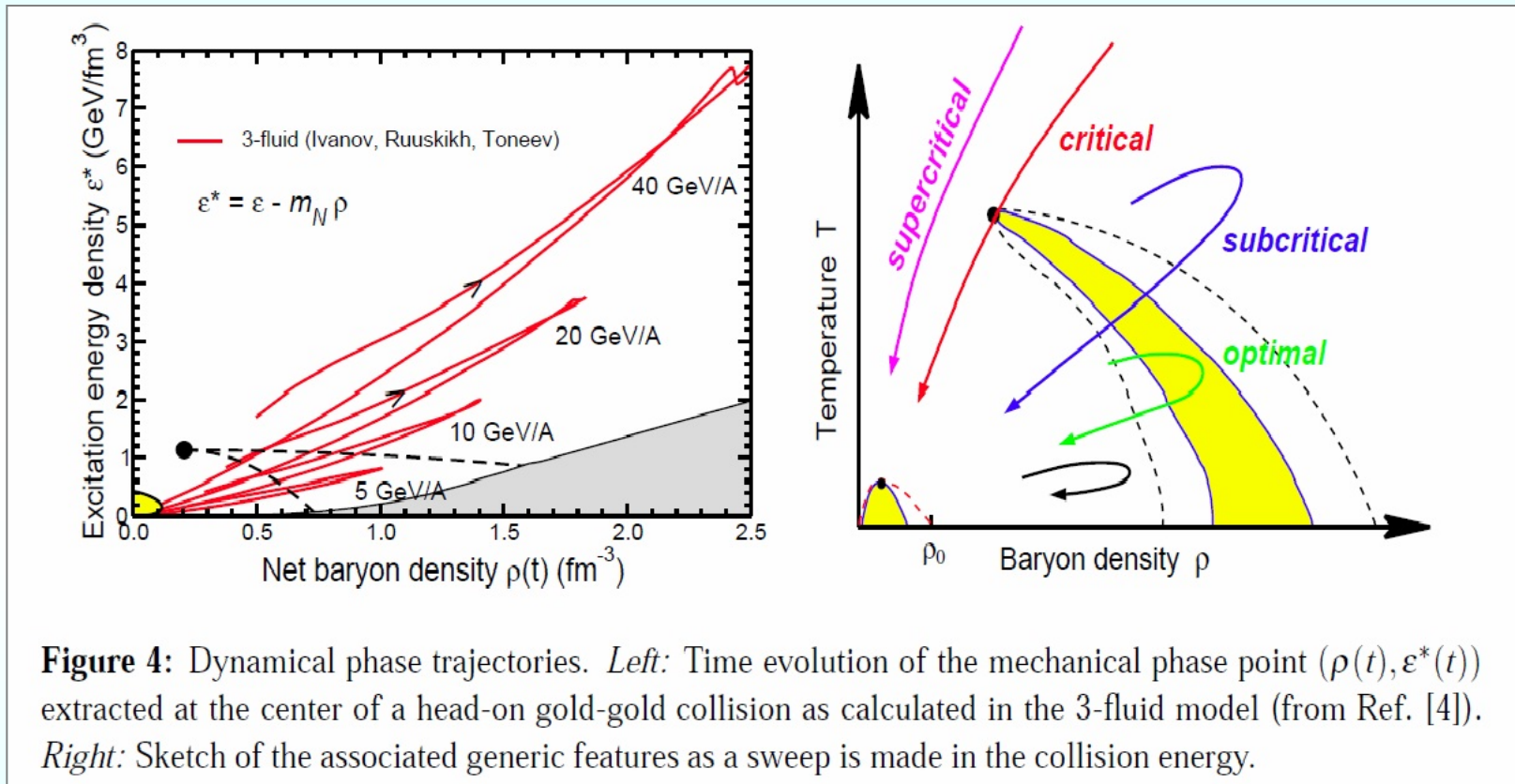
J. Steinheimer & J. Randrup, CPOD-2013

Metastable

Spinodal region

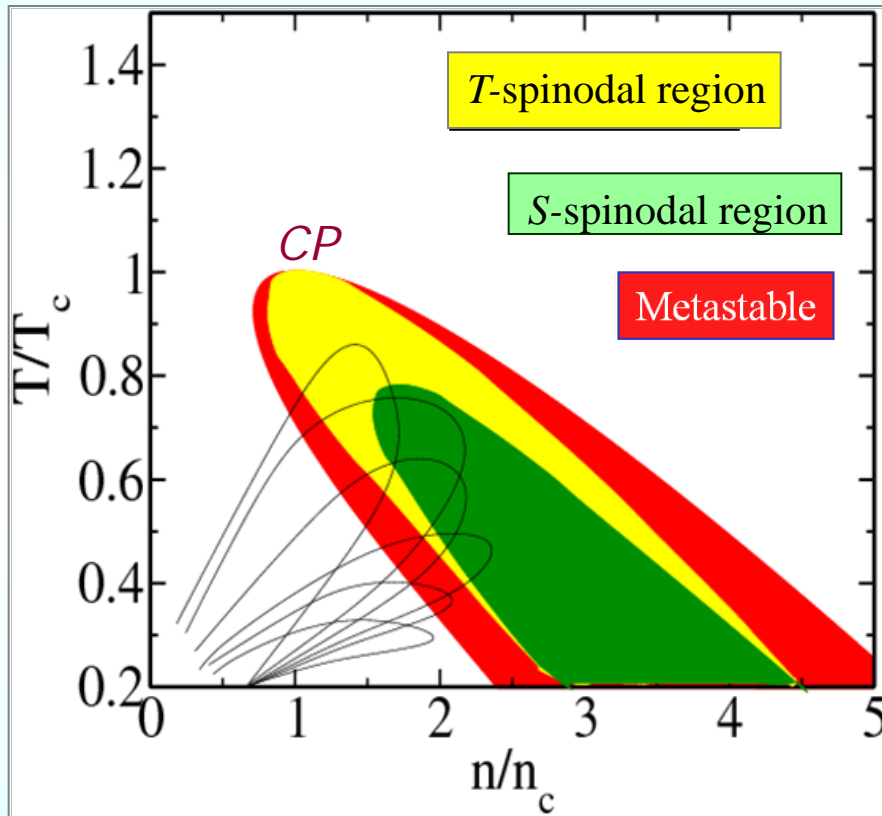
Metastable

Jorgen Randrup



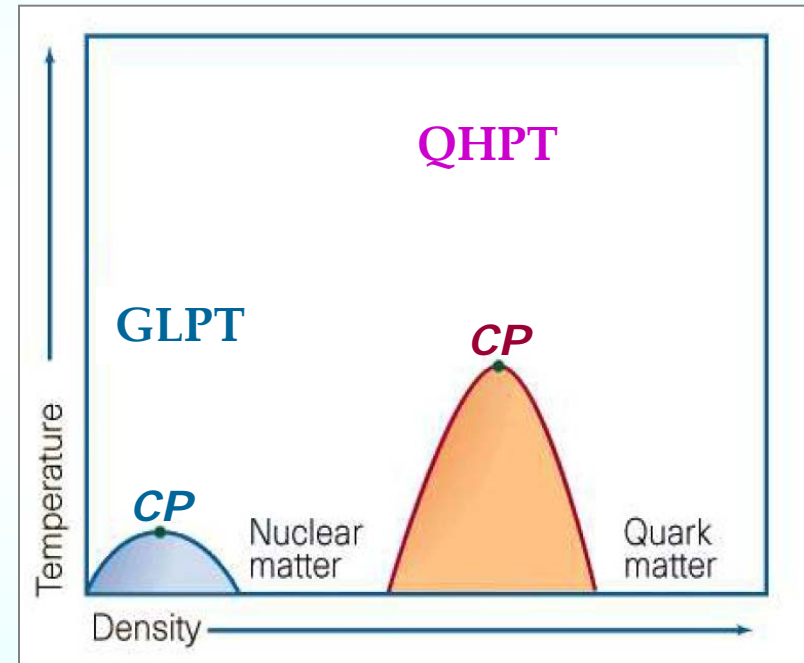
Dubna, Russia, 2009

Dense QCD Phases in Heavy Ion Collisions and Supernovae,
11 October, 2009



Vladimir Skokov (GSI, Darmstadt)

Jan Steinheimer & J. Randrup, *CPOD-2013*

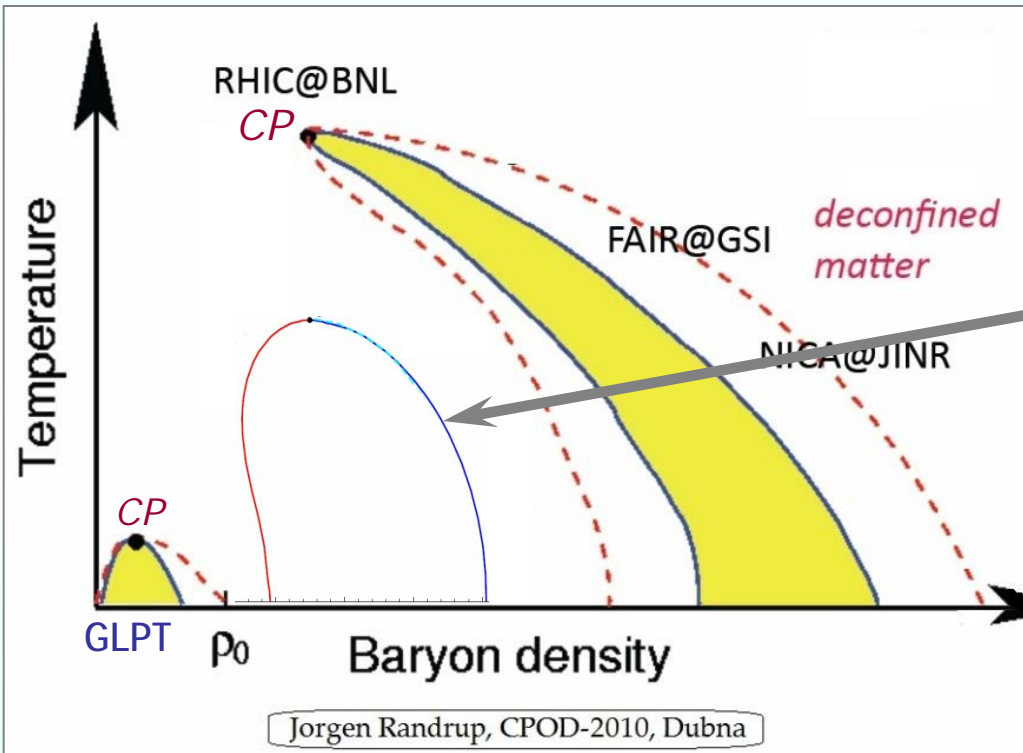


QHPT is expected naturally as a little bit bending VdW-like PT

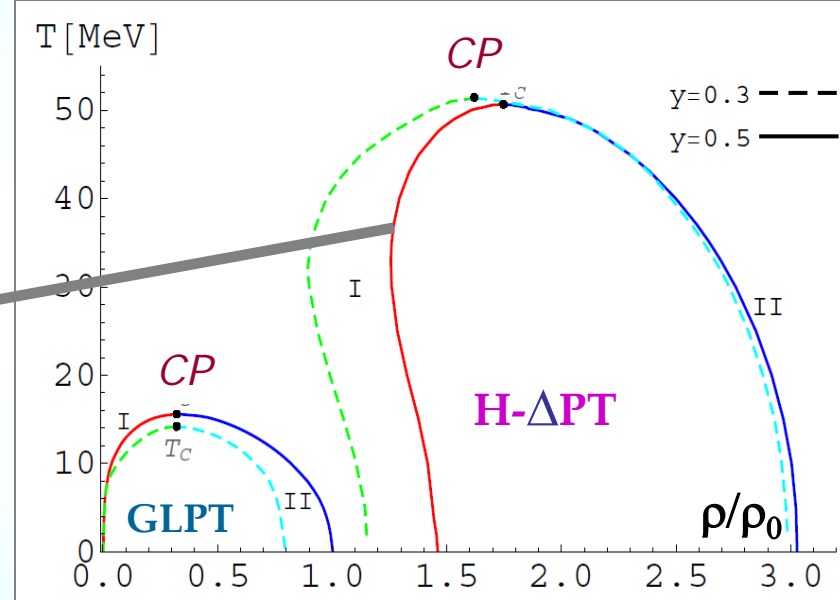
Gas-liquid, Hadron- Δ -meson and Quark-hadron phase transitions are often considered as similar

Prerow 2009

“Critical Point and Onset of Deconfinement”
Dubna, Russia, 2009



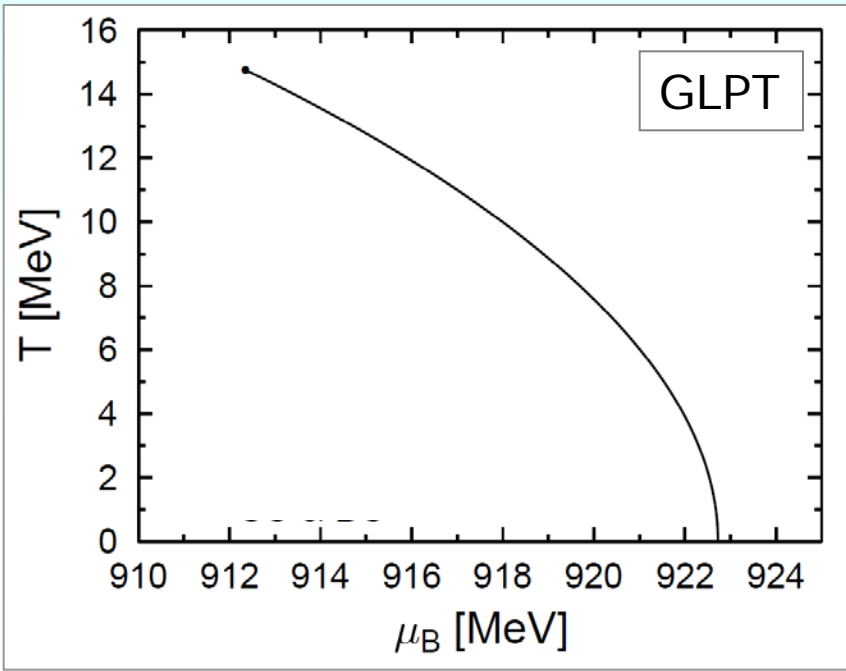
Phase diagram of the liquid-gas and the nucleon- Δ matter phase transition



Lavagno A., Drago A., Pagliara G., Pigato D.
J. of Phys. **527** (2014)
**Thermodynamic instability in nuclear matter
and in compact stars**

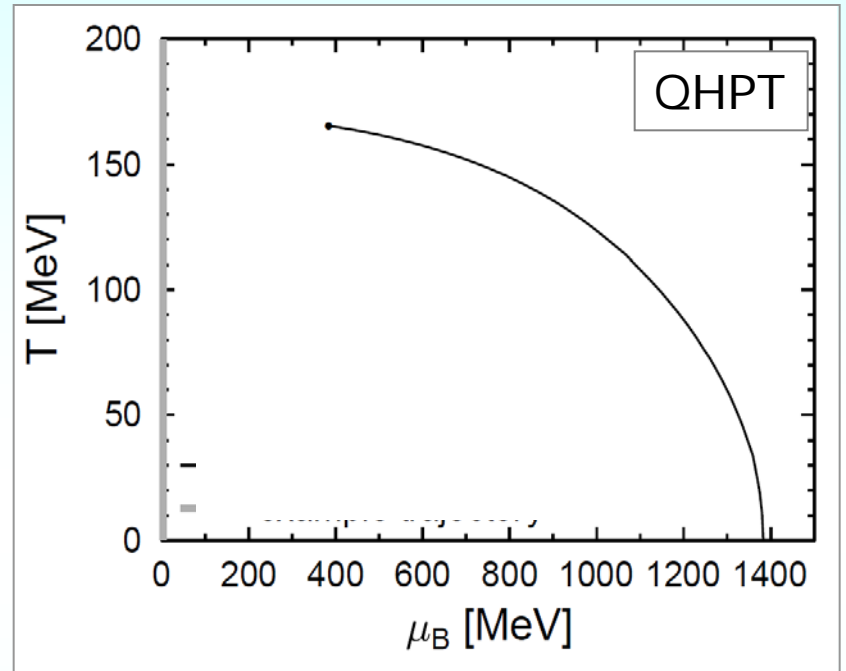
What type of this new phase transition: - enthalpic or entropic ?

GLPT *and* QHPT look *like* equivalent in $T-\mu$ phase diagram
(*symmetric case*)



FSUGold (Matthias Hempel (*))

Gas-liquid PT $\{p, n, N(A, Z)\}$



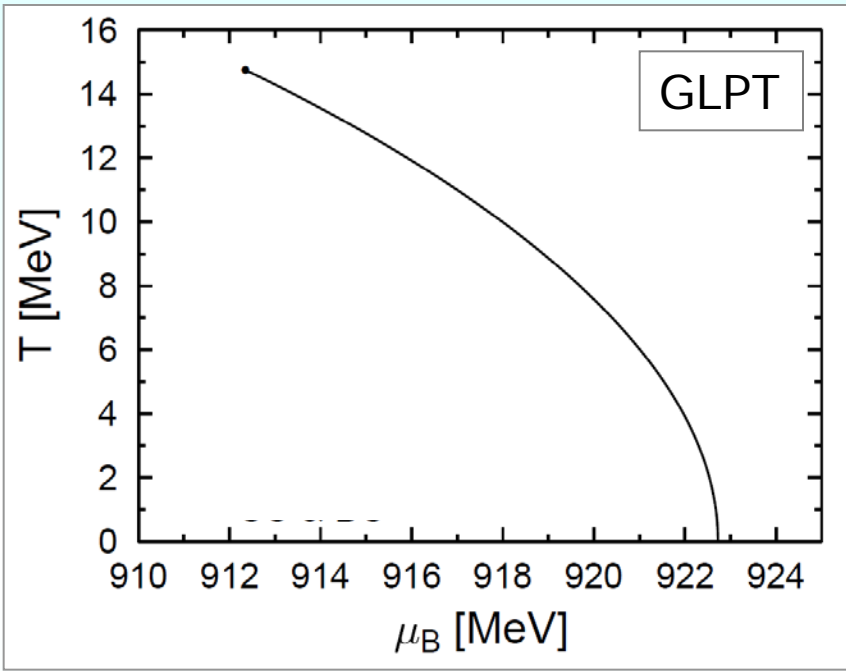
SU(3) model (V. Dexheimer & S. Schramm (*))

Quark-hadron PT



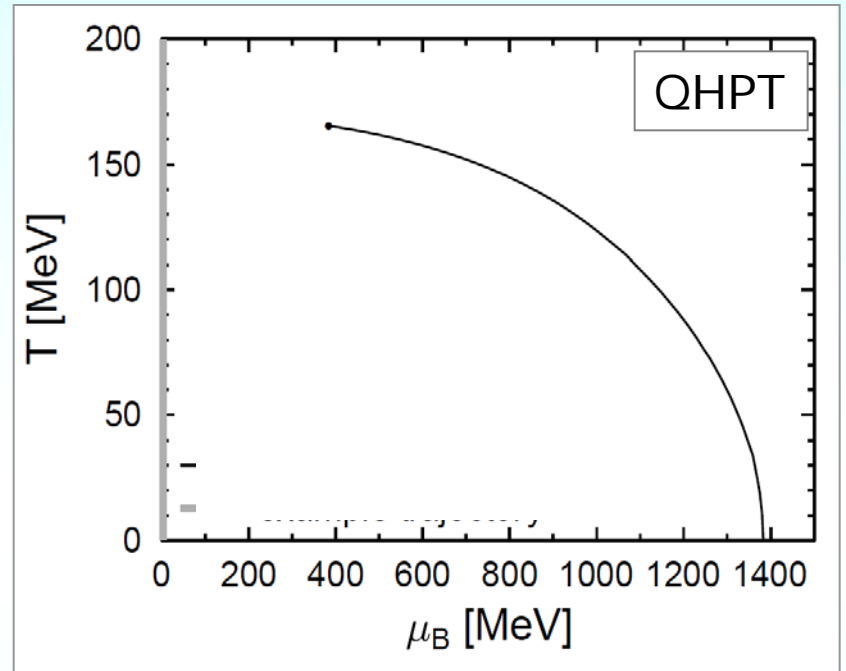
(*) M. Hempel, V. Dexheimer, S. Schramm *and* I. Iosilevskiy // (*Phys. Rev. C* **88**, (2013))

GLPT *and* QHPT look *like* equivalent in $T-\mu$ phase diagram
(symmetric case)



FSUGold (Matthias Hempel (*))

Gas-liquid PT $\{p, n, N(A, Z)\}$



SU(3) model (V. Dexheimer & S. Schramm (*))

Quark-hadron PT



(*) M. Hempel, V. Dexheimer, S. Schramm *and* I. Iosilevskiy // (Phys. Rev. C 88, (2013))

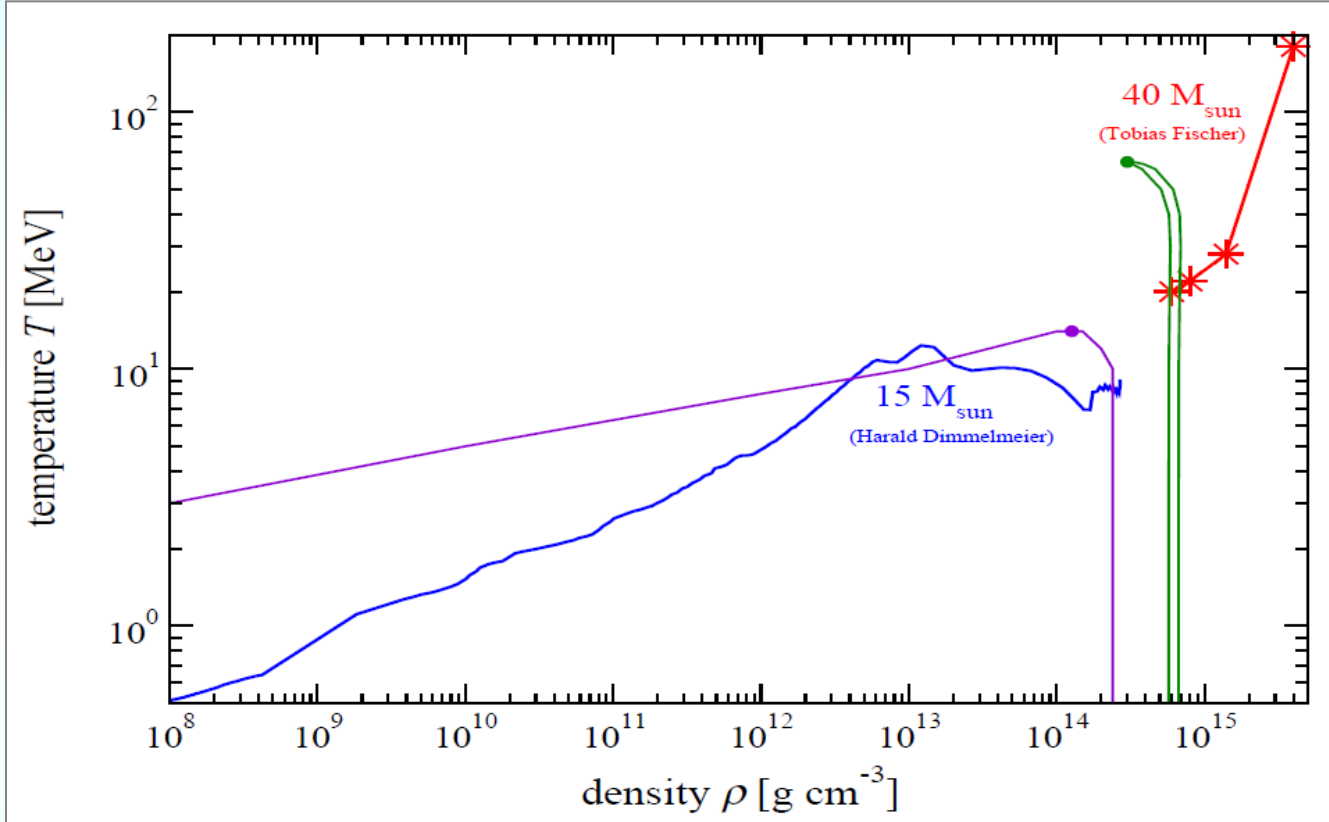
No!

Enthalpic PT



Entropic PT

Supernova Collapse in the Phase Diagram (III)



David Blaschke, “*Extreme State of Matter*”, *Elbrus-2010*

Supernova trajectories are taken from: Harald Dimmelmeier *and* Tobias Fischer

Gas-Liquid Phase Transition:

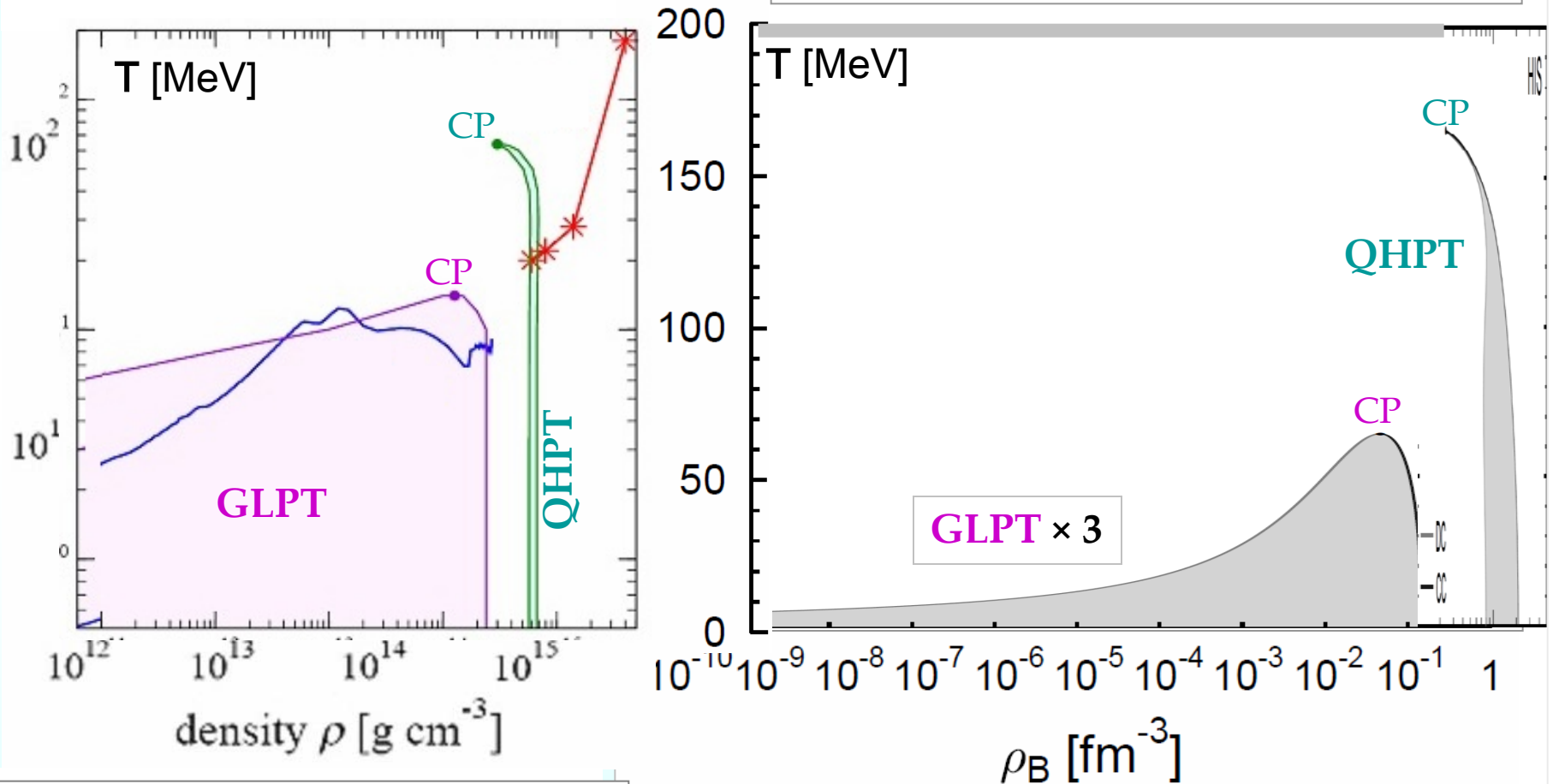
- G. Roepke et al., *Nucl.Phys.A* **399** (1983)

Quark-Hadron Phase Transition:

- D. Blaschke, T. Klähn, F. Weber, “*Compact Star constraints on the EOS*”, *Lecture Notes in Physics*, **814**, Springer (2011)

$T - \rho$ phase diagram of symmetric Coulombless GLPT and QHPT

M. Hempel, V. Dexheimer, S. Schramm, I. Iosilevskiy
Phys. Rev. C **88** (2013)



after David Blaschke *et al.*

Acta Phys. Pol. Supp. **3** (2010)

GLPT - G.Roepke *et al.*, *Nucl.Ph.* (1983)

QHPT - D.Blaschke, T.Klaehn, F.Weber... (2011)

SN path calcs: - Tobias Fisher

FSUGold (Matthias Hempel)

SU(3) model (Veronica Dexheimer)

GLPT

QHPT

Phase transitions *in* high energy density matter

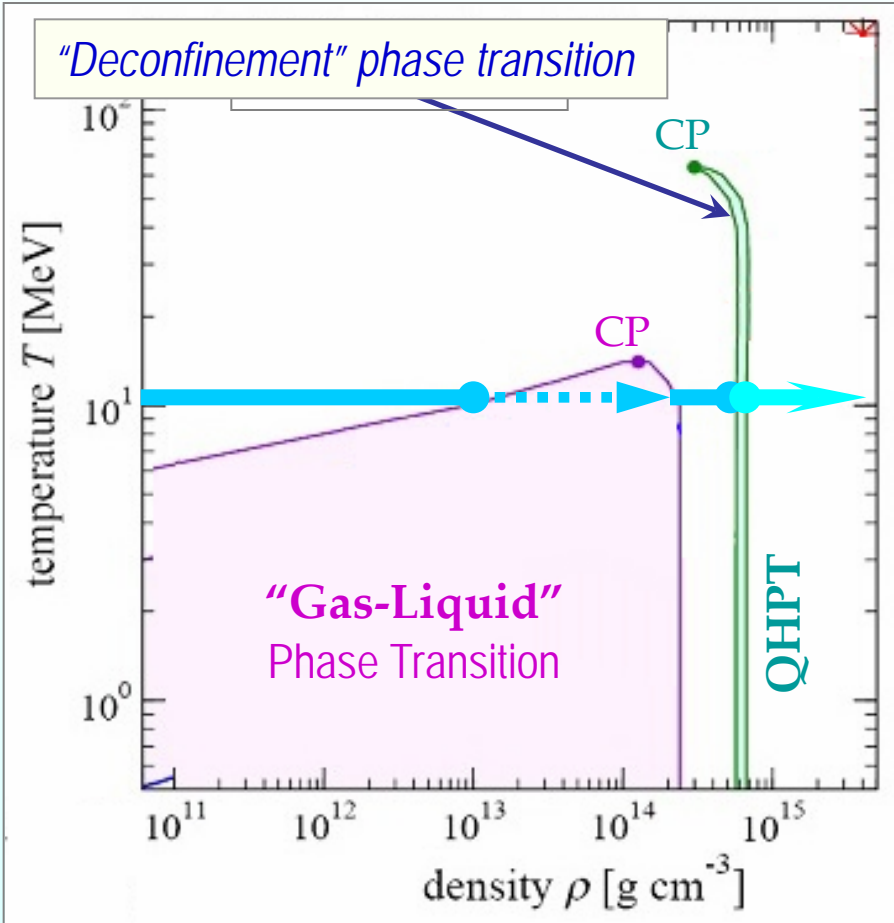
Enthalpic *vs* Entropic
?

Enthalpic *and* entropic phase transitions in nuclear matter *and* in electromagnetic plasma

PT under isothermal compression

$$\text{GLPT} \Leftrightarrow \Delta H < 0 \Leftrightarrow \text{GLPT}$$

$$\text{QHPT} \Leftrightarrow -T\Delta S < 0 \Leftrightarrow \text{PPT}$$



Hypothetical "Plasma" phase transition (PPT) in hydrogen

H. Kitamura und S. Ichimaru, J.Phys.Soc. of Japan **67** (1998)

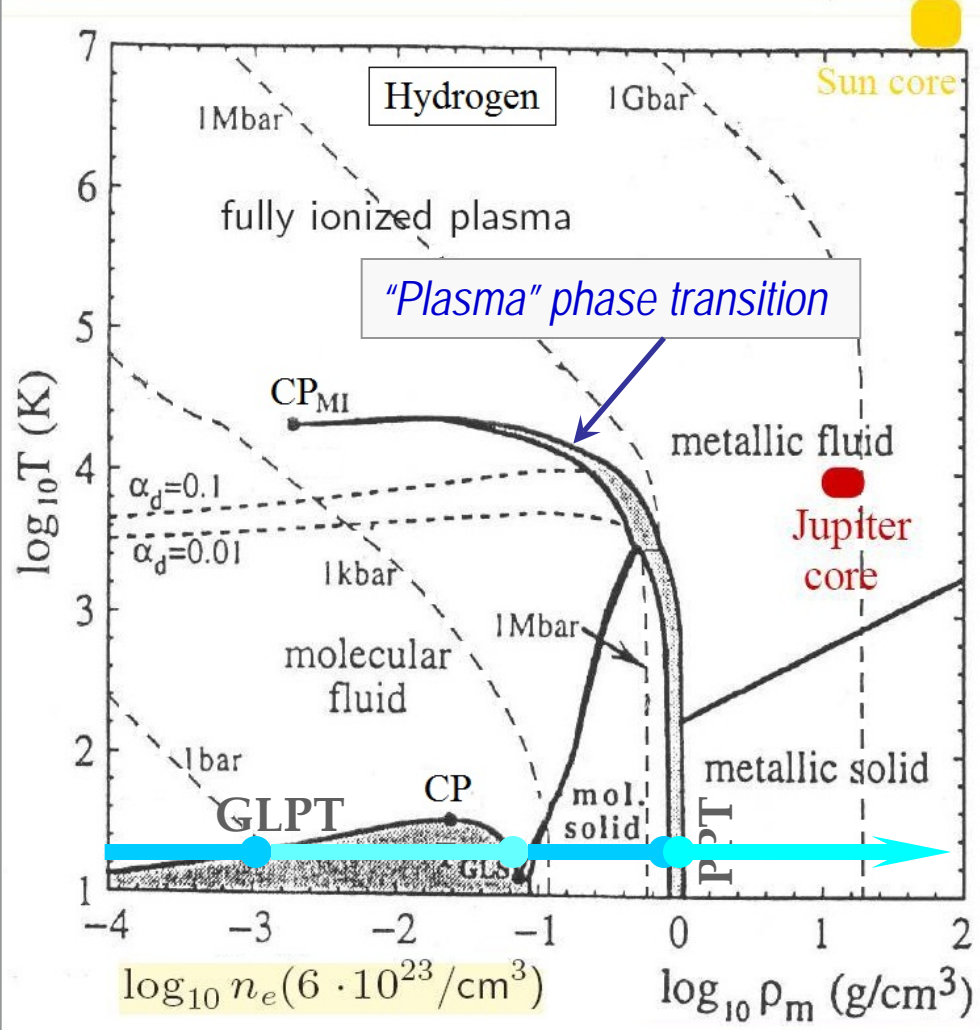
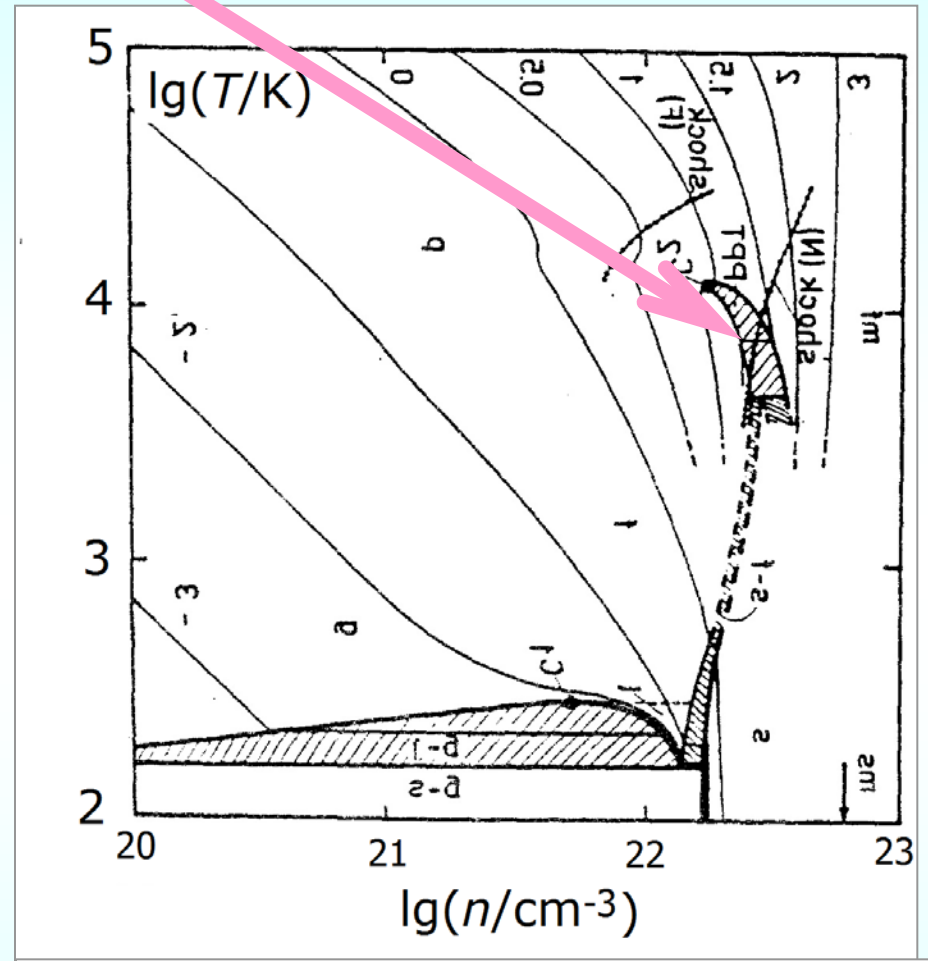
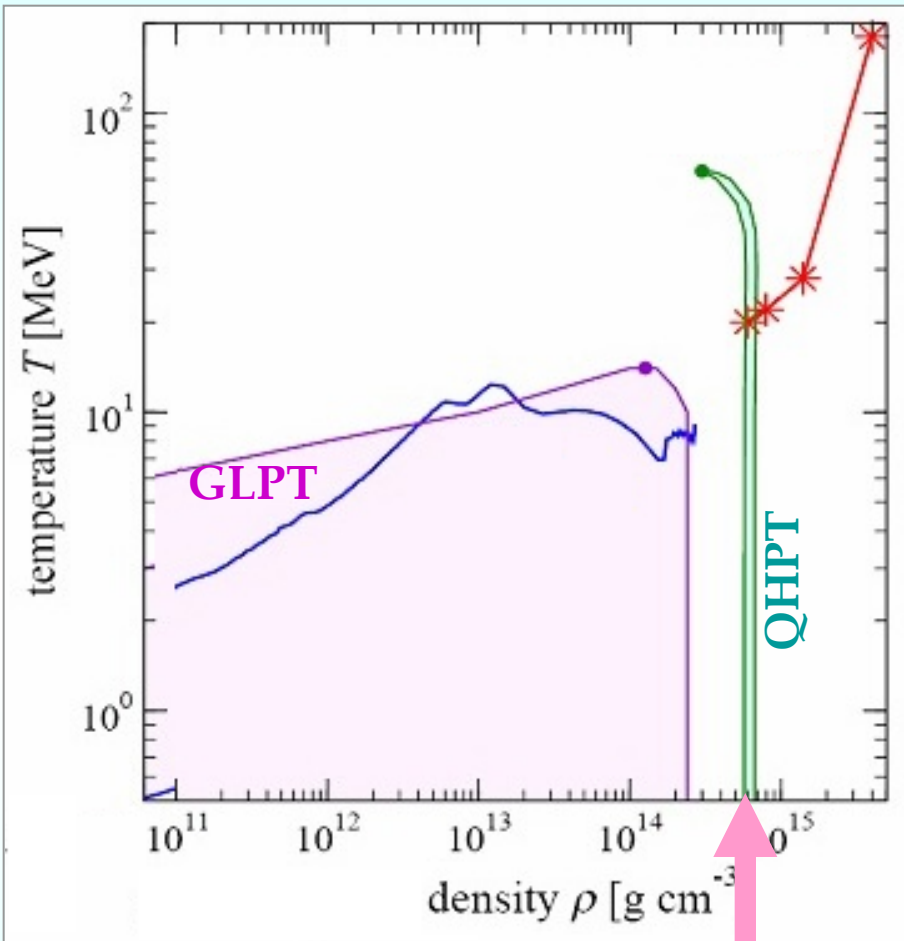


Figure after David Blaschke

Gas-liquid *and* **ionization-driven** phase transitions *in* xenon



Dienemann H, Clemens G, Kraeft W. D. *Annalen der Physik* 7, (1980)

Gas-liquid *and* **deconfinement-driven** PT *in* dense nuclear matter

General: "**Delocalization-driven**" PT-s *in* matter of **extreme state**

Basic point

Most of **entropic** 1st-order fluid-fluid phase transitions are “**driven**” by **forced decay** (*delocalization under compression*) of some kind of **bound complexes** :

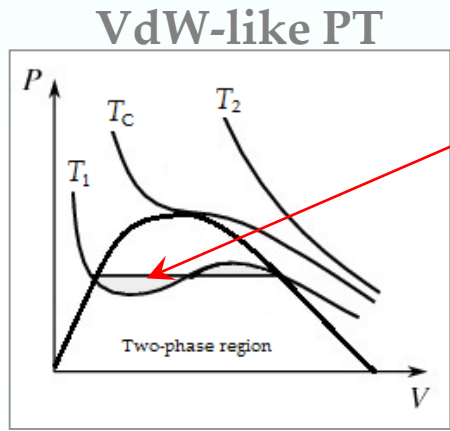
=== «» ===

(“*pressure*” ionization, “*pressure*” dissociation...
... “*pressure*” quark deconfinement” ...etc)

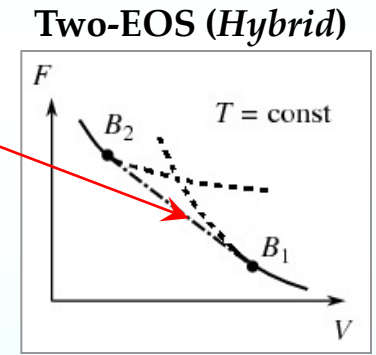
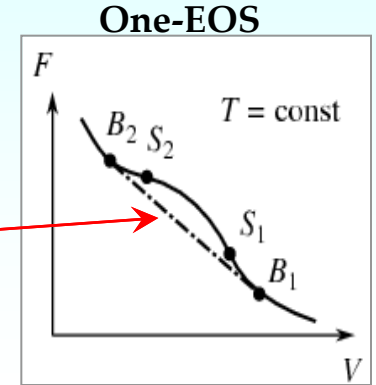
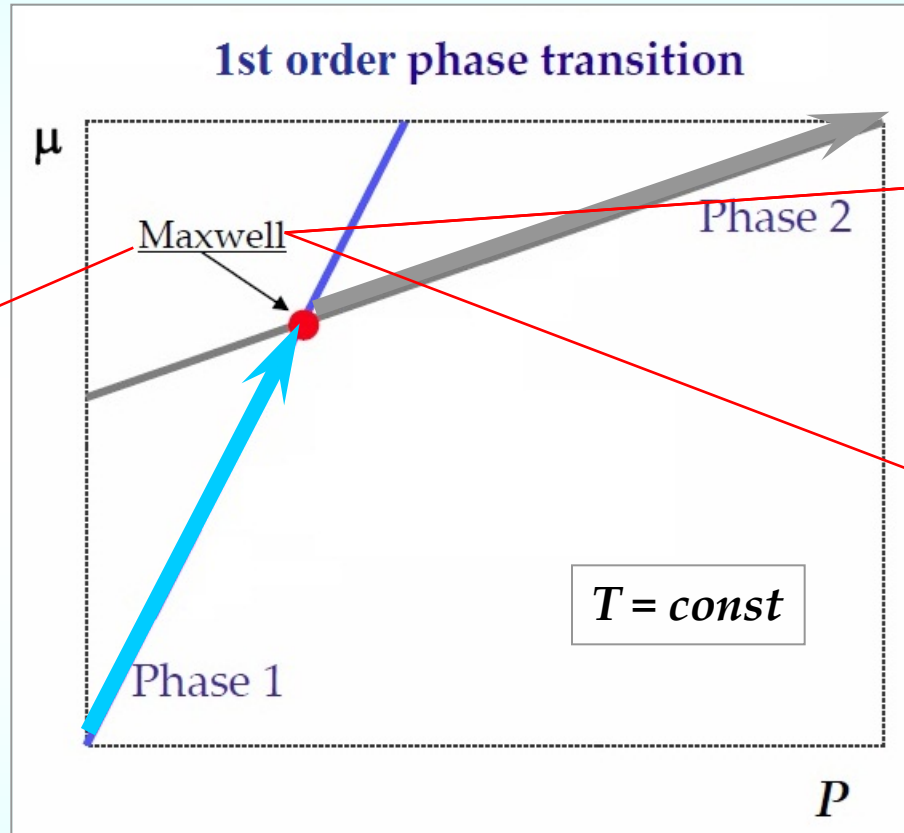
Phase transitions: **Enthalpic** *or* **Entropic** ?

(definition)

$$G = H - TS$$



Maxwell "Equal squares"



"Double tangent"

Enthalpic PT

$$\Delta H = T\Delta S < 0$$

$$(dP/dT)_{binodal} > 0$$

Exothermal PT

Phase equilibrium

$$G_1 = G_2 \Leftrightarrow \Delta H = T\Delta S$$

Entropic PT

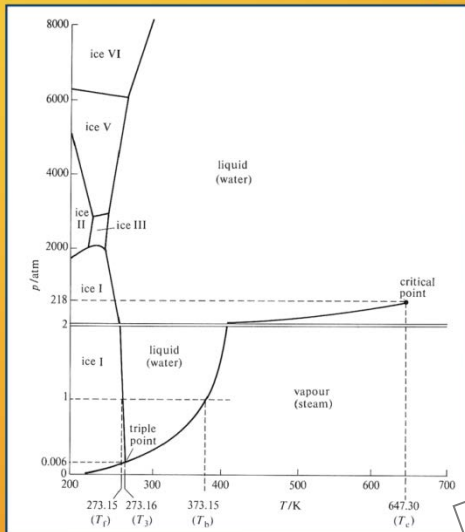
$$\Delta H = T\Delta S > 0$$

$$(dP/dT)_{binodal} < 0$$

Endothermal PT

Entropic Crystal-Crystal and Crystal-Fluid Phase Transitions

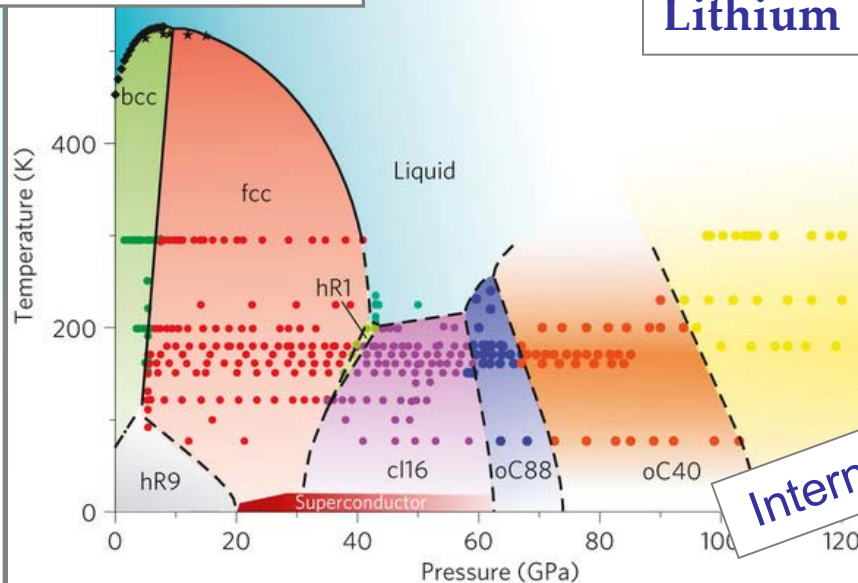
Water's Phase Diagram



Source: P.W. Atkins, *Physical Chemistry*, 2 ed., 1978

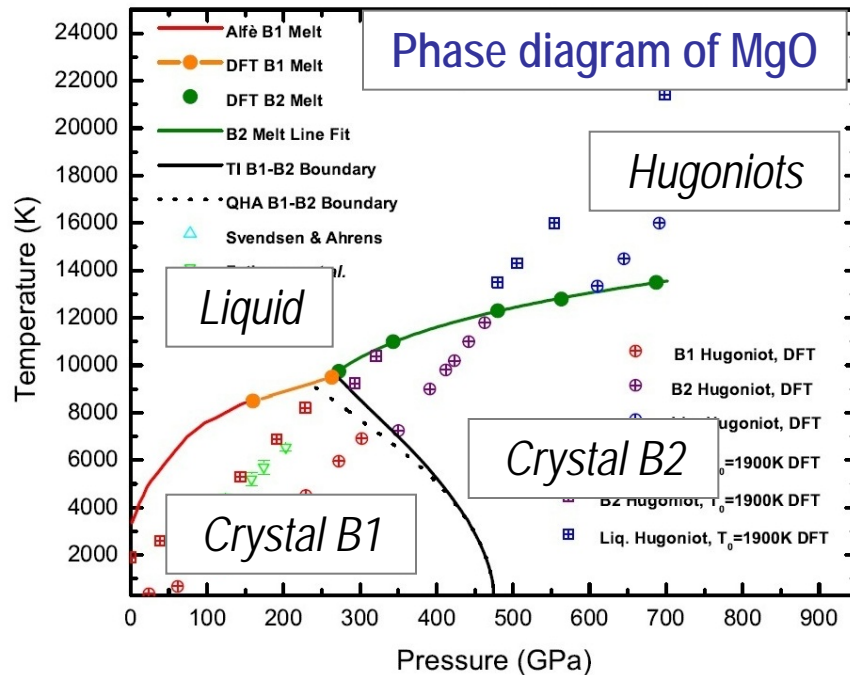
Internet

Lithium



Internet

Phase diagram of MgO



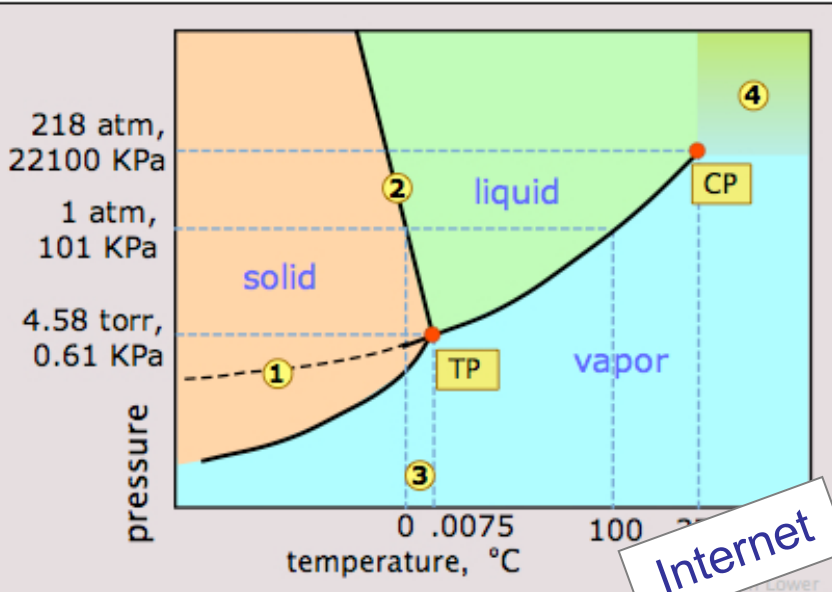
Hugoniots

Liquid

Crystal B2

Crystal B1

Root S. et al (Sandia) / [arXiv: 1502.0009](https://arxiv.org/abs/1502.0009)



Internet

The main subject of our interest

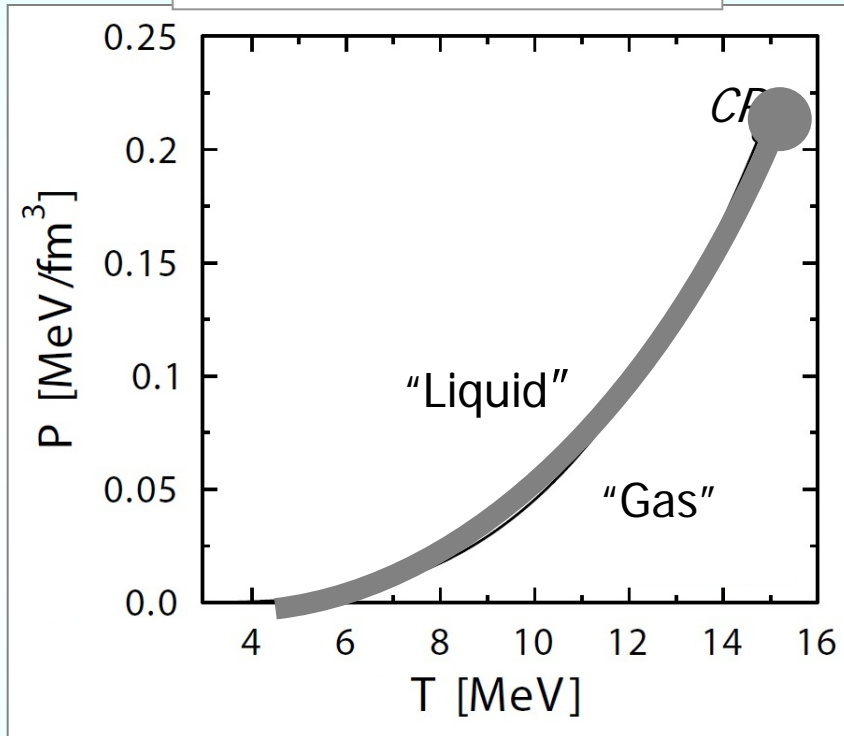
Isostructural 1st-order entropic
fluid-fluid phase transitions

P-T phase diagram *of* **GLPT** *and* **QHPT**

$P - T$ phase diagram of symmetric Coulomb-less GLPT and QHPT

One-EOS approach (*critical point*)

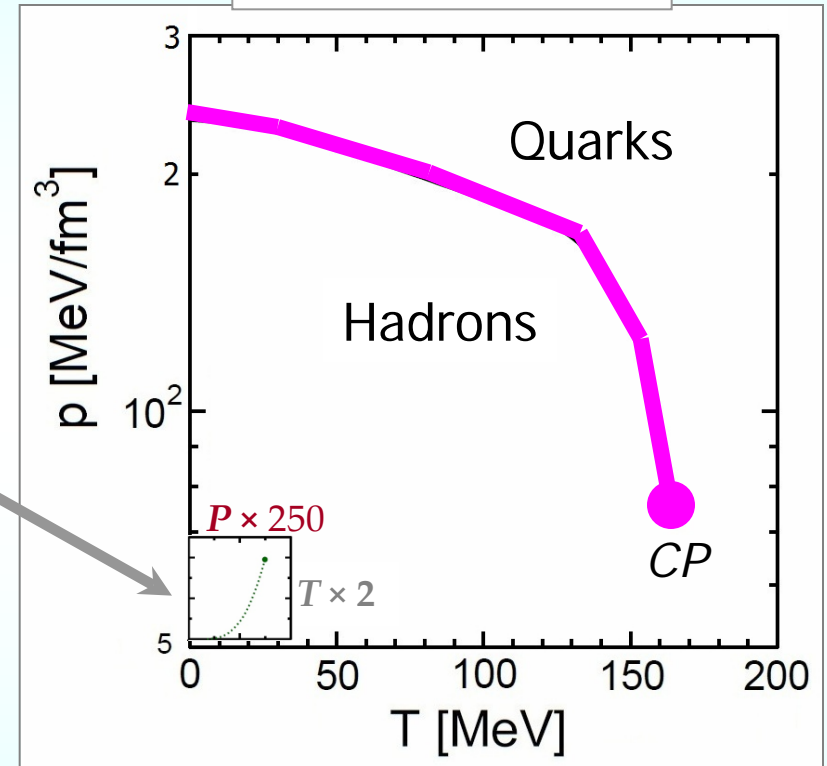
Nuclear Gas-Liquid PT



Standard VdW-like behavior

(*enthalpic PT*)

Quark-Hadron PT



Non-standard behavior: $(dP/dT)_{\text{binodal}} < 0$

(*entropic PT*)

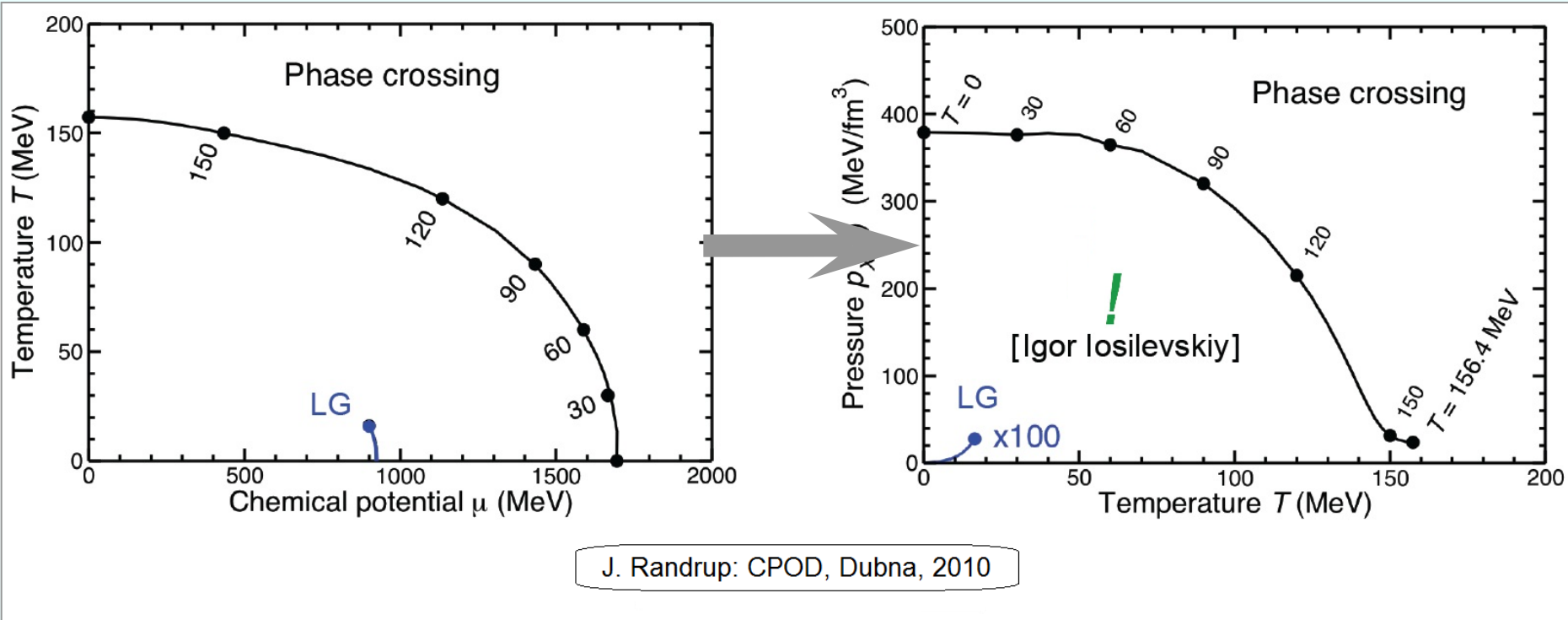
Non-congruence of the nuclear liquid-gas and the deconfinement phase transitions

M.Hempel, V.Dexheimer, S.Schramm and I.Iosilevskiy // PRC, 88 (2013)

P - T phase diagram of symmetric GLPT and QHPT

Jørgen Randrup, LBNL

GLPT vs. QHPT



GLPT

Standard VdW-like behavior: $(dP/dT)_{\text{binodal}} > 0$



QHPT

Non-standard behavior: $(dP/dT)_{\text{binodal}} < 0$

Critical Point and Onset of Deconfinement (CPOD)

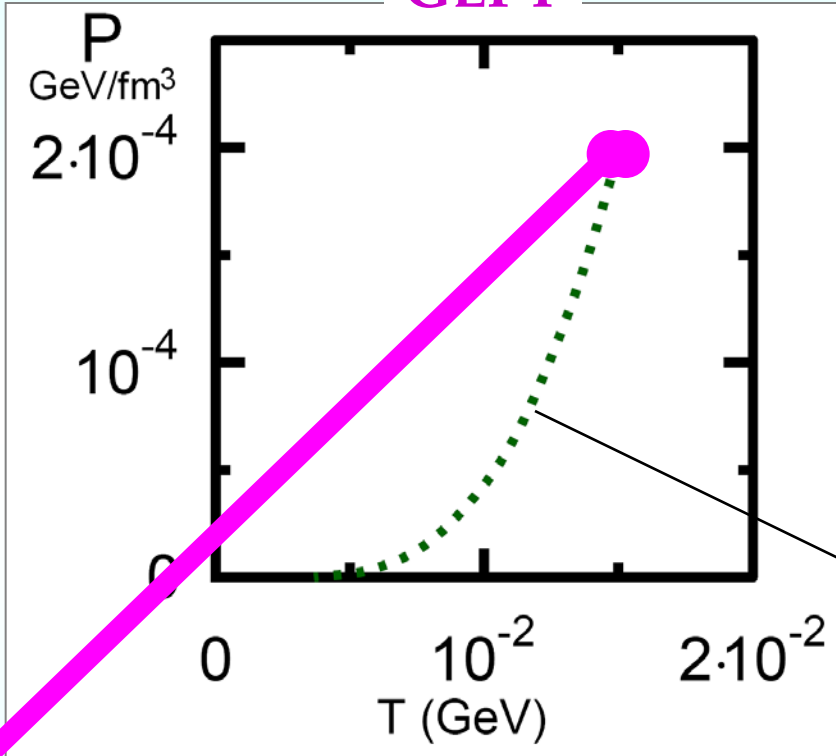
23 - 29 August 2010 at Joint Institute for Nuclear Research

(Dubna-2010)

P - T phase diagram of symmetric GLPT and QHPT

One-EOS approach (*critical point*)

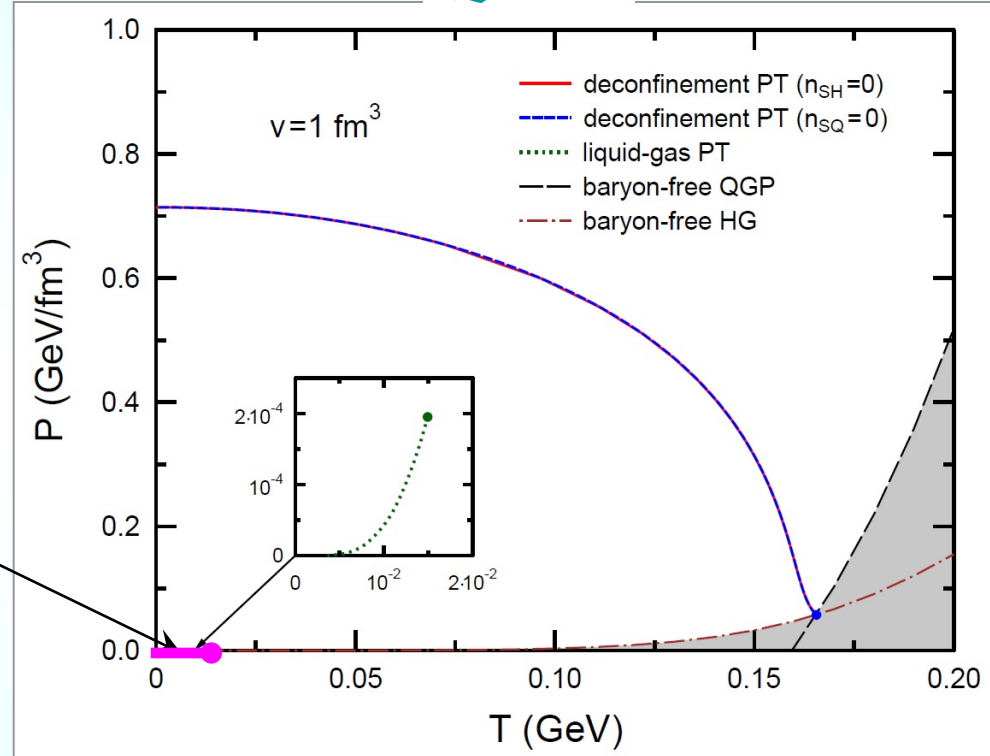
GLPT



Standard VdW-like behavior

Two-EOS approach (*no critical point*)

QHPT



Non-standard behavior: $(dP/dT)_{\text{binodal}} < 0$

Figures after: Satarov L., Dmitriev M., Mishustin I.
Phys. At. Nucl. (2009)

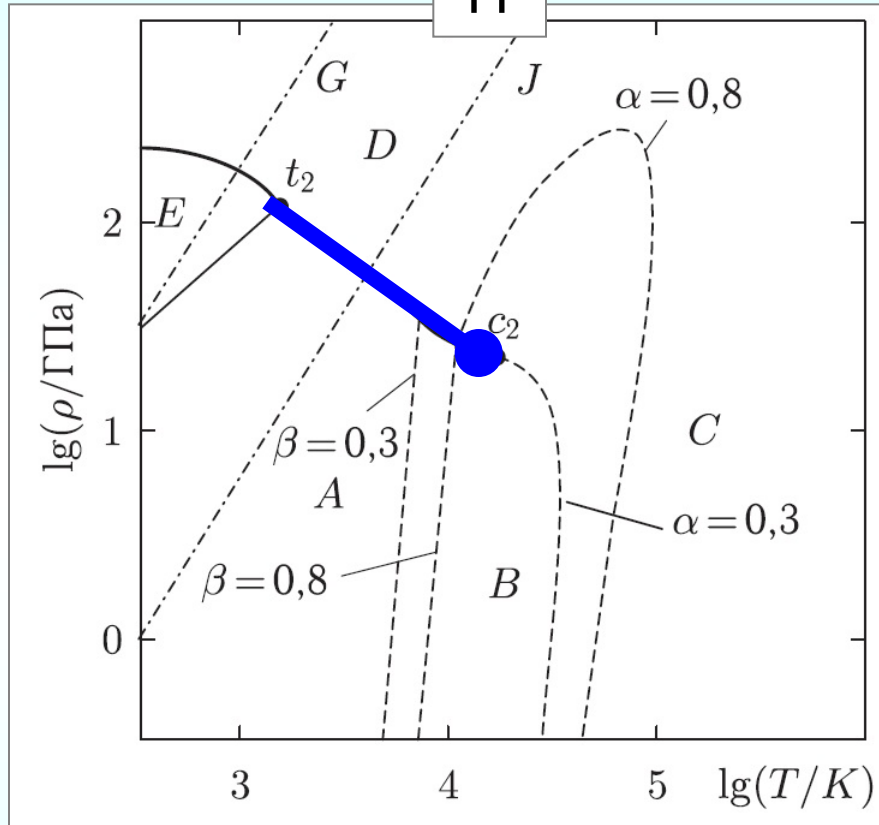
Phase transitions *in* high energy density matter

Enthalpic *vs* Entropic
?



("Plasma" PT vs VdW-like PT)

Entropic vs Enthalpic phase transitions ("plasma" vs VdW-like PTs)

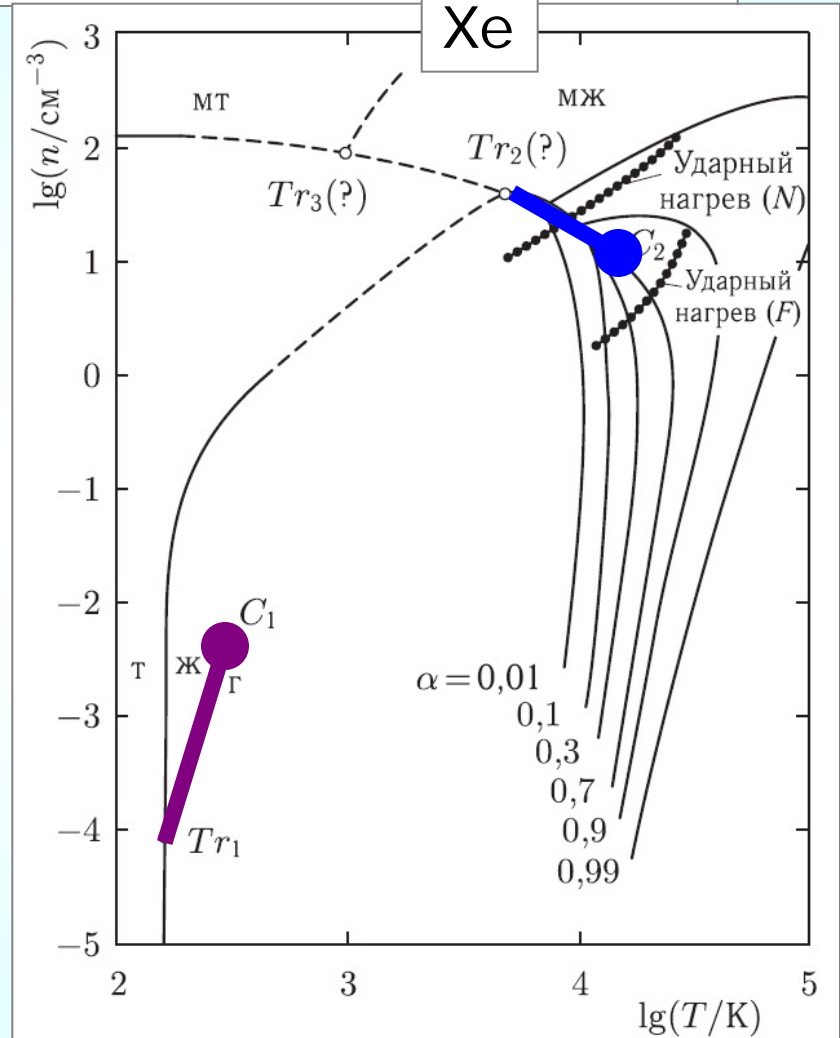
H



Ebeling W., Reichert W.
Phys. Lett. A, **80** (1985)

-  Plasma PT (*entropic*) ($dP/dT < 0$)
-  Gas-liquid PT (*enthalpic*) ($dP/dT > 0$)

Xe

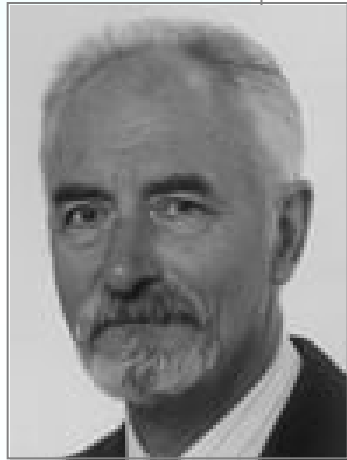


Ebeling W., Foerster A., Reichert W.
Physica A, **150** (1988)

Fifty years of predictions for plasma phase transitions

(non-ideality models via "chemical picture" (1968 – 2017))

(*) Beulle, Ebeling
et al. (1999)



Werner Ebeling

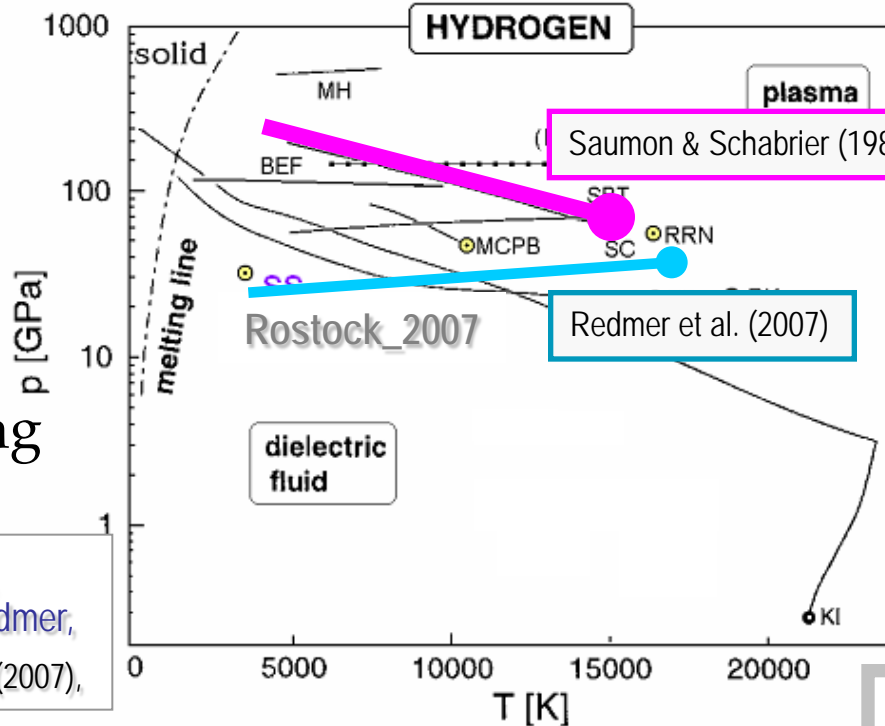
Rostock - 2007

Holst, Nettelmann, Redmer,

Contrib. Plasma Phys. 47 (2007),

Hydrogen EOS and Plasma Phase Transition
(coexistence lines and critical points of the PPT)

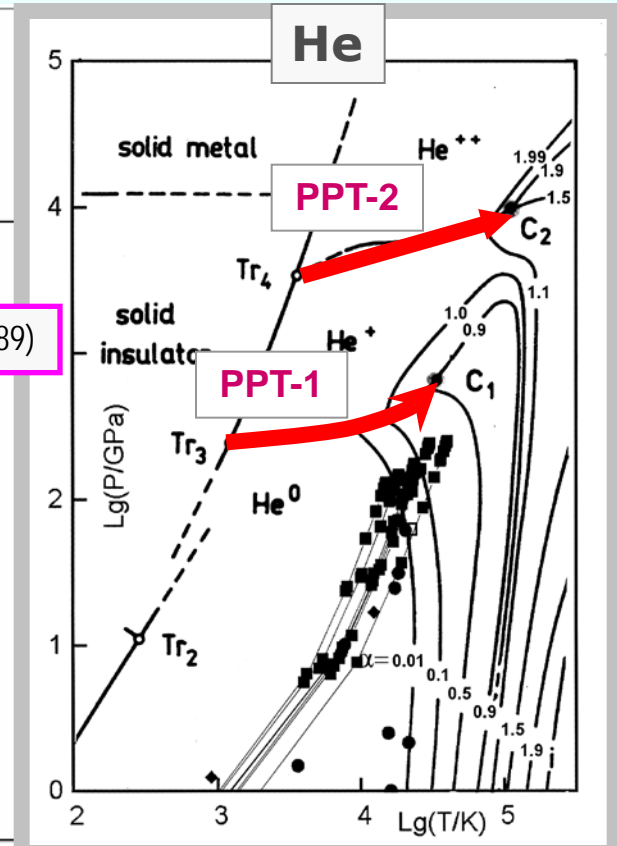
D. Beulle, W. Ebeling and A. Foerster
Phys. Rev. B 59 14177-14181 (1999)



Saumon & Schabrier (1989)

Redmer et al. (2007)

SS - Stevenson D, Salpeter E. (1977) *ApJ*. Sp.35,221

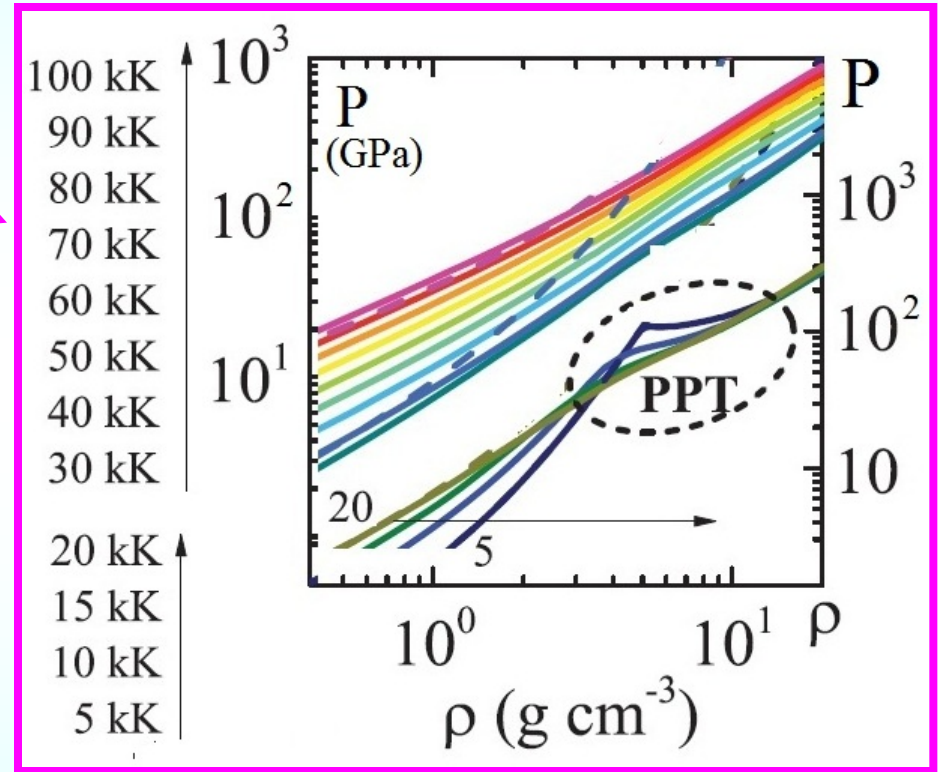
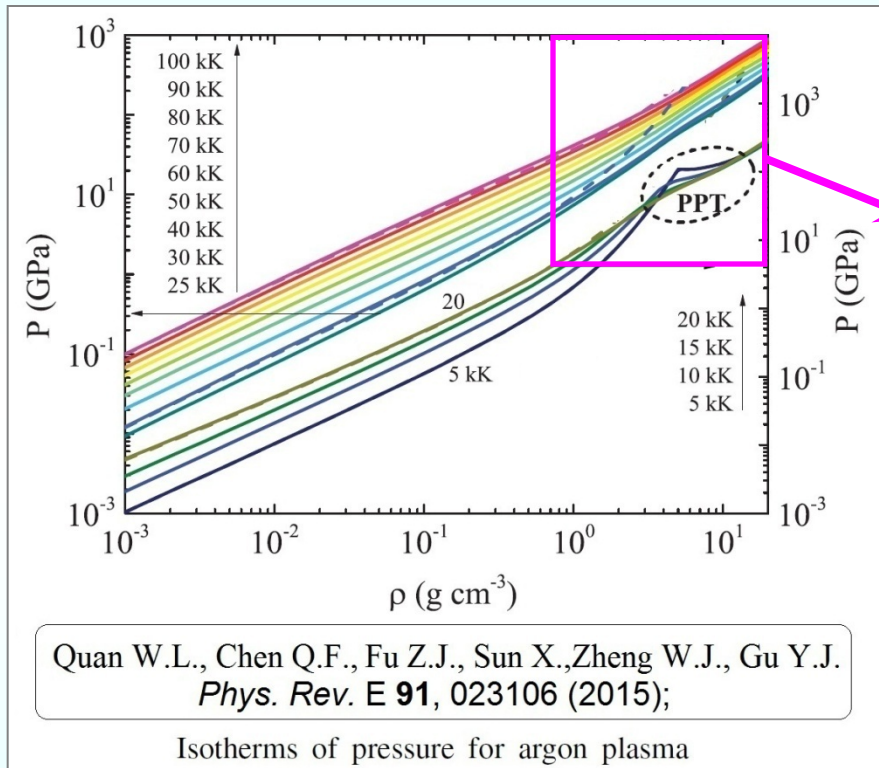


Two separate plasma phase transitions
(under 1st and 2nd ionization in He)

Ebeling, Foerster *et al.* (1991)

Ionization-driven (*entropic*) phase transition in Ar

(*Very recent example: Plasma model in chemical picture*)



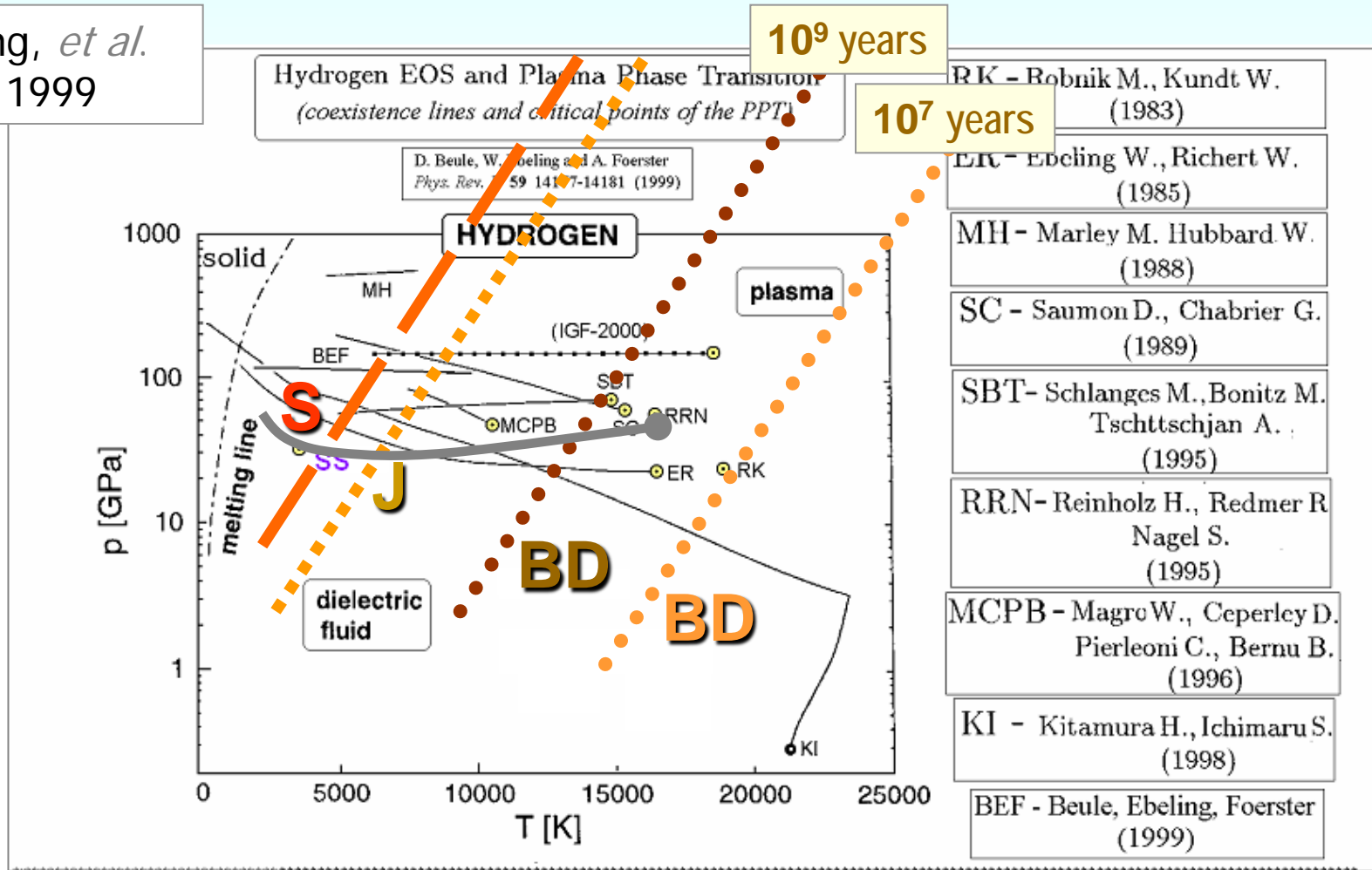
NB !

Abnormal order of isotherms

Hypothetical "plasma phase transition" in hydrogen

Relevant to the problem of formation for Giant and Extrasolar Planets and Substellar objects

W. Ebeling, *et al.*
PRB, 1999



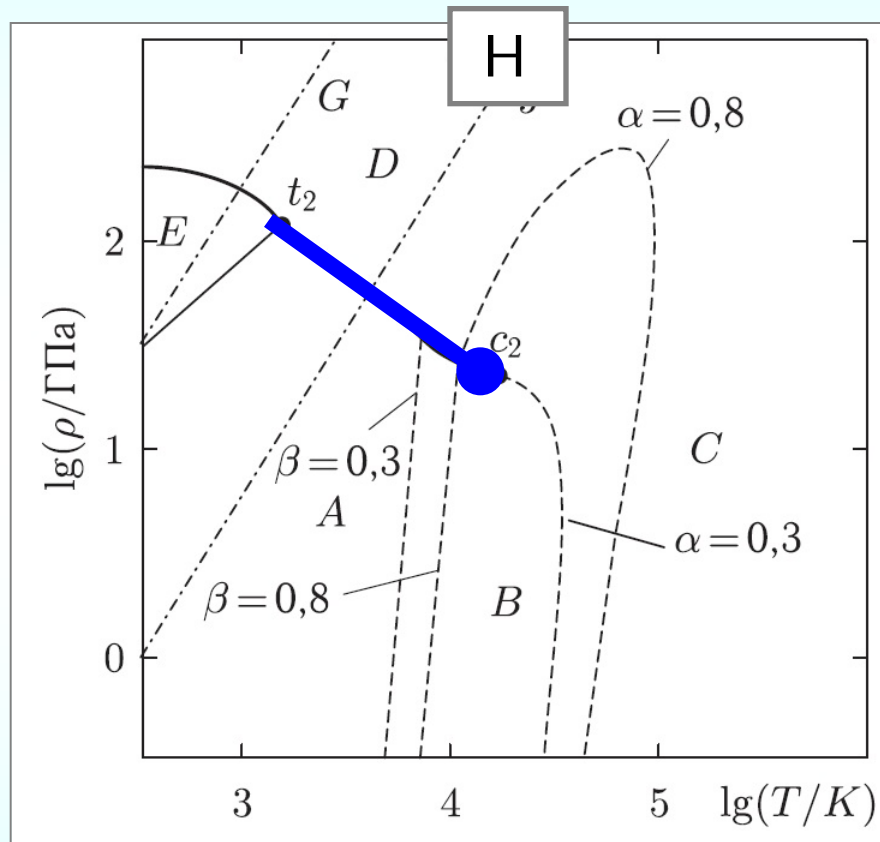
Redmer *et al.* 2007

S - Saturn
J - Jupiter
BD - Brown Dwarfs

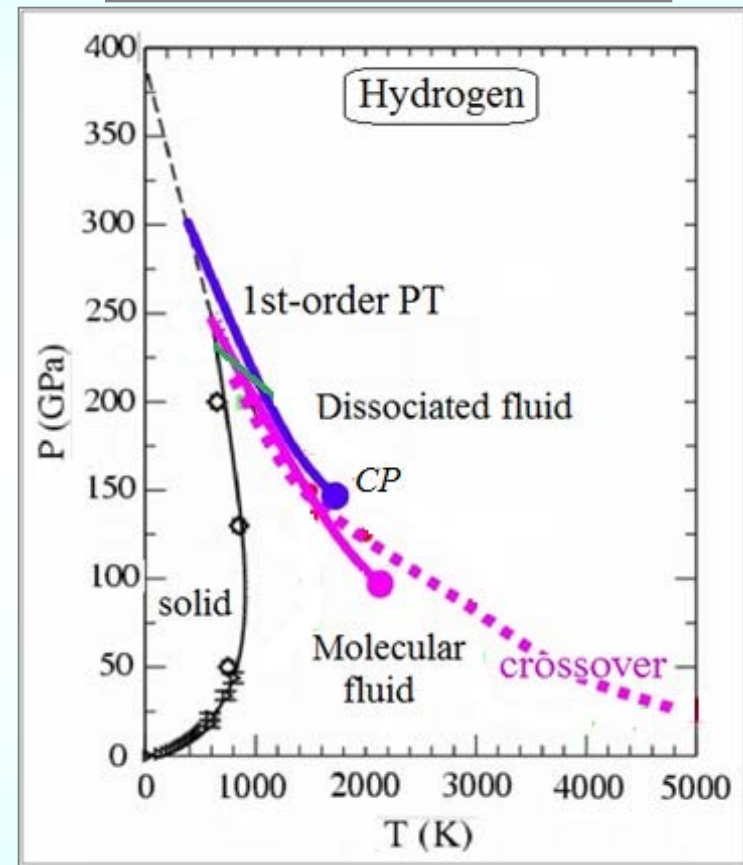
Ionization- and Dissociation-driven phase transitions in H_2

$$(dP/dT)_{\text{binodal}} < 0$$



(Chemical model)






(*ab initio* - DFT/MD)



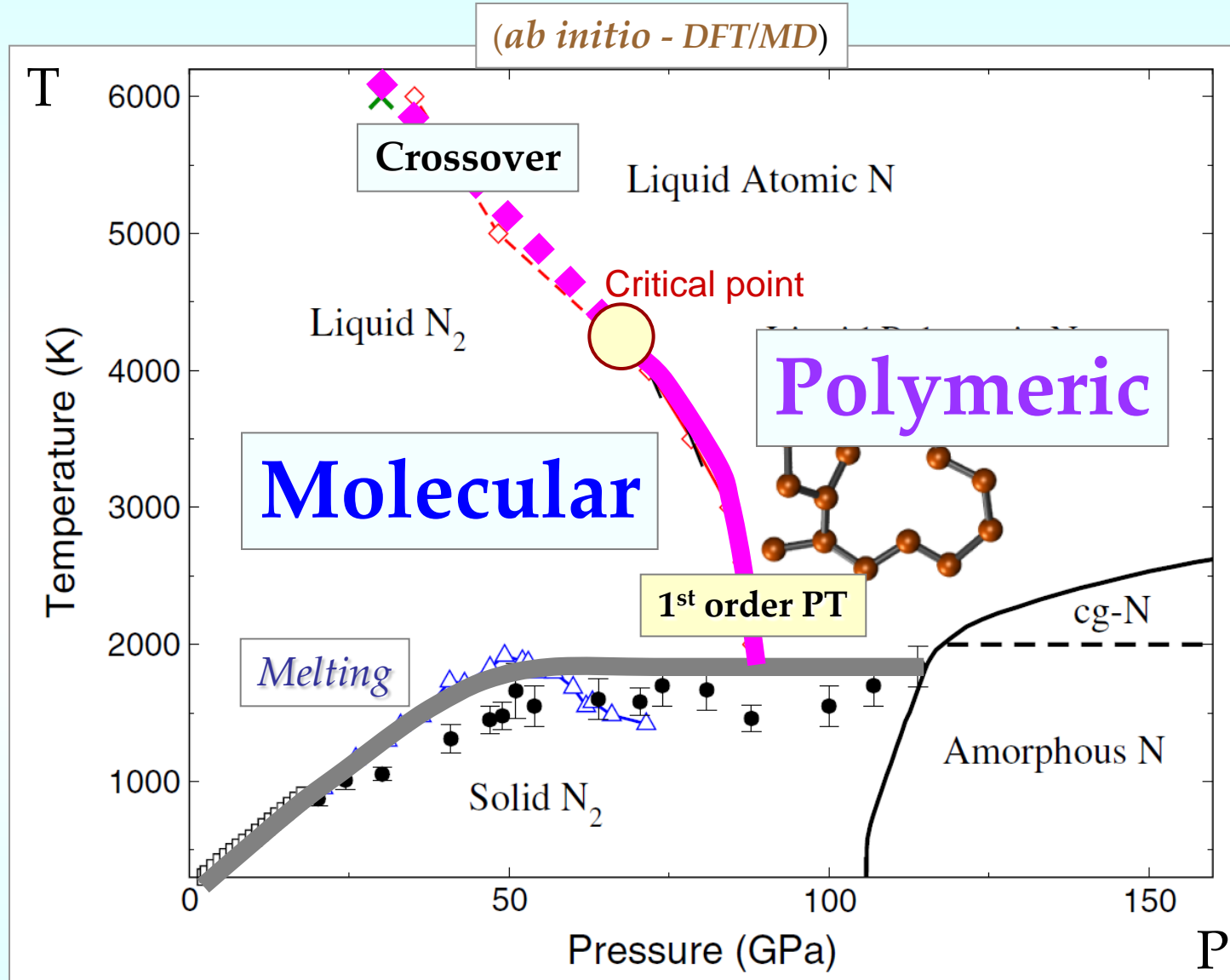
Dissociation-driven PT (evidently entropic)

-  Plasma PT (*entropic*) ($dP/dT < 0$)
-  Gas-liquid PT (*enthalpic*) ($dP/dT > 0$)

DFT/MD:

-  Bonev S., Militzer B. *et al.*, *PRB* 69 (2004)
-  Morales M. *et al.*, *PNAS* 107, (2010)
-  Lorenzen W., Holst B., Redmer R. *PRB* (2010)

Entropic fluid-fluid phase transition in N₂



B. Boates, S. Bonev, *Phys. Rev. Lett.*, **102** (2009) // *ab initio* – DFT/MD

Ionization- and Dissociation-driven phase transitions in H₂

(mostly entropic)

Non-standard behavior: $(dP/dT)_{\text{binodal}} < 0$ or $(dP/dT)_{\text{binodal}} > 0$

Dissociation-driven PT

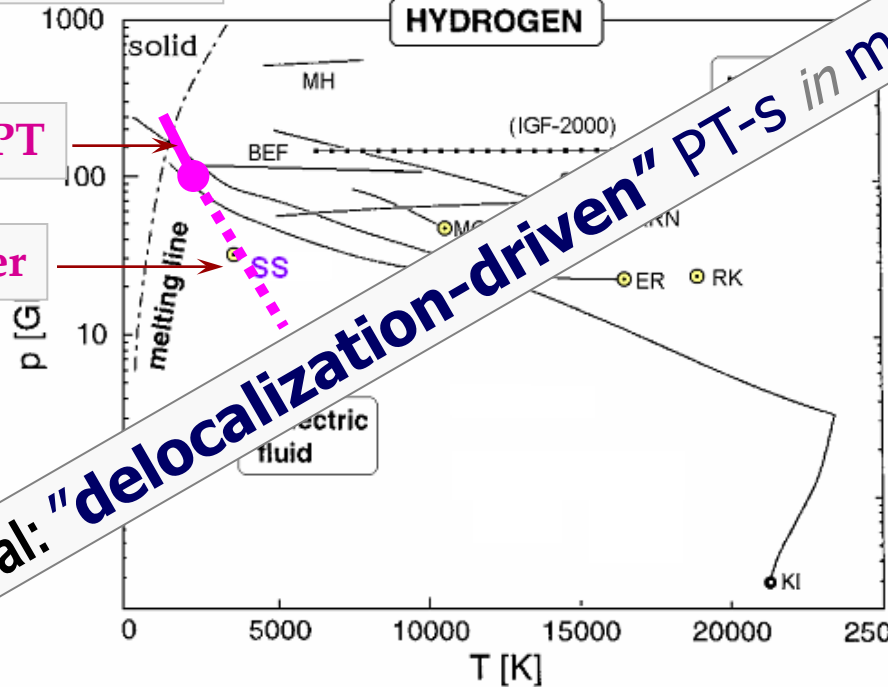
1st-order PT

Crossover

General: "delocalization-driven" PT-S in matter of extreme state

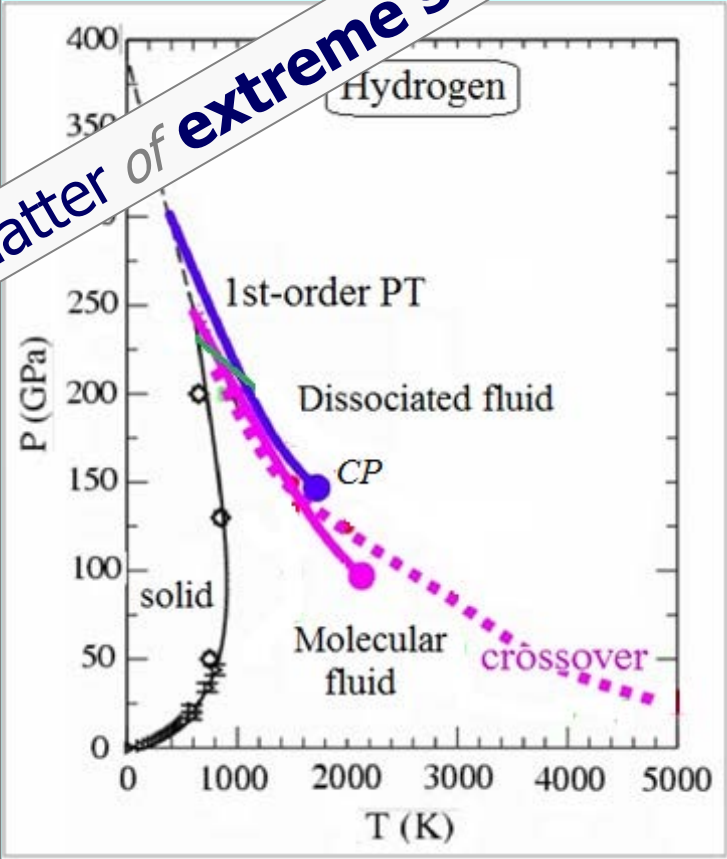
Hydrogen EOS and Plasma Phase Transition
(coexistence lines and critical points of the PPT)

D. Beule, W. Ebeling and A. Foerster
Phys. Rev. B 59 14177-14181 (1999)



SS - Stevenson D, Salpeter E. (1977) *ApJ*. Sp.35,221

IGF-2000 - Iosilevski I, Gryaznov V., Fortov V. "Thermodynamics of HYDROGEN and Deuterium via..."



Dissociation-driven PT (*ab initio*)

DFT/MD:

- Bonev S., Militzer B. *et al.*, *PRB* 69 (2004)
- Morales M. *et al.* *PNAS* 107, (2010)
- Lorenzen W. *et al.* *PRB* (2010)

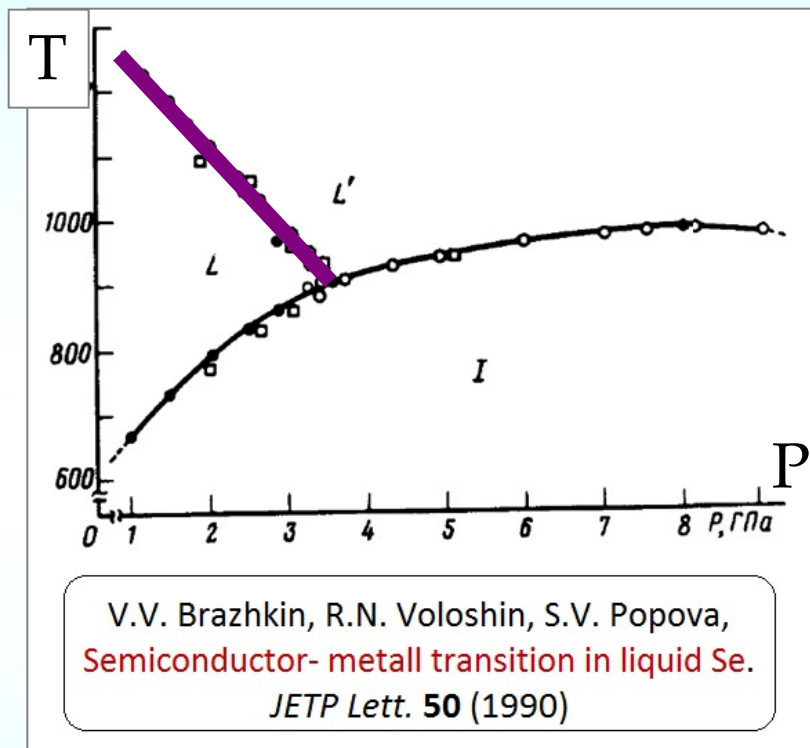
Phase transitions *in* high energy density matter

Experiment

Enthalpic *vs* Entropic
?

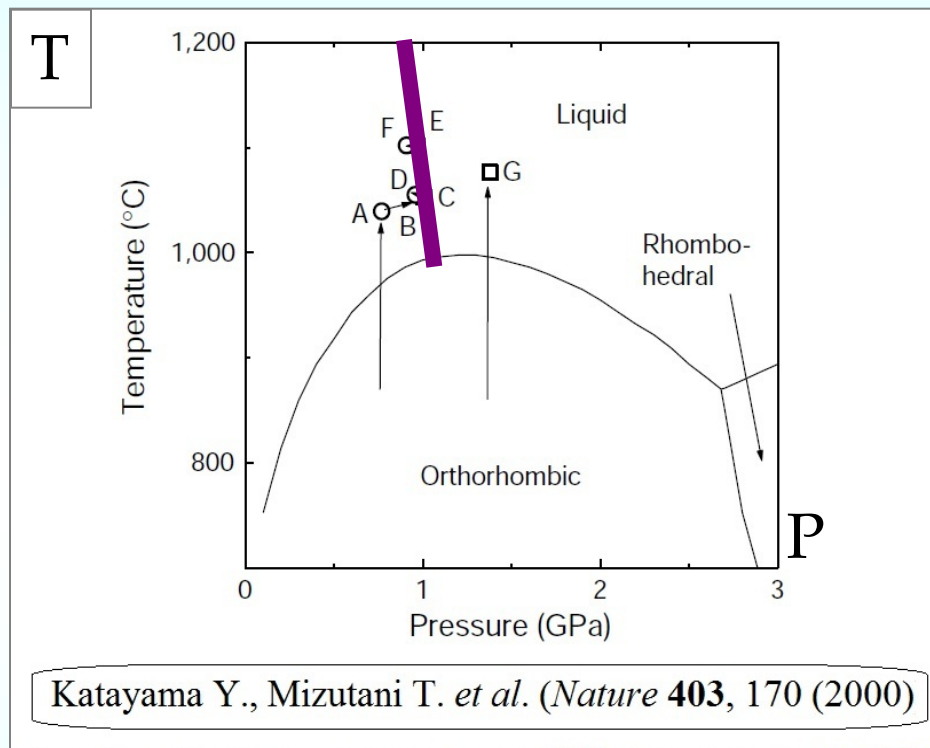
Entropy-driven fluid-fluid phase transitions

Selenium



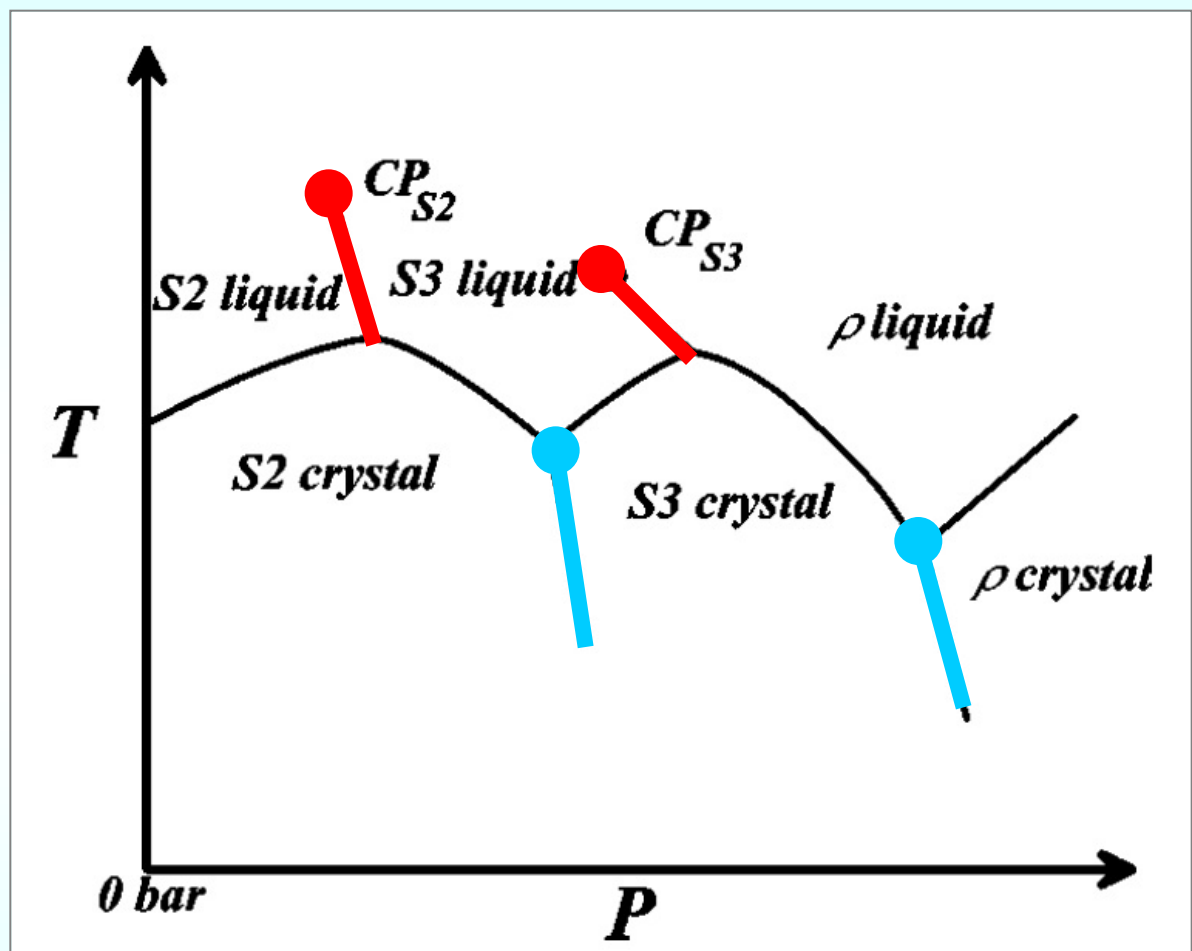
Experiment

Phosphor



Experiment

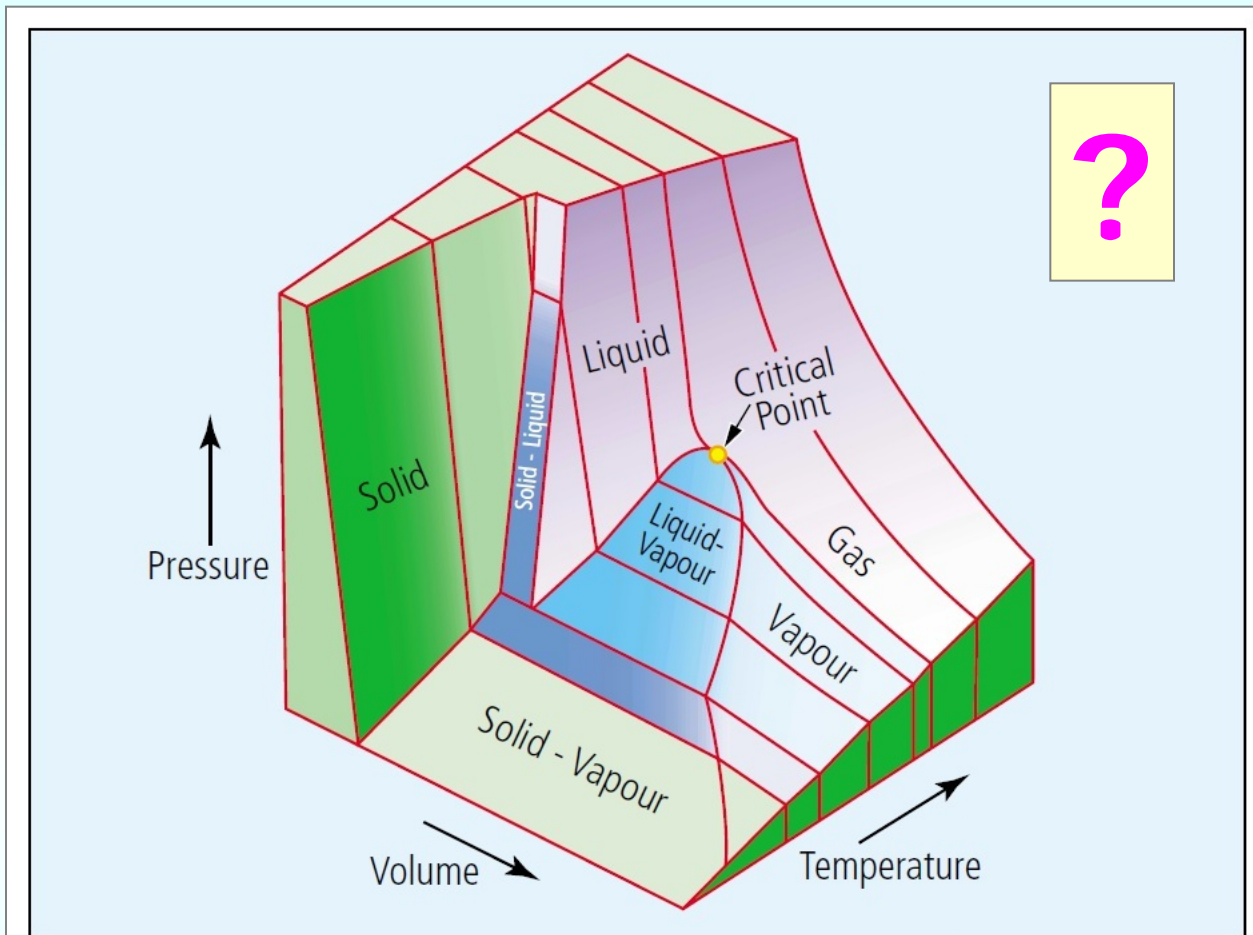
Enthalpic *and* Entropic Phase Transitions ?



Hajime Tanaka // Phys. Rev. E, **62** (2000)
General view of a liquid-liquid phase transition

**Entropic phase transitions are not exception,
but they are general rule instead !**

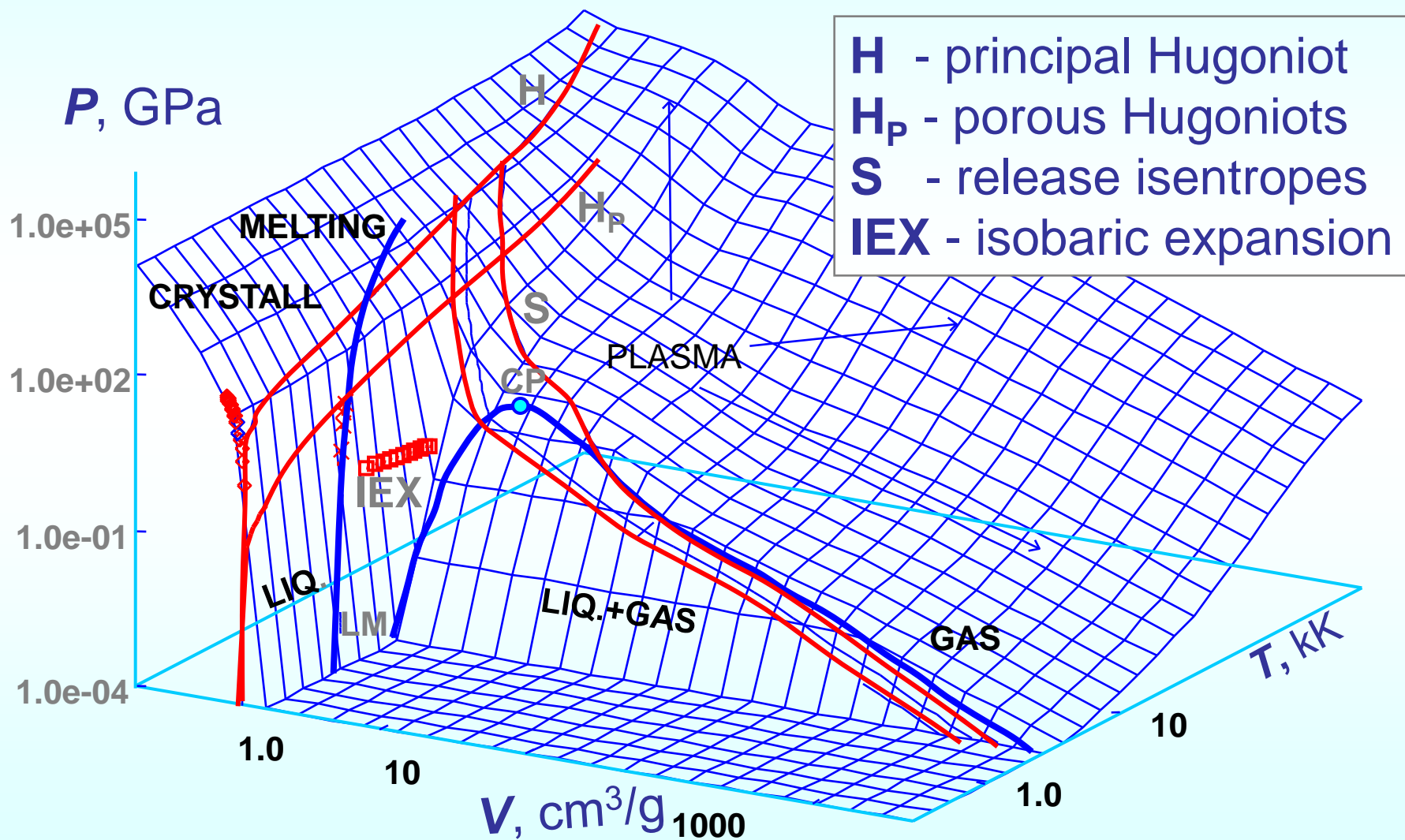
**Where are entropic PTs located at standard
phase diagrams ?**



Discovery • The Science & Technology Journal

Figure 1: The three-dimensional pressure-temperature phase diagram for a simple material. The $P(V,T)$ surface shown describes all possible states attainable for the material in question.

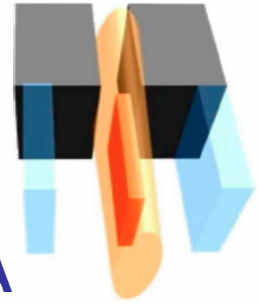
Dynamic Experiments (general phase diagram)



Wide-range EOS - A. Bushman, I. Lomonosov, V. Fortov

WDM community

HIHEX Heavy Ion Heating and Expansion



FAIR
NICA

p

Melting γ_1

Hugoniot

Shock compression
(high explosive)

WDM

Isentropic release

Plasma

HIB isochoric heating (HIHEX)

Isentropic release (HIHEX)

T_0

Solid

Liquid

$S=const$



CP

Gas

LG

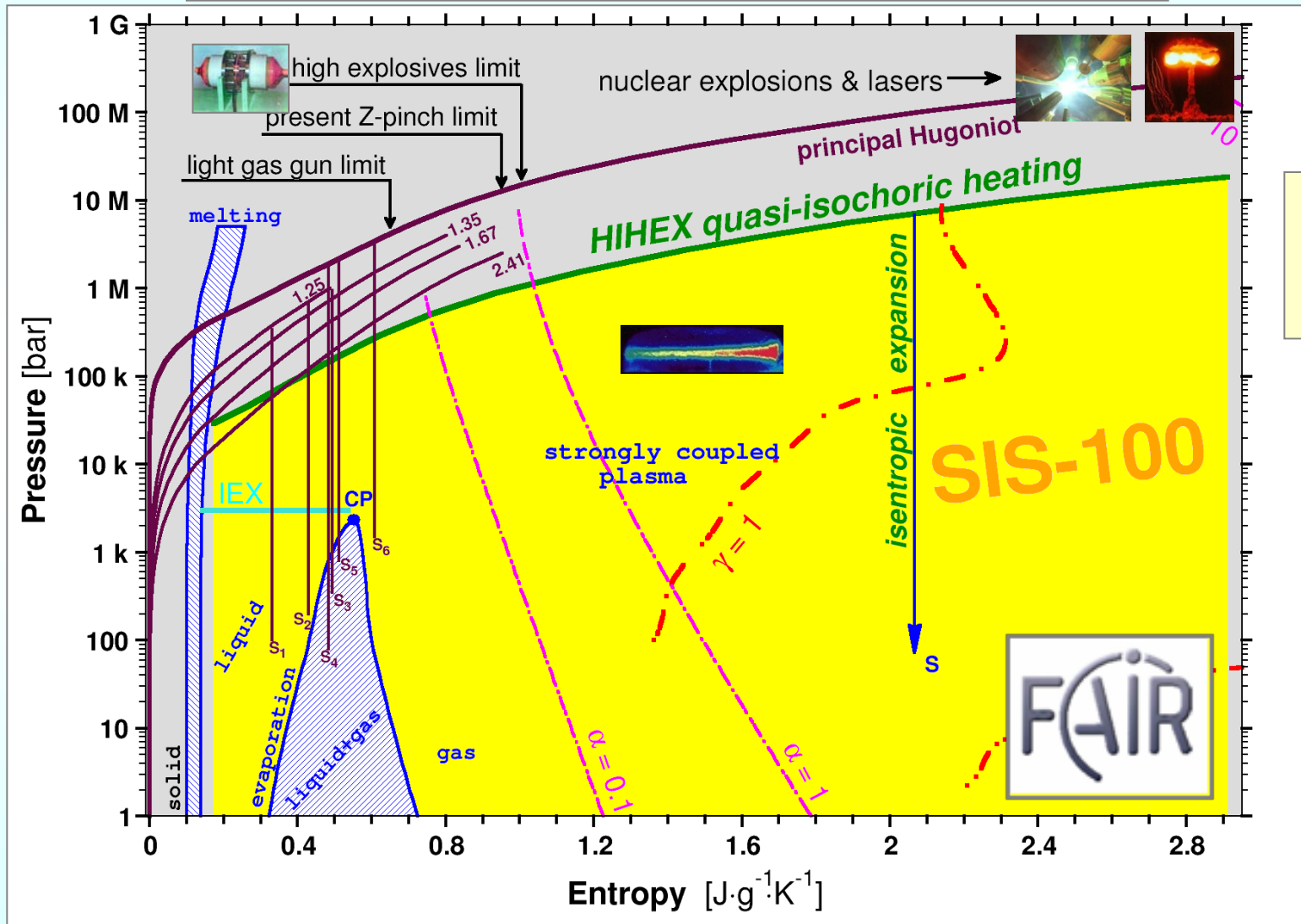
V

- uniform quasi-isochoric heating of a large-volume dense target
- isentropic expansion in 1D plane or in 2D



"*Terra Incognita*" regions of the phase diagram accessible in experiments at **FAIR**

D.D,H. Hoffmann, V.E. Fortov et al. *Phys. Plasmas* **9** (2002)



Pressure – Entropy diagram (*I. Lomonosov*)

Anomalous Properties of Entropic Phase transitions

*What's a matter in falling P - T diagram
for entropic phase transitions . . . ?*

Why should we be worried about it ?

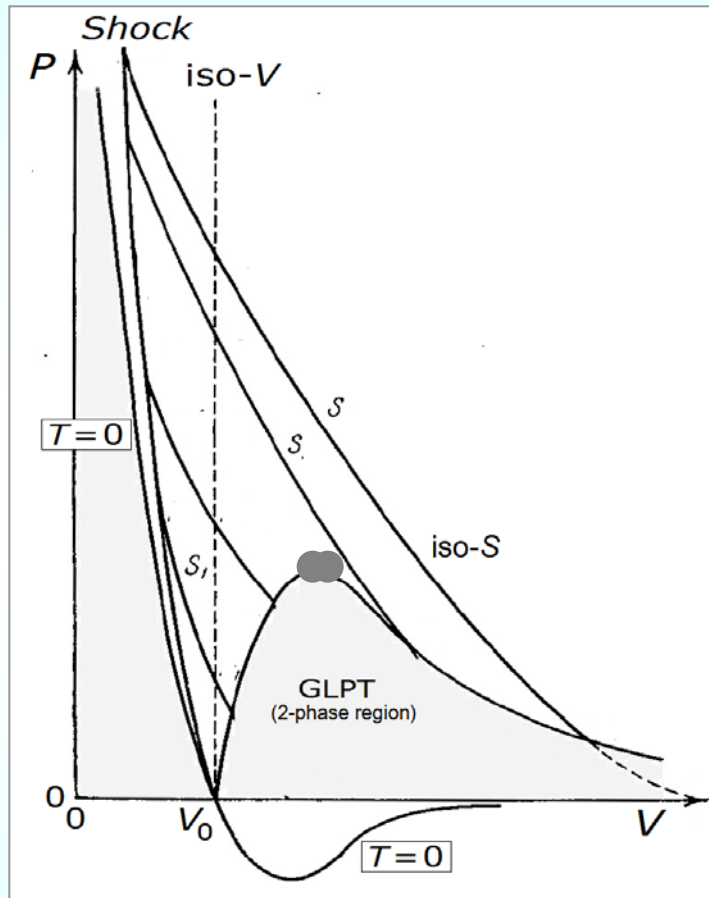


Enthalpic vs. Entropic phase transitions

in **P - V** phase diagram

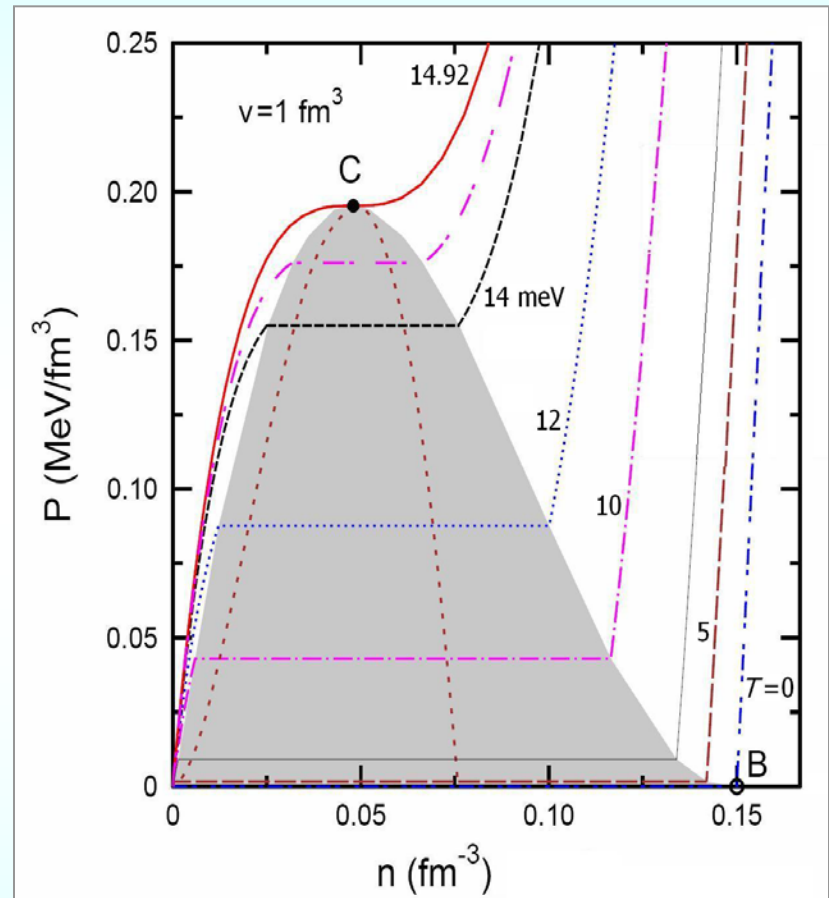
P - ρ phase diagram of symmetric Coulomb-less GLPT

Standard VdW-like PT



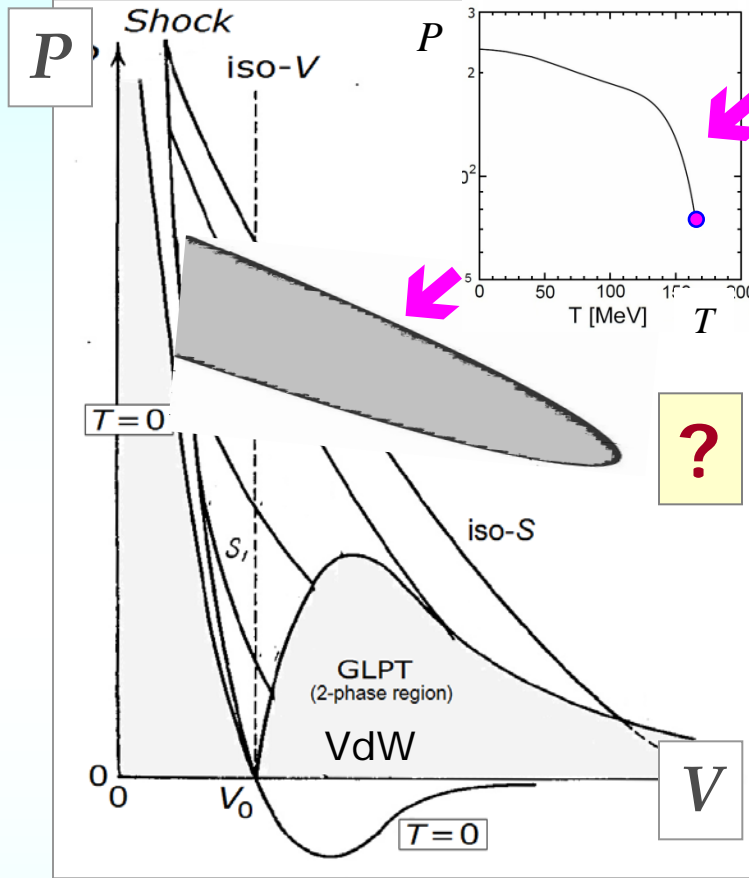
Zeldovich and Raizer
Moscow (1966)

"Gas-Liquid" PT in symmetric nuclear matter

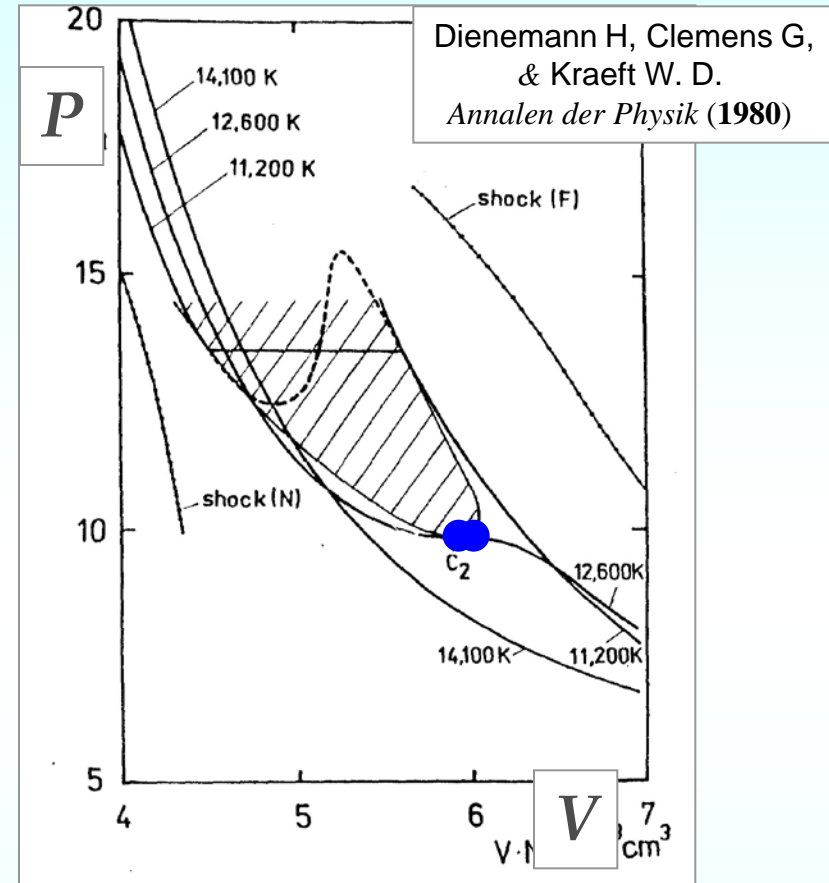


Satarov L., Dmitriev M., Mishustin I.
Phys. At. Nucl. (2009)

Ionization-driven (“plasma”) phase transition



Typical
Entropic
phase
transition



Entropic (ionization-driven) phase transition in Xe

Enthalpic (gas-liquid) phase transition

NB!

Entropic phase transition has **lower** (on pressure) **critical point!**

p

Melting H_1

Shock compression
(high explosive)

Isentropic release

WDM

Plasma

HIB isochoric heating

Isentropic release

T_0

$S=const$

Solid

Liquid

CP

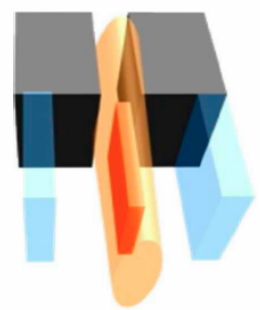
Gas

LG

17

HIHEX

Heavy Ion Heating and Expansion



- uniform quasi-isochoric heating of a large-volume dense target
- isentropic expansion in 1D plane or



Heavy-ion beams for exploring of phase transitions *(in progress)*

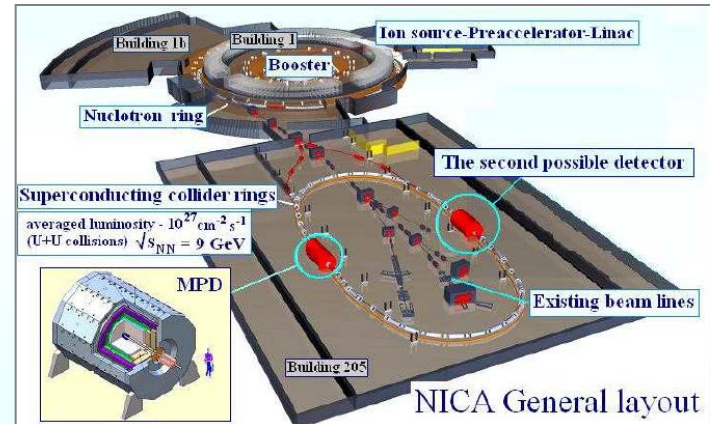
Heavy-ion Colliders



RHIC
(BNL)



LHC
(Cern)



Nuclotron-Based Ion Collider Facility
(NICA)
JINR, Dubna, Russia



FAIR

(after A.A.Golubev / Hirscheegg-2017)

Dissociation-driven (*entropic*) phase transitions

Hydrogen

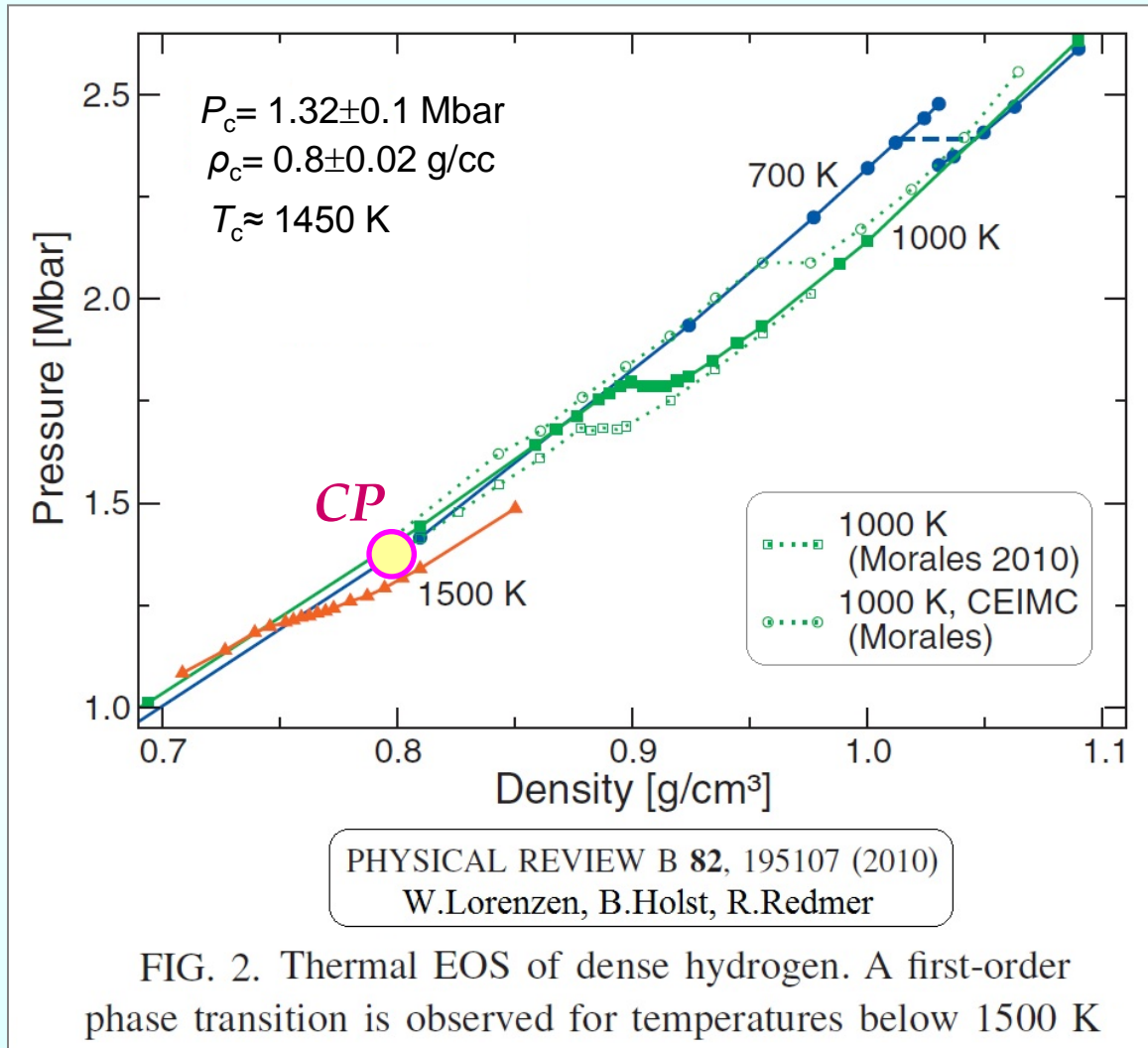


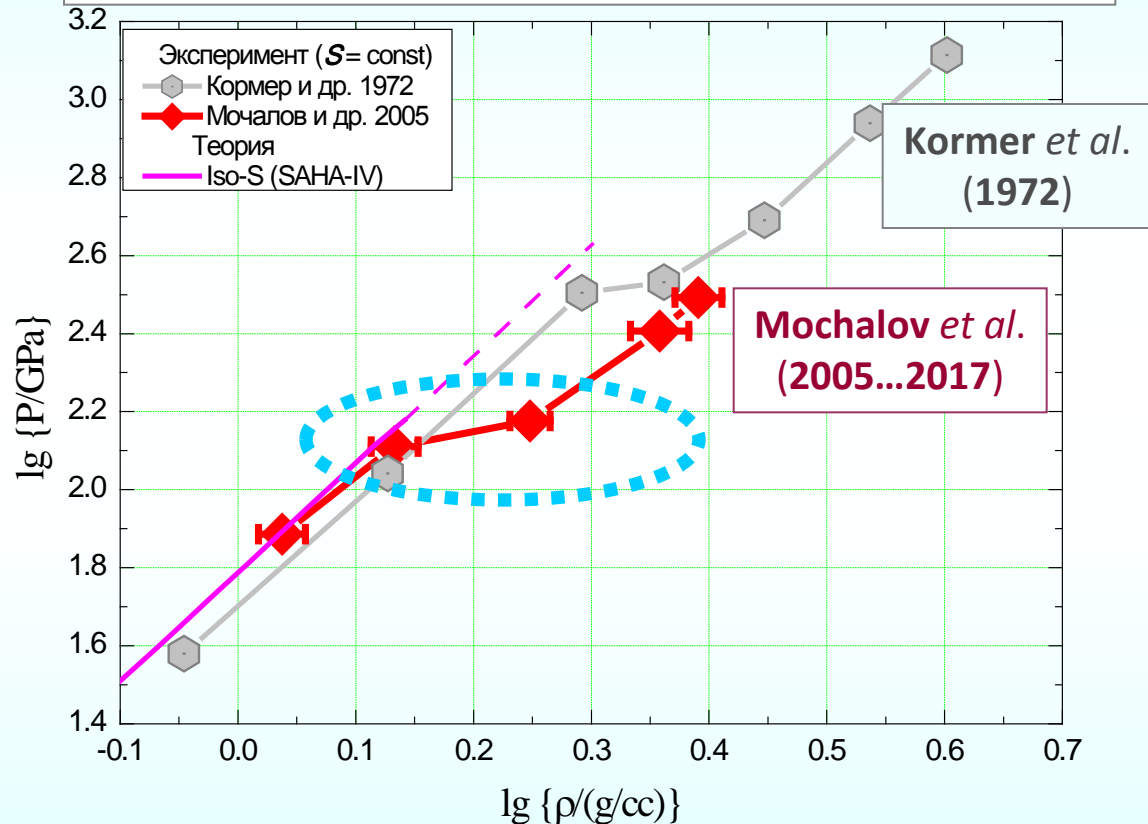
FIG. 2. Thermal EOS of dense hydrogen. A first-order phase transition is observed for temperatures below 1500 K

Anomalous order + crossing of isentropes !

Quasi-isentropic compression of deuterium up to the pressure 500 GPa

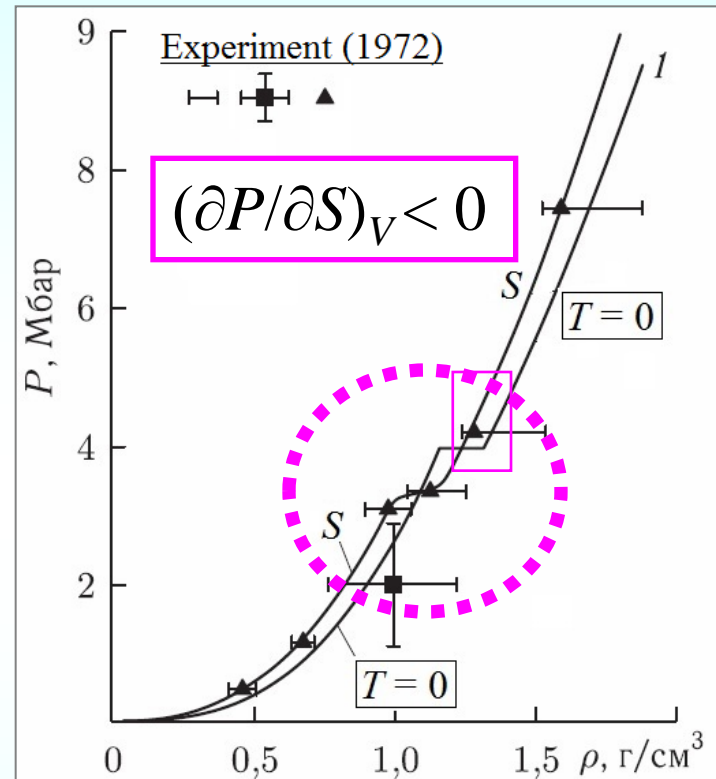
Experiments in VNIIEF (Sarov)

Density jump at quasi-isentropic compression



Fortov V., Mochalov M. *et al.* *Phys. Rev. Lett.* 99, 2007

Mochalov M., Il'kaev R., Fortov V. *et al.* *JhETP* 124, 2017

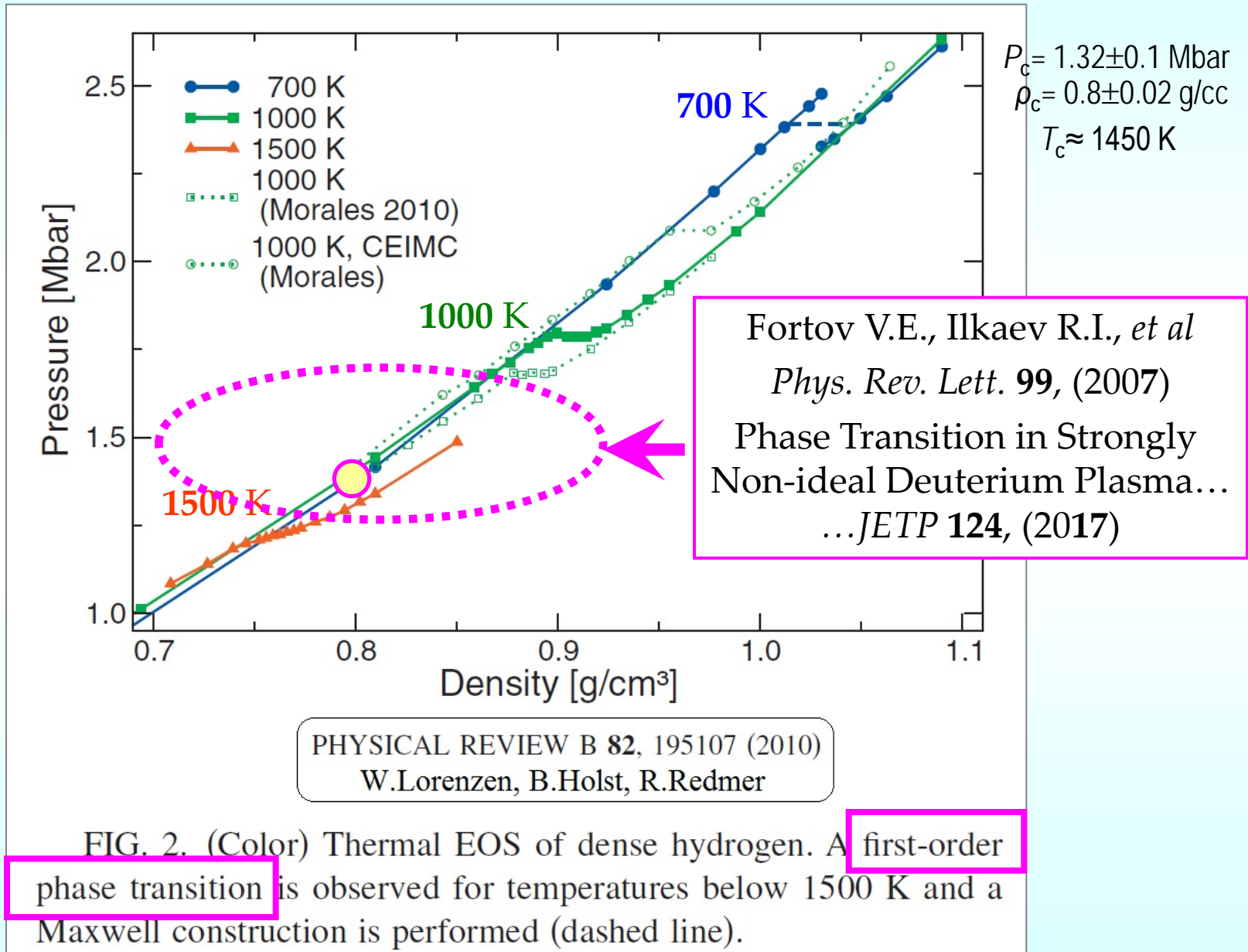


Фортвов В.Е. *Уравнения Состояния*
М.: Физматлит, 2013

Нулевые изотермы (1) и изэнтропы (2) молекулярного и металлического водорода [50]

Semiempirical EOS (VNIIEF)
Kopyshv & Khrustalev

Entropic fluid-fluid phase transition in H₂



*“...Так из смешенья стихий бесконечные сонмы созданий
странных и многообразных на вид происходят...”*

Lucretius (De rerum natura)

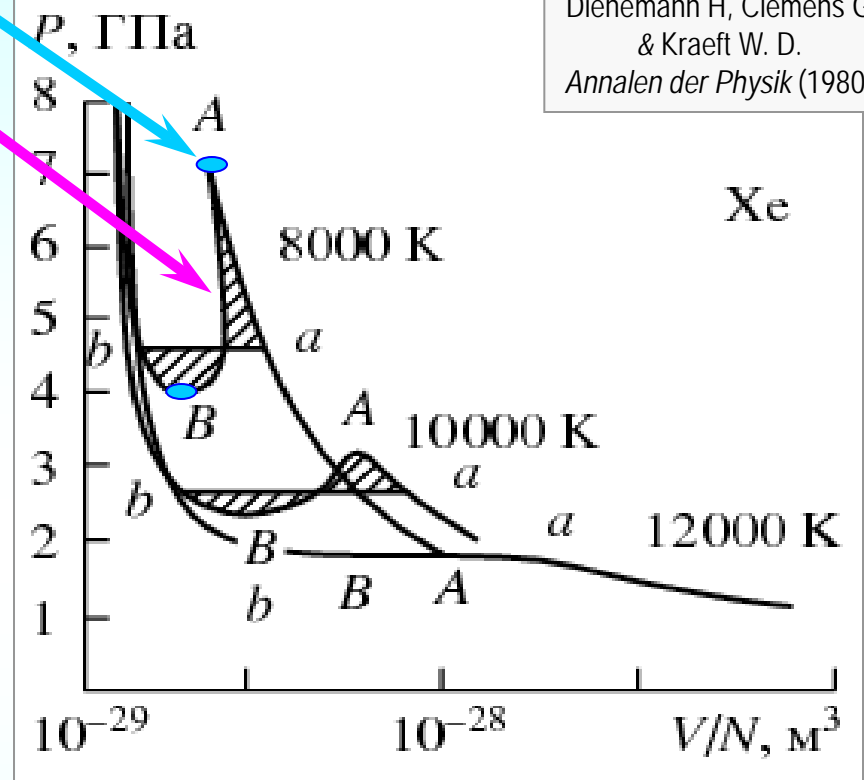
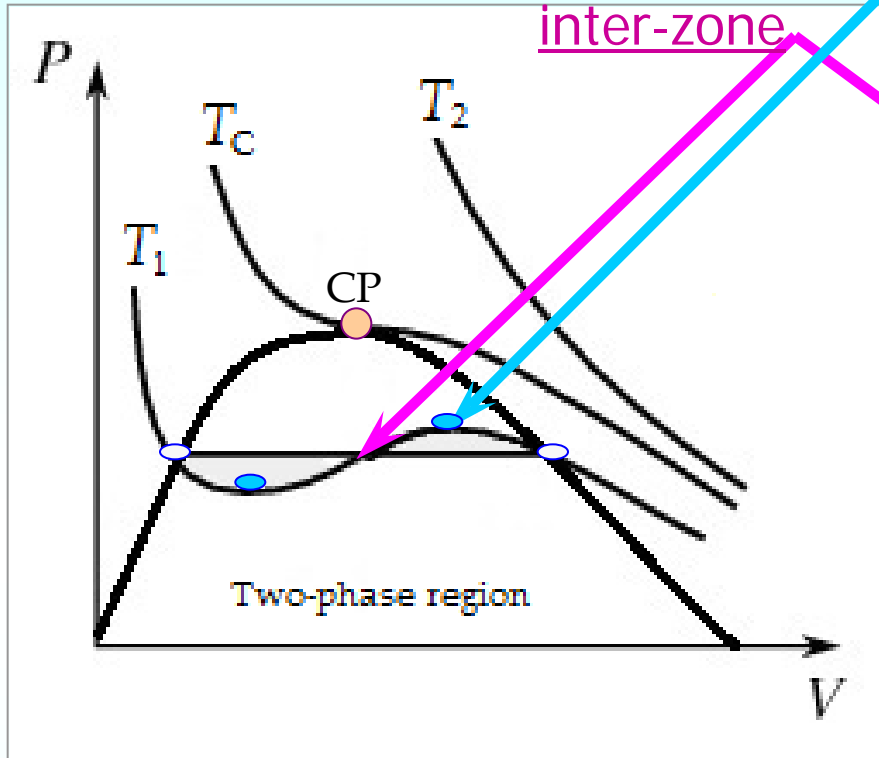
Anomalous structure
of **stable, unstable** *and* **metastable domains**
in **entropic phase transitions**

Enthalpic (GLPT) vs Entropic (PPT)

(continued)

spinodal points

Dienemann H, Clemens G,
& Kraeft W. D.
Annalen der Physik (1980)



VdW-like phase transition

Ionization-driven phase transition

NB!

(enthalpic PT)

$T \ll T_c$

(entropic PT)

Abnormal form of isotherms in spinodal region of entropic PT!
 { **beak-shaped spinodal point** (in contrast to VdW-PT) }

Third branch with $(\partial P/\partial V)_T < 0$ appears on isotherms in spinodal region!

Hot dense matter in “chemical” representation

Code SAHA-D

Gryaznov V., Iosilevskiy I. *J. Phys. A*, **42** (2009) *Thermodynamics of hot dense hydrogen*

Example – Non-ideal hydrogen plasma

$\Leftrightarrow \approx$ Nuclear statistical equilibrium

Model of composition: – $H_2, H, H^+, H_2^+, H_3^+, H^-, e^- \dots$

Effective Interaction Potentials – *Modified Coulomb, Short-range repulsion and attraction (\approx “excluded volume effect”)*

Electron degeneracy (in ideal-gas contribution and in screening length –
– Modified Debye screening)

Non-ideality corrections: – *Modified pseudopotential approach for Coulomb correction // Soft spheres app. for short-range repulsion // Simplified “Bound” correction for S-R attraction*

Helmholtz Free Energy minimization – *Complicated numerical algorithm*

Equilibrium composition

Thermodynamics (EoS)

Transport prop.

Opacity

Hydrodynamics of matter under extreme impact

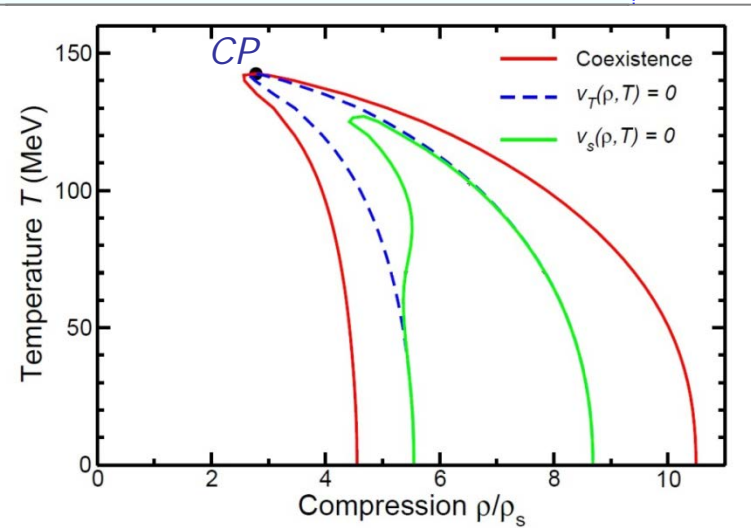
Chemical representation /EOS-code SAHA/

Gryaznov V., Iosilevskiy I. Fortov V. *Encyclopedia of Low-Temperature Plasmas* / Moscow, Fizmztlit (2004)

Hypothetical dissociation-driven (*entropic*) PT

Randrup J., *Phys. Rev. C*, **82**, (2010)

CP
Binodal
T-spinodal
S-spinodal

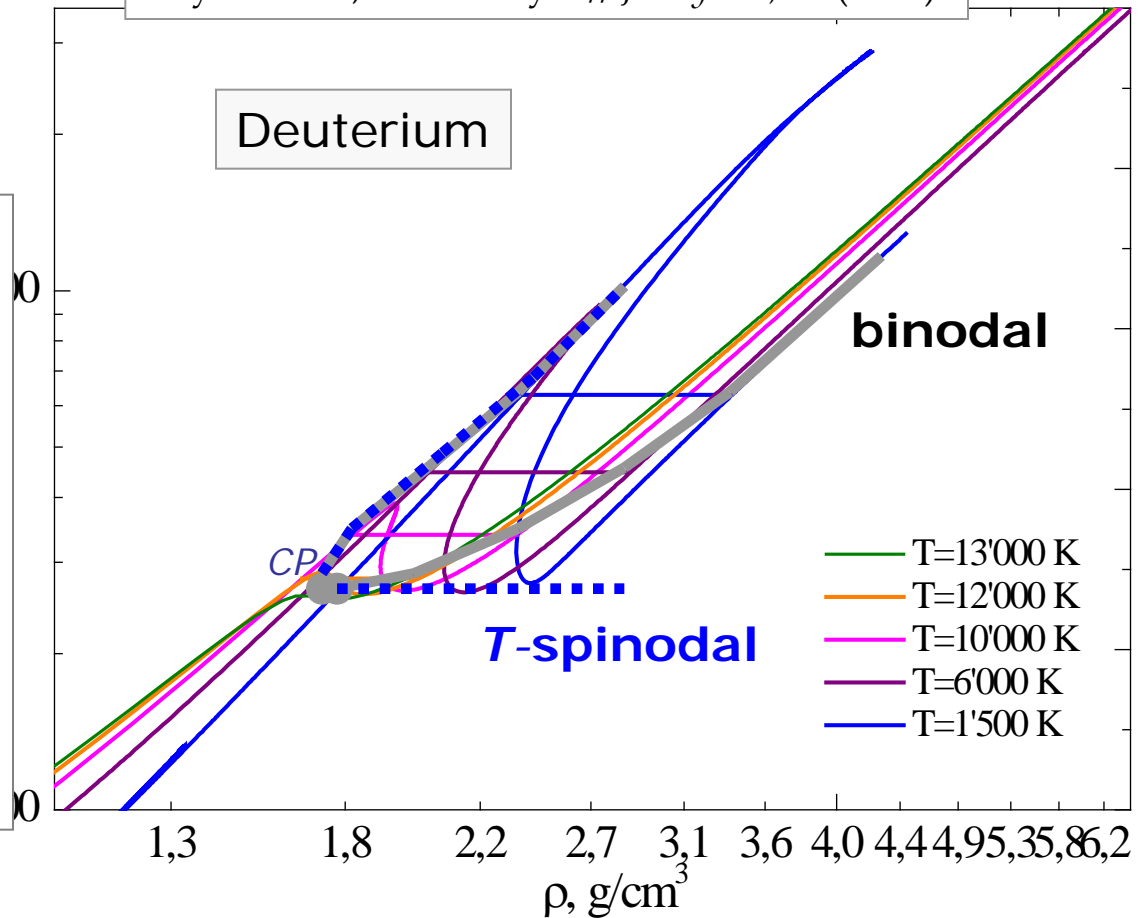


Randrup J. *Phys. Rev. C*, **82** (2010)
 Spinodal phase separation in relativistic nuclear

phase transition

Code SAHA-D

Gryaznov V., Iosilevskiy I. // *J. Phys. A*, **42** (2009)



Deuterium

binodal

T-spinodal

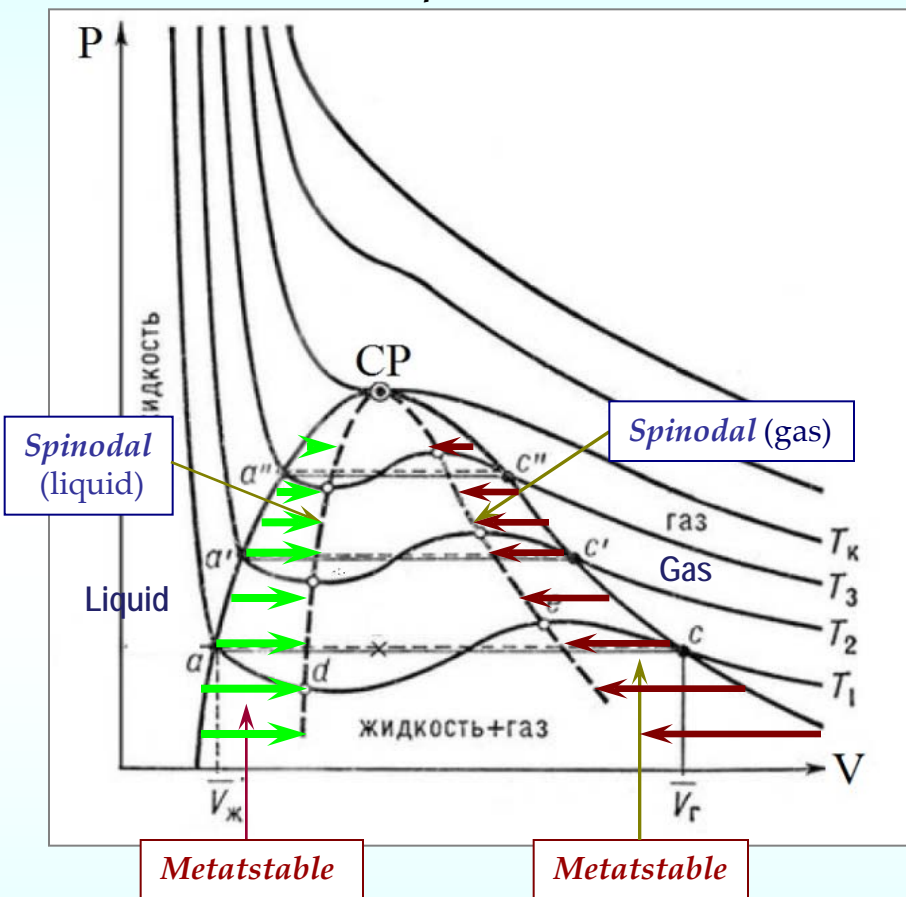
- T=13'000 K
- T=12'000 K
- T=10'000 K
- T=6'000 K
- T=1'500 K

NB! Iso-*T* spinodal $\{(\partial P/\partial V)_T = 0\}$ is located **outside** of **binodal**

Iso-*S* spinodal $\{(\partial P/\partial V)_S = 0\}$ is located **outside** of **iso-*T* spinodal!**

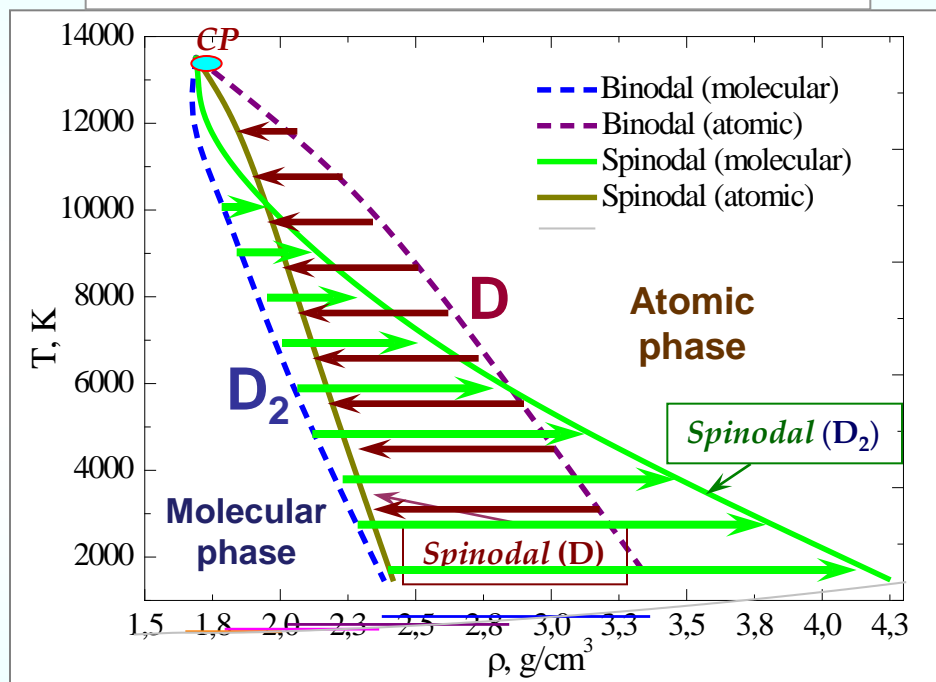
Anomalous topology of binodals and spinodals in the two-phase region of entropic phase transition ($T - \rho$ diagram)

VdW (enthalpic) Phase Transition



Dissociation-driven (entropic) Phase Transition in hydrogen

Code SAHA-D
Gryaznov V., Iosilevskiy I., *J. Phys. A*, **42** (2009)



"Night bat" structure of metastable "wings"

NB!

Abnormal features of entropic phase transition are due to multi-layered structure of thermodynamic surfaces!

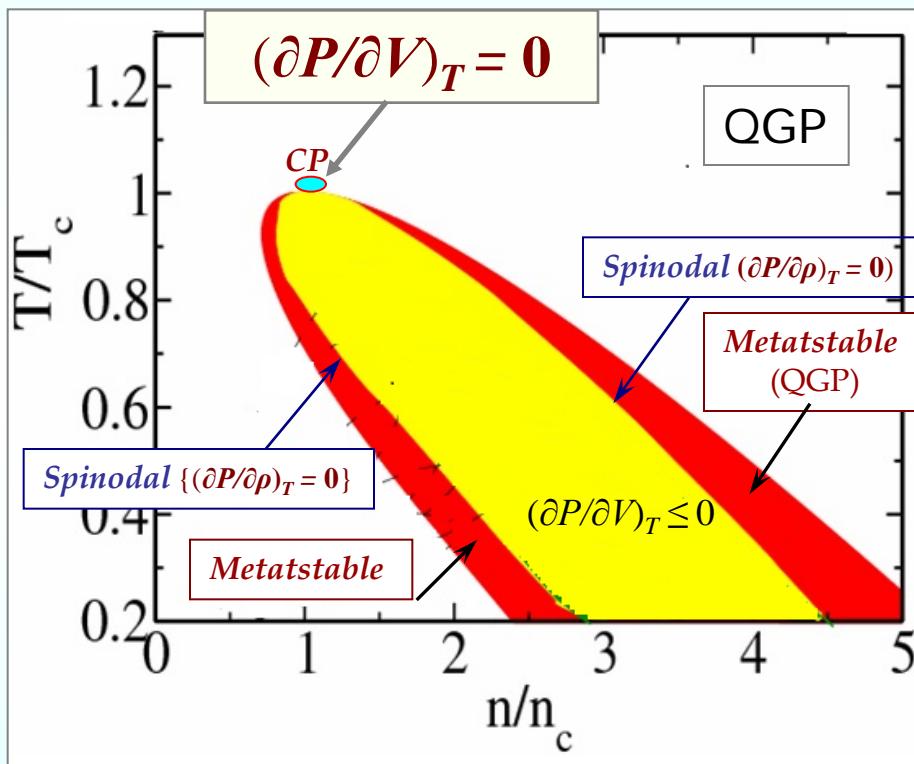
Anomalous features of entropic phase transition

(due to multi-layered structure of thermodynamic surfaces !)

($T - \rho$ diagram)

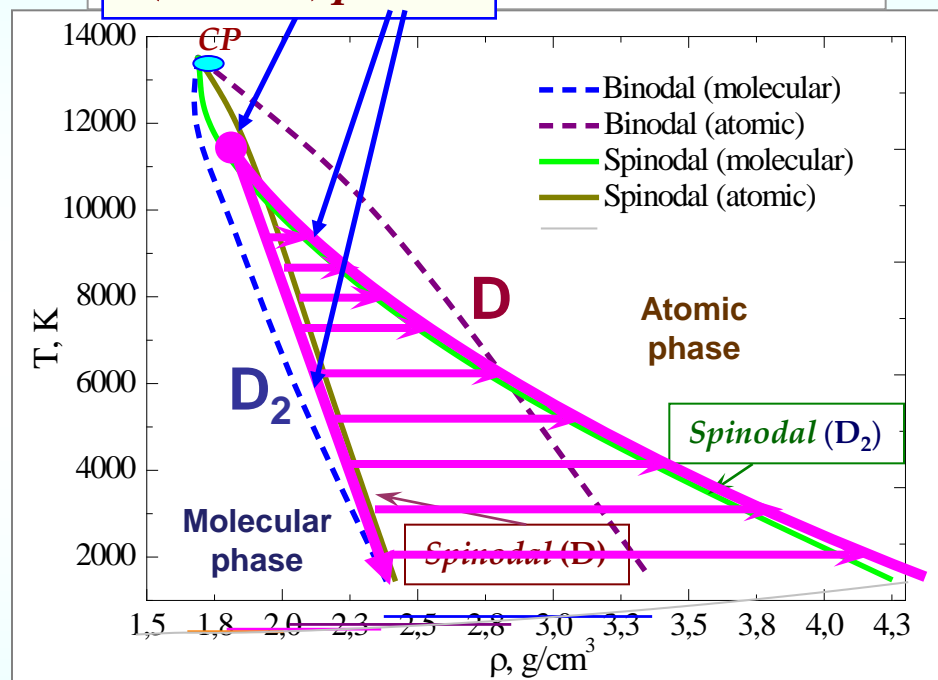
Quark-Hadron Phase Transition

After Vladimir Skokov, *Int. Conf. "Prerow-2009"*



Dissociation-driven Phase Transition

(MHA-D) $(\partial P/\partial V)_T = \infty$ // *J. Phys. A*, 42 (2009)



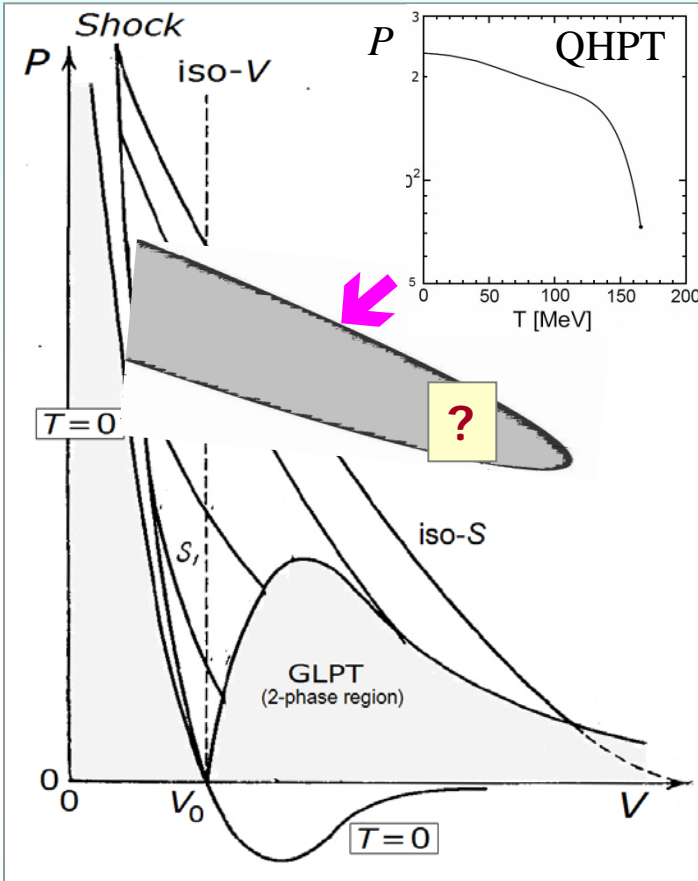
{ Iosilevskiy I. // (in preparation) }

NB !

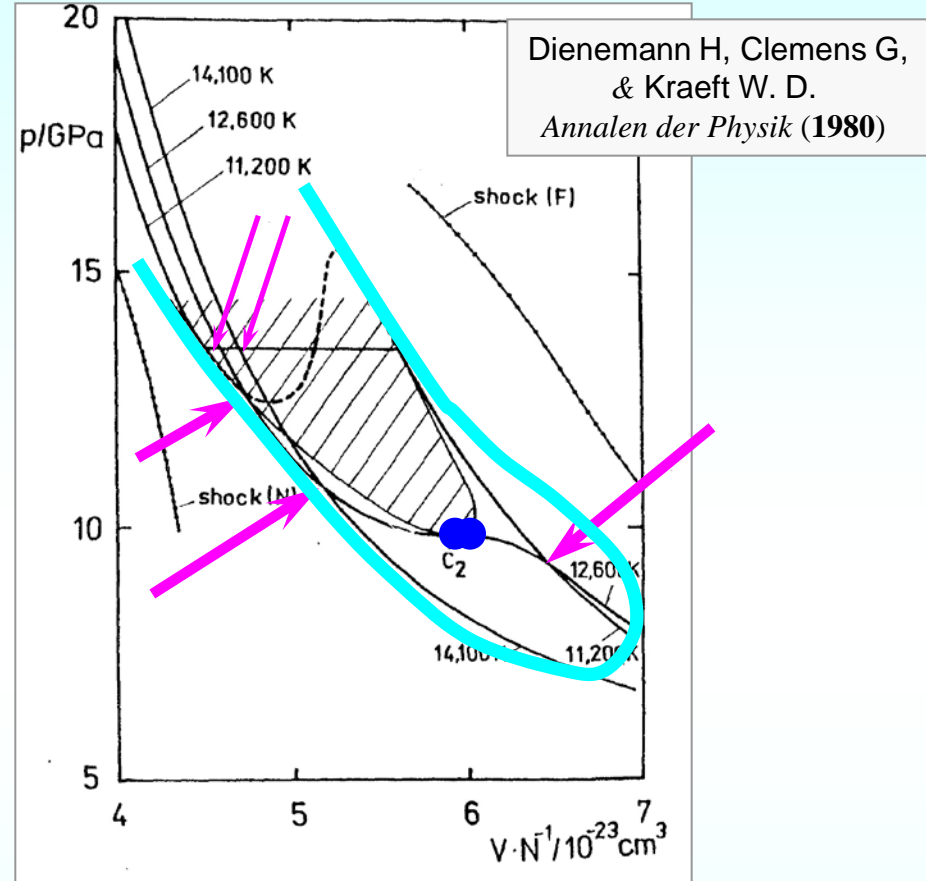
- New (additional) region of metastable state $\Leftrightarrow (\partial P/\partial V)_T < 0$
- New (additional) spinodal lines $\Leftrightarrow (\partial P/\partial V)_T = \infty !$
- New (additional) singular point (no-named still) $\Leftrightarrow (\partial P/\partial V)_T = \infty !$

Entropic Phase Transitions
and
Anomalous Thermodynamics Region

Ionization-driven (“plasma”) phase transition



$P(V)$



Enthalpic (gas-liquid) phase transition

Entropic (ionization-driven) phase transition in Xe

NB!

Abnormal order and **crossing** of **isotherms!**

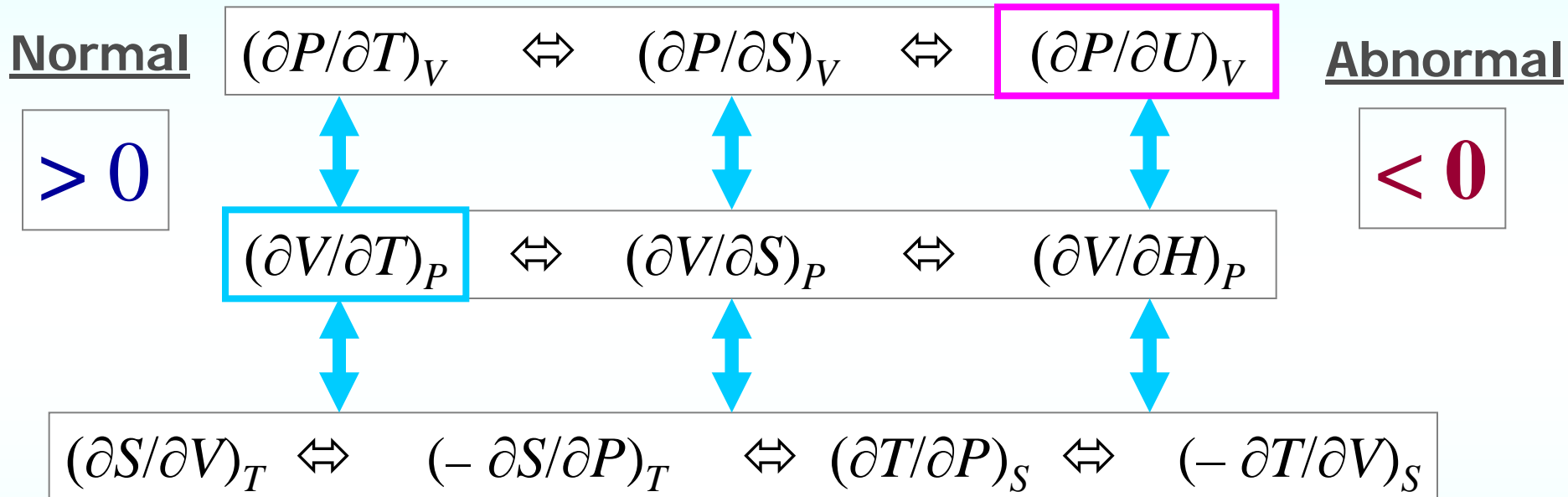
$$(\partial P / \partial T)_V < 0 \rightarrow V(\partial P / \partial U)_V < 0 \Leftrightarrow (\partial V / \partial T)_P < 0 \Leftrightarrow (\partial T / \partial P)_S < 0$$

In the **vicinity** of **entropic PT** one meets **abnormal thermodynamics!**

New **boundary** exists with **zero cross derivatives** – “**Zero-Boundary**” (ZB)!

Anomalous Thermodynamics Region - *ATR*

Normally positive cross derivatives became *negative simultaneously!*



$(\partial P/\partial U)_V$ - thermodynamic Gruneizen parameter, $Gr \equiv V(\partial P/\partial U)_V$

$(\partial V/\partial T)_P$ - thermal expansion coefficient, $\alpha_T \equiv V^{-1}(\partial V/\partial T)_P$

All these cross derivatives are equal to *ZERO simultaneously!*

Features of entropic phase transitions

(ionization- and dissociation-driven)

Entropic PT obeys to anomalous thermodynamics !

- *negative Gruneizen parameter* $V(\partial P/\partial U)_V < 0$
- *negative thermal pressure coefficient* $(\partial P/\partial T)_V < 0$
- *negative entropic pressure coefficient* $(\partial P/\partial S)_V < 0$
- *negative thermal expansion coefficient* $(\partial V/\partial T)_P < 0$
- *..... etc. etc.*
- *anomalous order of isotherms (!)*
- *anomalous order of isentropes (!)*
- *anomalous order of shock adiabats (!)*
- *..... etc. etc.*
- *anomalous form of isotherms in two-phase region*
- *anomalous interconnection of spinodals and binodals*
- *..... etc. etc.*

Anomalous thermodynamics *in the* neighborhood of entropic phase transition -- (*AT-region*)



$$(\partial P/\partial T)_V < 0$$



Abnormal order + crossing of isotherms !

$$(\partial P/\partial S)_V < 0$$



Abnormal order + crossing of isentropes !

$$= = \ll \gg = =$$



Shock adiabats go less steeper than isentropes !

$$V(\partial P/\partial U)_V < 0$$



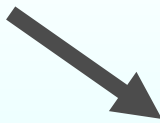
**Abnormal order + crossing of Hugoniot
(shock adiabats) !**

See e.g. A.Medvedev & R.Trunin, *Uspekhi (UFN)* **182** (2012) and V.Brazhkin's critique (=“=)

$$(\partial T/\partial P)_S < 0$$



**Abnormal decreasing (increasing) temperature
under isentropic compression (expansion) !**



**Abnormal conditions of convection
instability !**

See e.g.

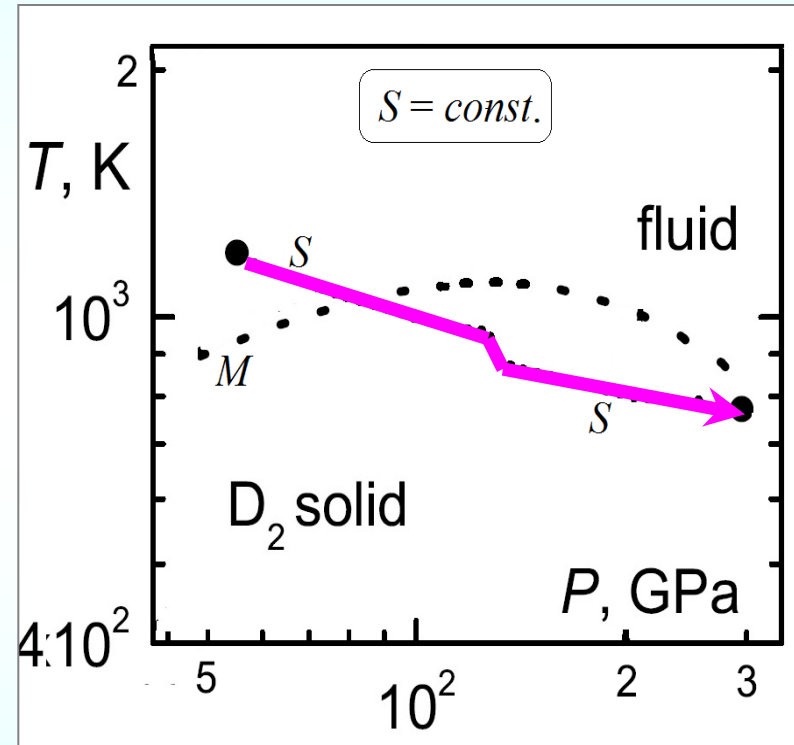
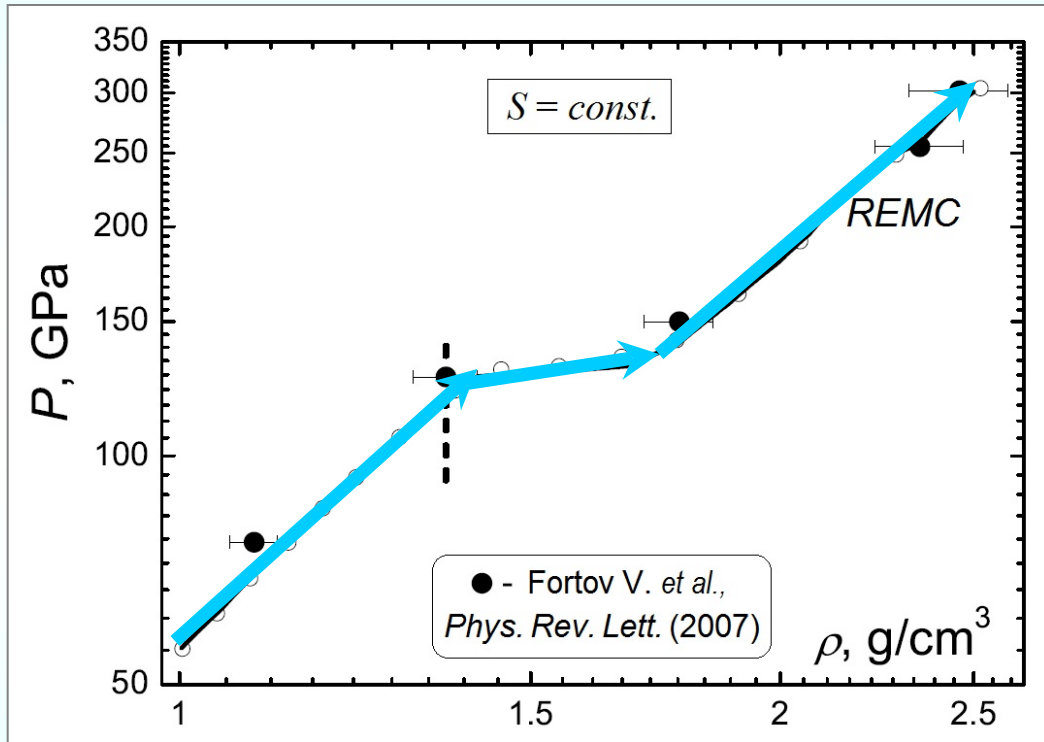
Hempel M., Heinemann O., Yudin A., Iosilevskiy I., Liebendoerfer M., Thielemann F-K.
Physical Review D, 94 (2016)

A Hot Third Family of Compact Stars and the Possibility of Core-Collapse Supernova Explosions

Reactive Ensemble Monte-Carlo - REMC

(*isentropic compression*)

Deuterium (2009)



J. Phys. A.: Math & Theor., **42**, (2009)
 Filinov V., Levashov P., Bonitz M., Botsan A., Fortov V.
*Monte-Carlo calculations of thermodynamic properties
 of deuterium under high pressures%*

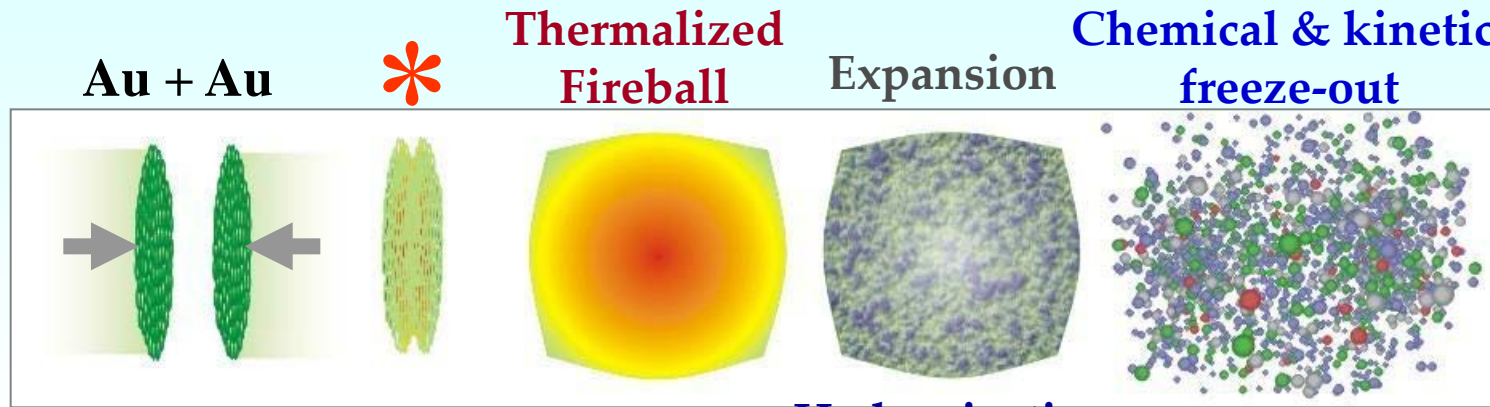
NB ! $(\partial T / \partial P)_S < 0$

**Температура S -сжимаемого
 дейтерия *падает*, а не растет !**

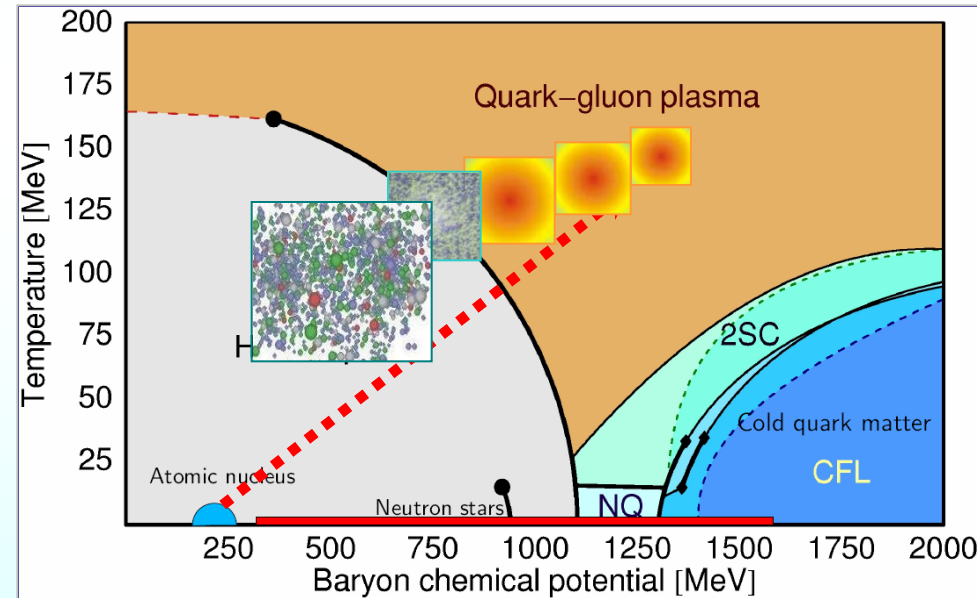
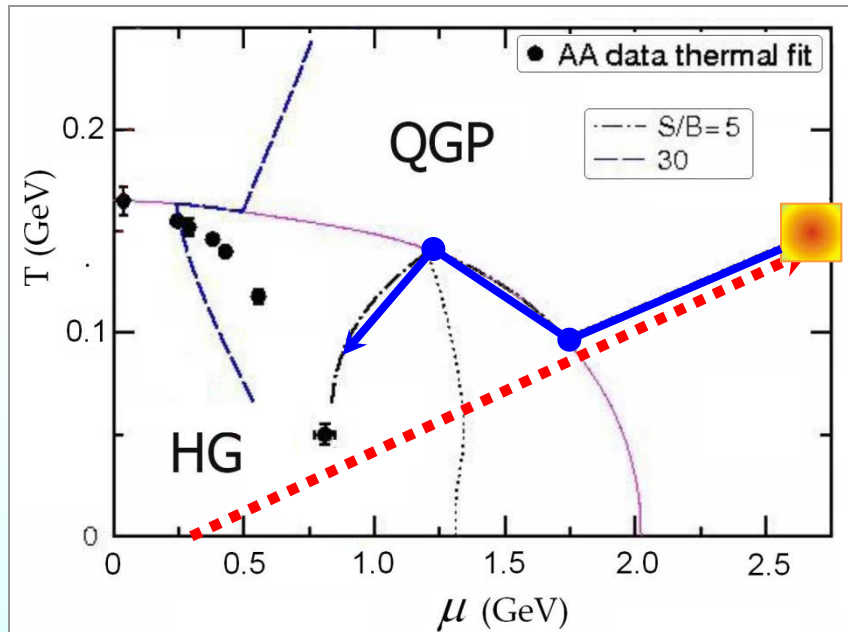
NB!

What are consequences of anomalous properties of entropic phase transitions for hydrodynamic stability of adiabatic processes: *shock compression and isentropic expansion* ?

Impact *and* fireball hydrodynamics *in* RHIC



Hadronization



L. Satarov, M. Dmitriev, I. Mishustin // [arXiv: 0901.1430](https://arxiv.org/abs/0901.1430)

Widely accepted phase diagram of matter

Shock adiabat of Renkin-Hugoniot-Taub

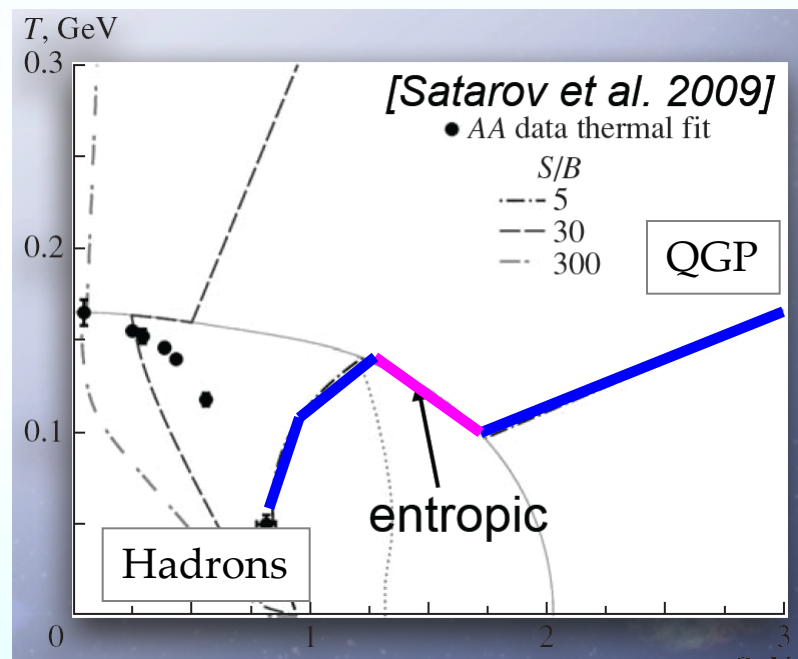
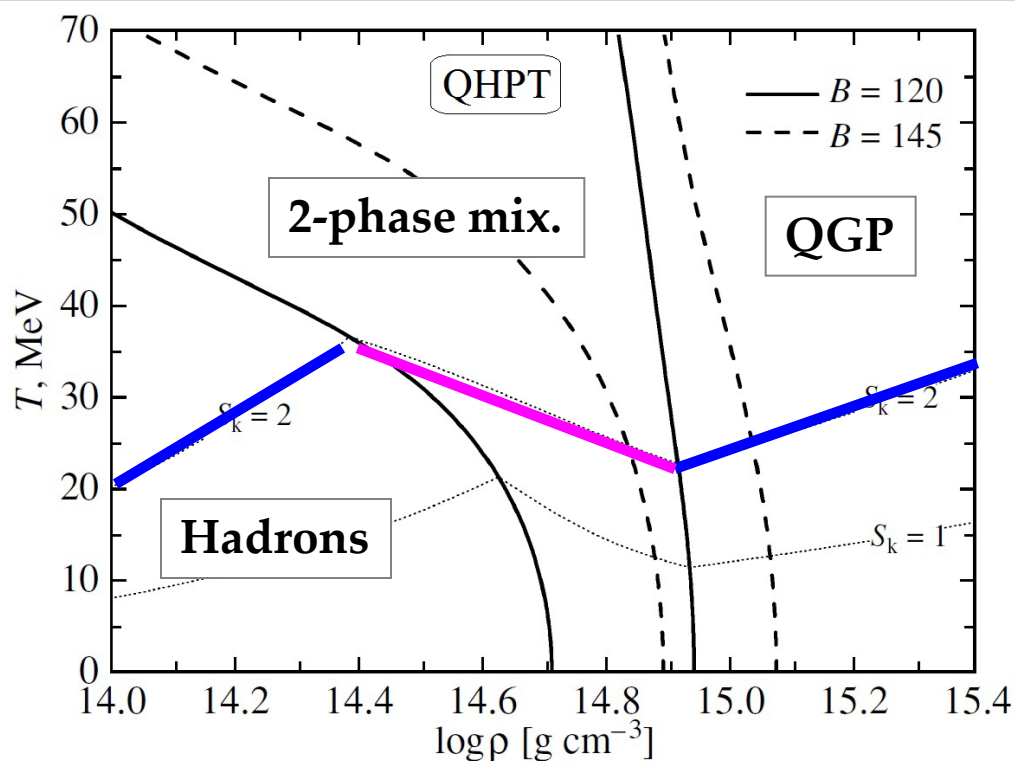
Landau L. & Lifshitz E., *Hydrodynamics*, (Moscow, 1986)

Negative Gruneizen parameter - - $Gr \equiv V(\partial P/\partial U)_V < 0$

Temperature fall under isentropic compression - - $(\partial T/\partial P)_S < 0$

Consequences of the *entropic* QCD PT:
Inverted convection in proto-hybrid stars

Yudin A., Hempel M., Nadyozhin D.
Razinkova T.L., *MNRAS*, 45,(2016)
Convection in hybrid stars



Matthias Hempel
Istanbul, 25.04.2016

Hempel M., Heinemann O., Yudin A., Iosilevskiy I., Liebendoerfer M. and Thielemann F.-K.
Third families of proto-compact stars, and the possibility of core-collapse supernova explosions
[arXiv:1511.06551](https://arxiv.org/abs/1511.06551)

Entropic phase transitions *are* always accompanied
by multilayered structure *of* thermodynamic surfaces

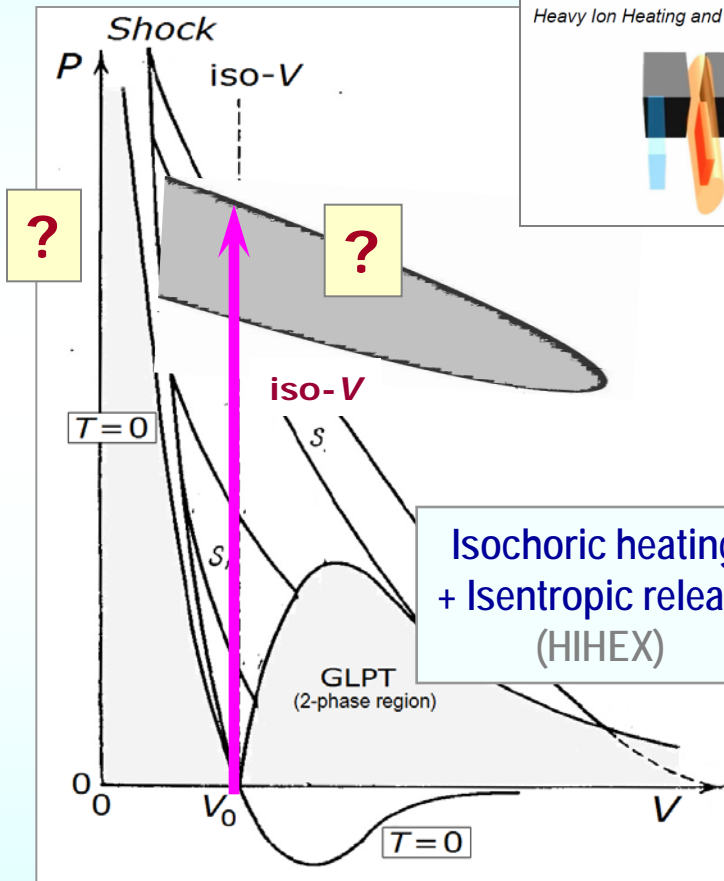
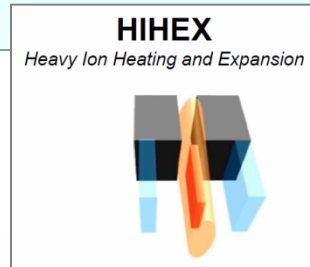
Multilayered structure *of* thermodynamic surfaces

$T(p, V), U(p, V), S(p, V) \dots$

in **entropic phase transition**

Multilayered structure of thermodynamic surfaces for entropic phase transitions

$T(p, V)$, $U(p, V)$, $S(p, V)$...

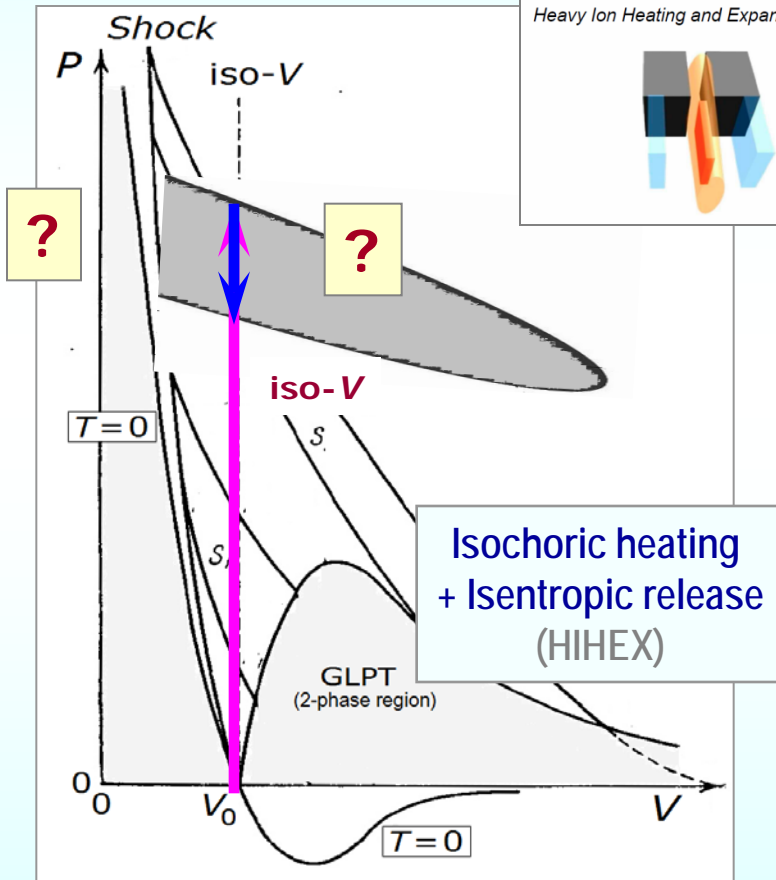
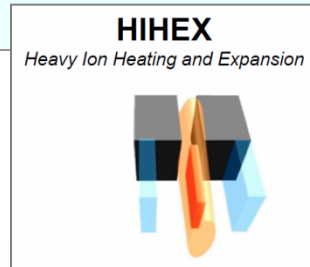


Isochoric heating
+ Isentropic release
(HIHEX)

Entropic phase transition and
enthalpic (*VdW-like*) one

Multilayered structure of thermodynamic surfaces for entropic phase transitions

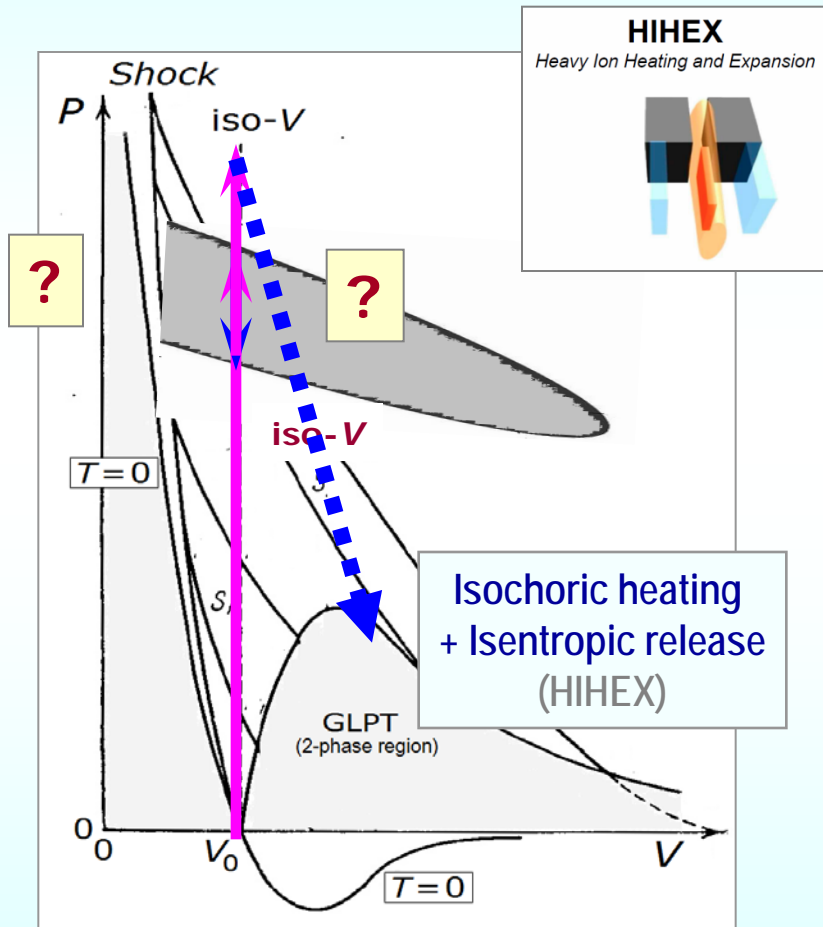
$T(p, V)$, $U(p, V)$, $S(p, V)$...



Entropic phase transition and
enthalpic (*VdW-like*) one

Multilayered structure of thermodynamic surfaces for entropic phase transitions

$T(p, V)$, $U(p, V)$, $S(p, V)$...



Entropic phase transition and
enthalpic (*VdW-like*) one

p

Melting H_1

Shock compression

Isentropic release

WDM

Plasma

HIB isochoric heating

Isentropic release

T_0

$\delta = const$

Solid

Liquid

CP

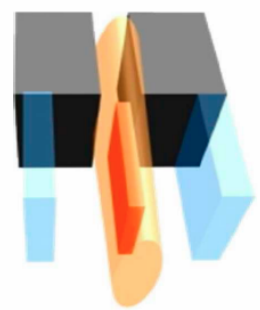
Gas

LG

17

HIHEX

Heavy Ion Heating and Expansion



- uniform quasi-isochoric heating of a large-volume dense target
- isentropic expansion in 1D plane or



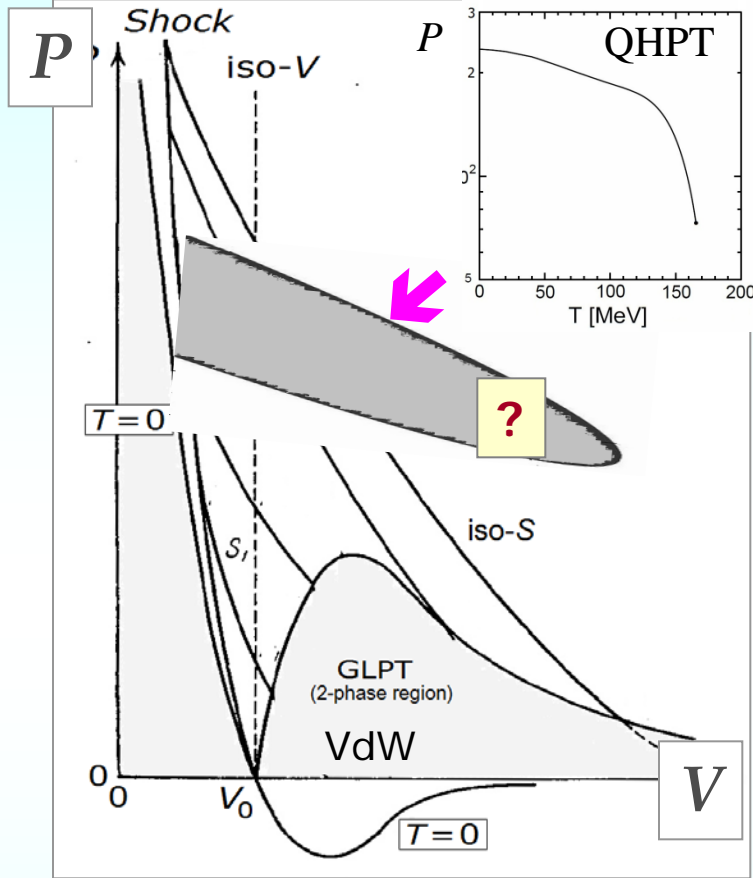
*Problem of anomalous thermodynamics
for entropic phase transitions*

Basic points

All entropic phase transitions are accompanied by thermodynamic **anomalies** in **two-phase** region

Most of entropic **fluid-fluid** phase transitions are accompanied by thermodynamic **anomalies** in area **nearby** the **critical point**

Ionization-driven (“plasma”) phase transition



Enthalpic (gas-liquid) phase transition

Entropic (ionization-driven) phase transition in Xe

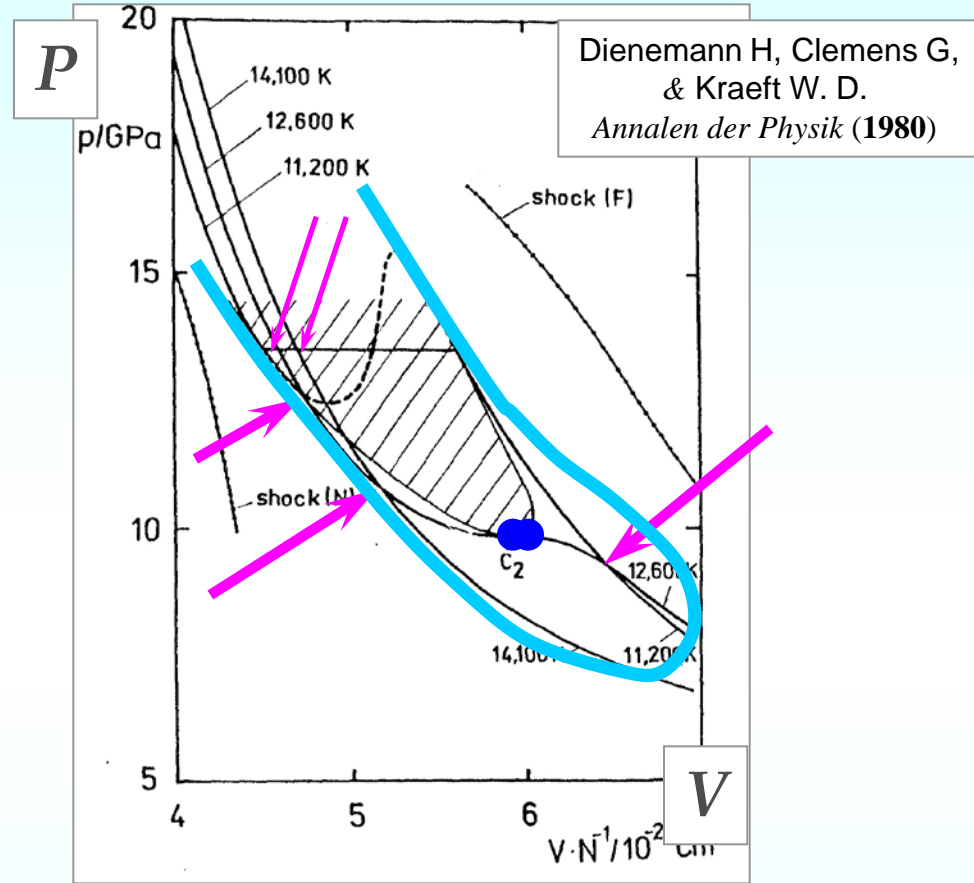
NB!

Abnormal order and **crossing** of **isotherms!**

$$(\partial P / \partial T)_V < 0 \rightarrow (\partial V / \partial T)_P < 0 \Leftrightarrow V(\partial P / \partial U)_V < 0 \Leftrightarrow (\partial T / \partial P)_S < 0$$

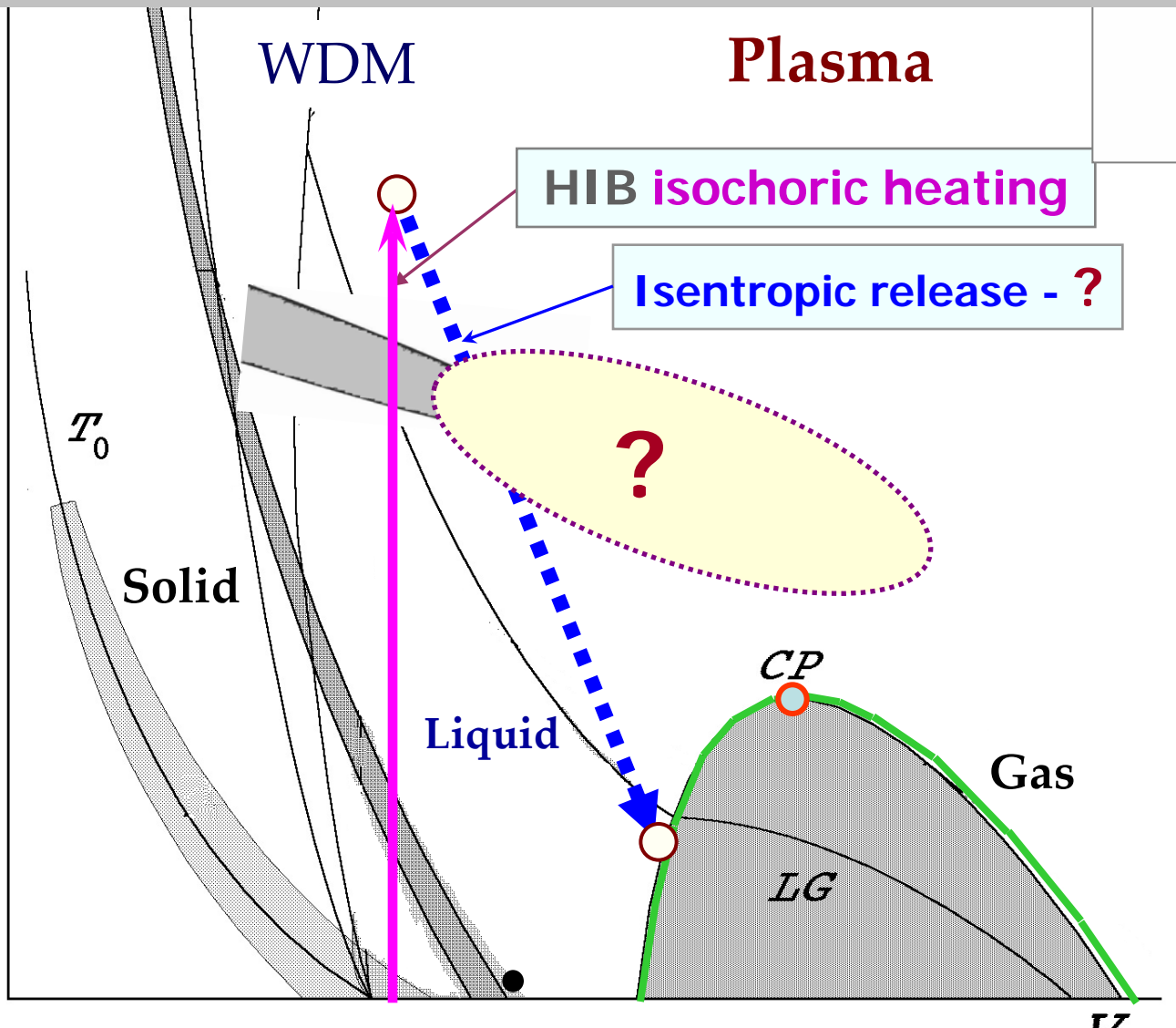
In the **vicinity** of **entropic PT** one meets **abnormal thermodynamics!**

New **boundary** exists with **zero cross derivatives** – “**Zero-Boundary**” (ZB)!



Entropic fluid-fluid phase transitions are accompanied by thermodynamic anomalies in area nearby the critical point

sion

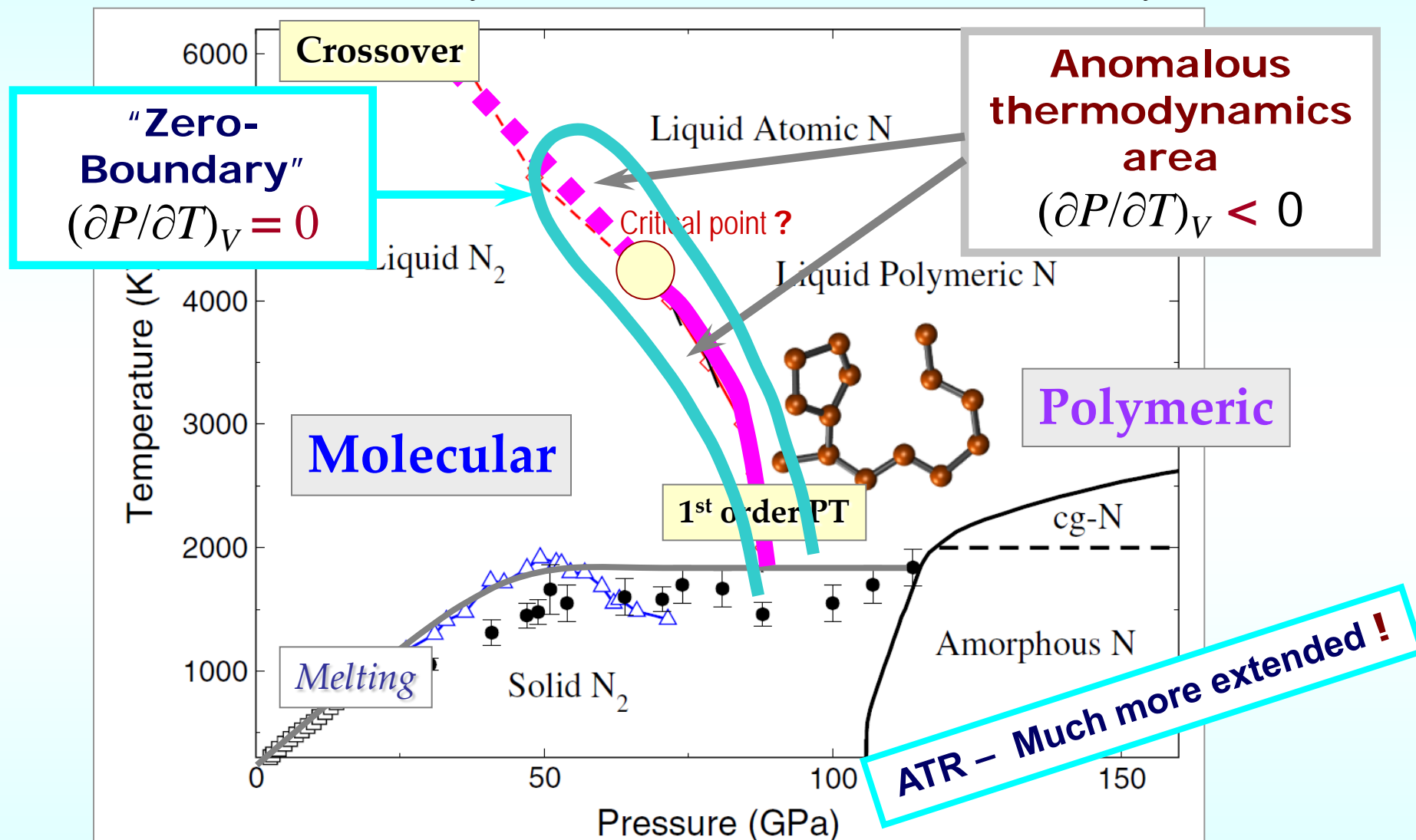


- uniform quasi-isochoric heating of a large-volume dense target
- isentropic expansion in 1D plane or



Entropy-driven fluid-fluid phase transitions (N_2)

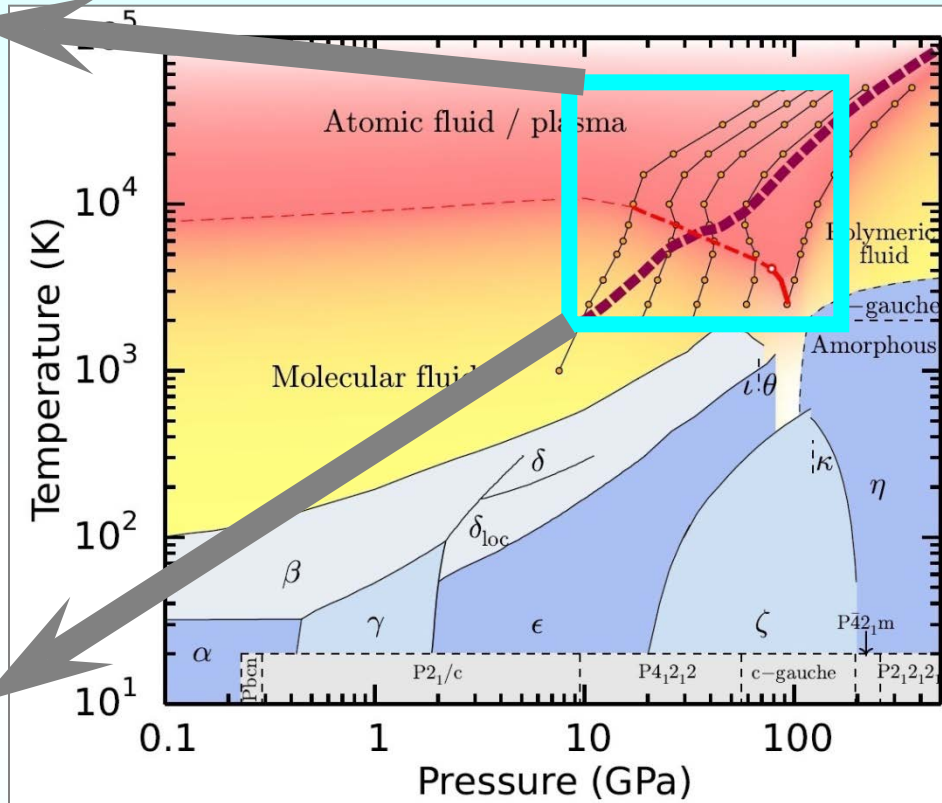
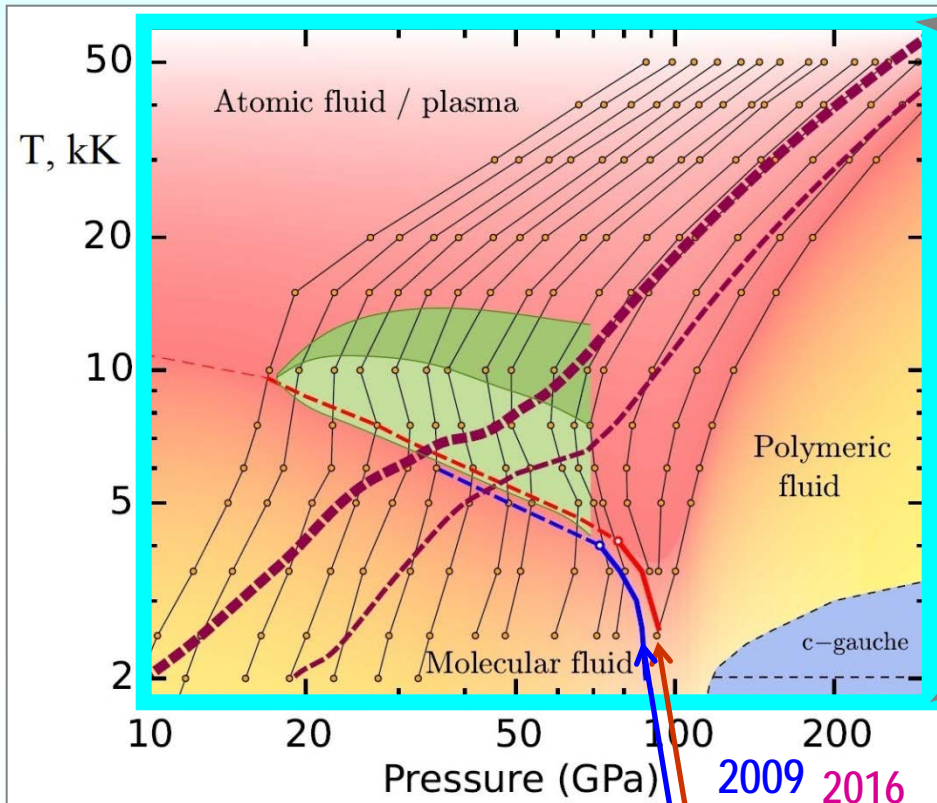
Boates B., Bonev S. *Phys. Rev. Lett.* **102** (2009)/ Quantum Molecular Dynamics



In the **vicinity** of **entropic PT** one meets **anomalous thermodynamics !**
New **boundary** exists with **zero cross derivatives** – **"Zero-Boundary"** (ZB)!

Phase Diagram of Warm Dense Nitrogen

(*ab initio approach*) Driver & Militzer, *Phys.Rev.B* 93 (2016)



● 1st order *fluid-fluid* phase transition
 ● $T_c = 4100 \text{ K}, P_c = 78 \text{ GPa}$

■ Liquid Hugoniot ($\rho_0 = 0.808 \text{ g/cc}$)
 ■ Solid Hugoniot ($\rho_0 = 1.035 \text{ g/cc}$)

Non-standard sign of $(\partial P/\partial T)_V < 0$!

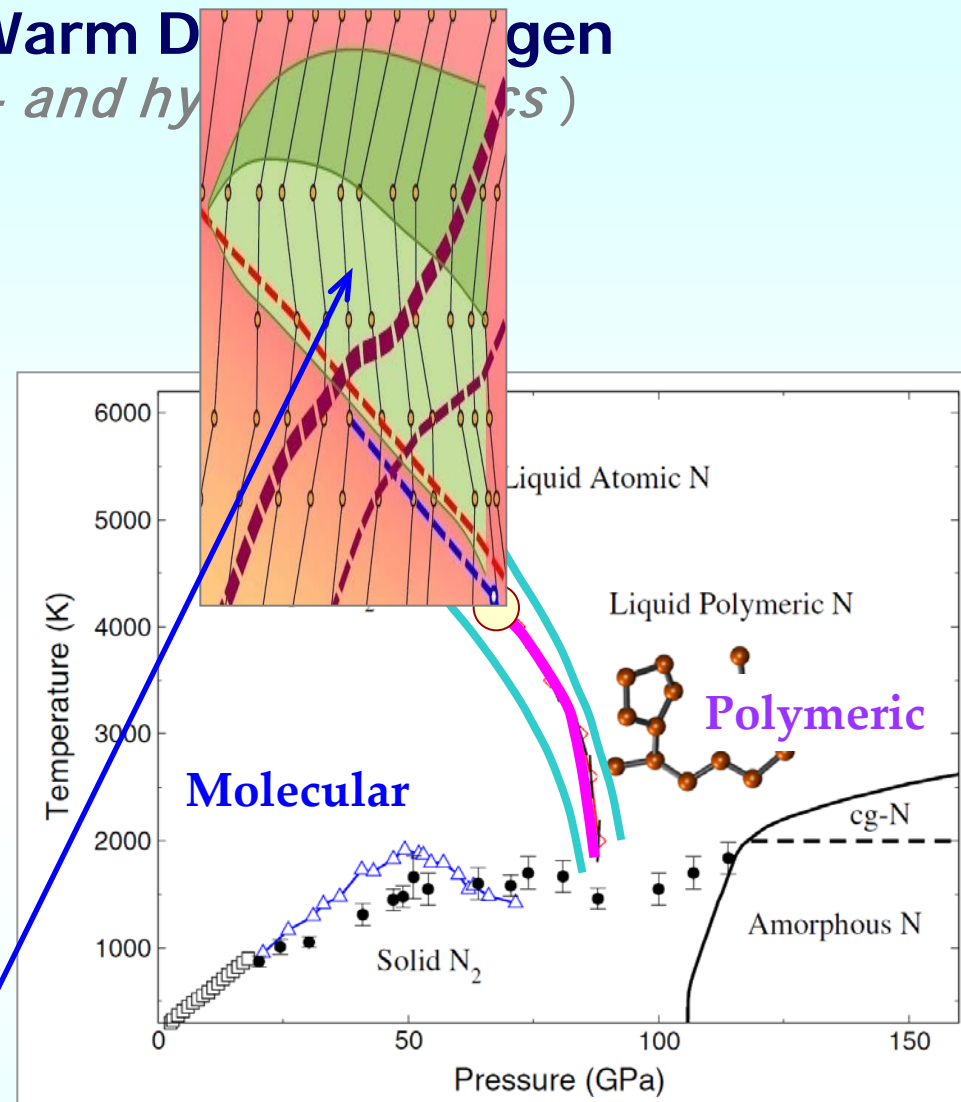
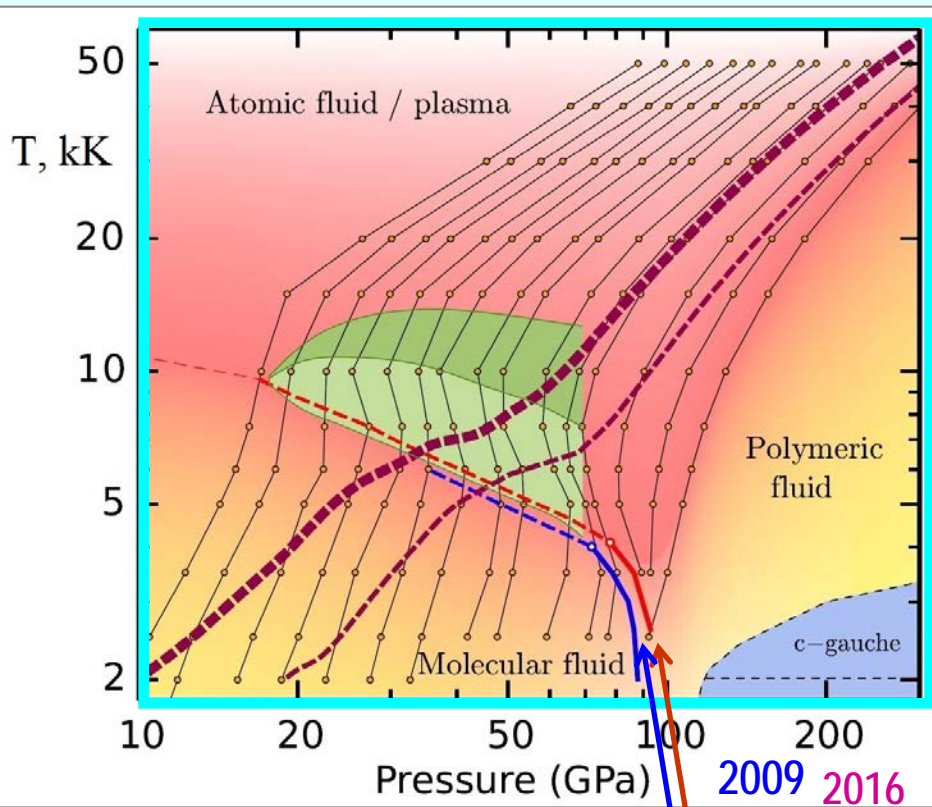
Driver K.P., Militzer B.
 First-Principles Equation of State Calculations of Warm Dense Nitrogen
 arXiv:1601.05787

Iosilevskiy / Hirschegg-2013
 "Anomalous Thermodynamics"

$Gr \equiv (\partial P/\partial U)_P < 0$ → $(\partial V/\partial T)_P < 0$

$(\partial T/\partial P)_S < 0$ [arXiv:1504.0585](https://arxiv.org/abs/1504.0585)

Phase Diagram of Warm Dense Nitrogen (anomalous thermo- and hydrodynamic properties)



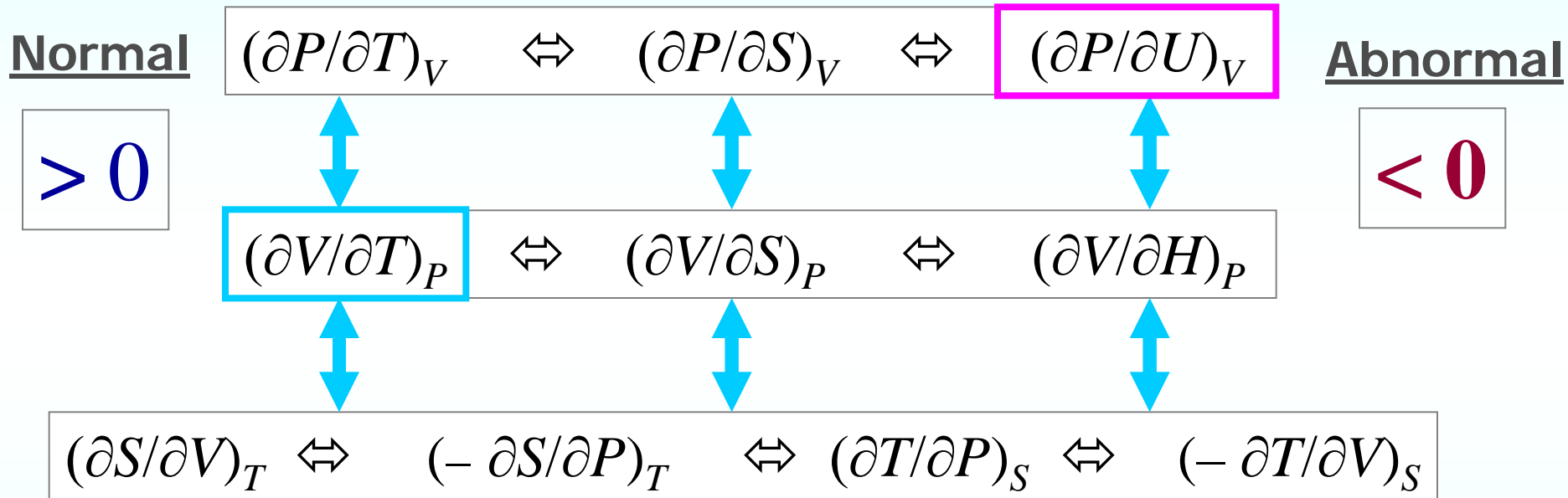
- (2016) 1st order *fluid-fluid* PT
- (2009) $T_c \approx 400$ K, $P_c = 70$ GPa

Anomalous thermodynamics area
 $(\partial P / \partial T)_V < 0$ & $(\partial T / \partial P)_S < 0$

- Liquid Hugoniot ($\rho_0 = 0.808$ g/cc)
- - - Solid Hugoniot ($\rho_0 = 1.035$ g/cc)

Anomalous Thermodynamics Region – *ATR*

Normally positive cross derivatives became *negative simultaneously!*

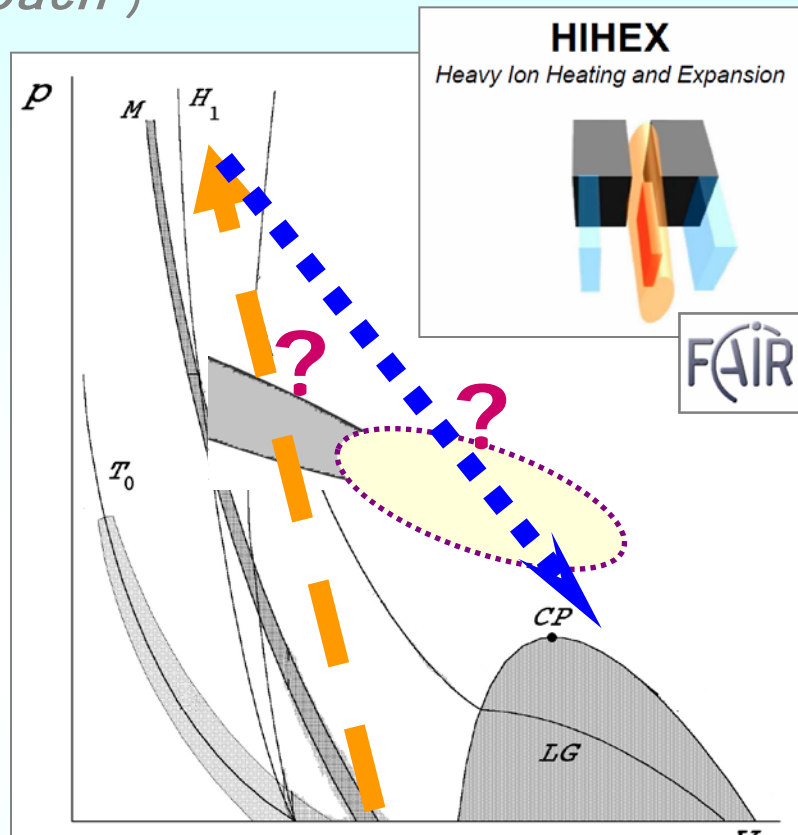
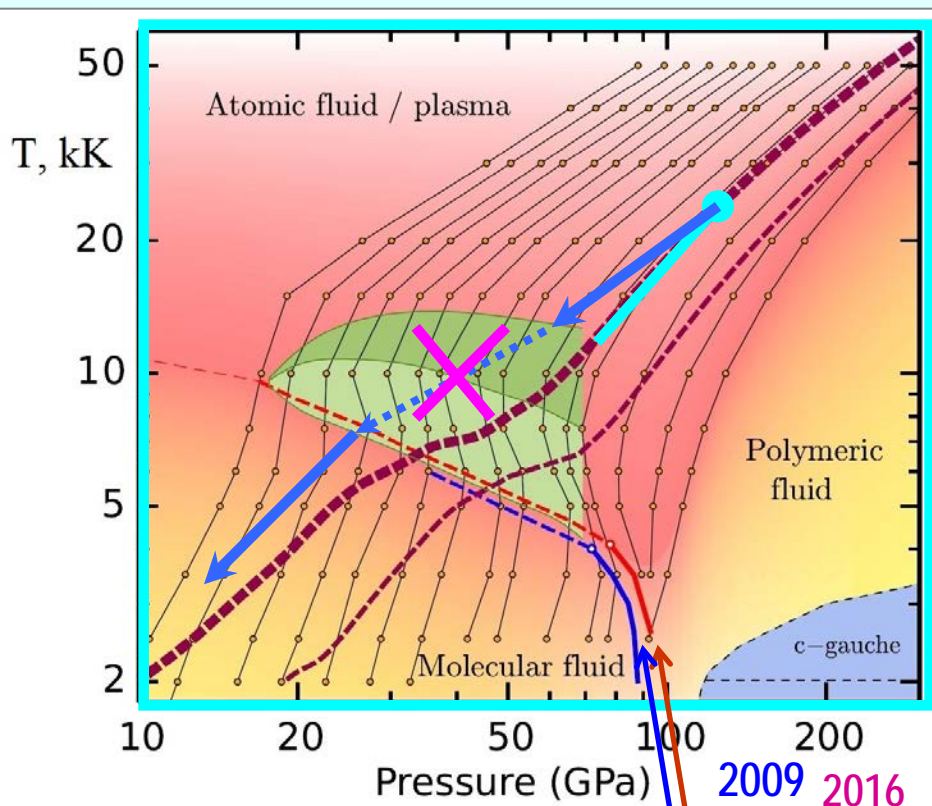


$(\partial P/\partial U)_V$ - thermodynamic Gruneizen parameter, $Gr \equiv V(\partial P/\partial U)_V$

$(\partial V/\partial T)_P$ – thermal expansion parameter, $\alpha_T \equiv V^{-1}(\partial V/\partial T)_P$

Anomalies in Isentropic Expansion of Warm Dense Nitrogen

(*ab initio approach*)



**Shock compression +
+ isentropic expansion**

Iosilevskiy / Hirscheegg-2013
"Anomalous Thermodynamics"

● 1st order *fluid-fluid* phase transition
● $T_c = 4100 \text{ K}, P_c = 78 \text{ GPa}$

■ ■ ■ ■ ■ Liquid Hugoniot ($\rho_0 = 0.808 \text{ g/cc}$)
● ● ● ● ● Solid Hugoniot ($\rho_0 = 1.035 \text{ g/cc}$)

■ Non-standard sign of
 $(\partial P / \partial T)_V < 0$!

$$(\partial T / \partial P)_S < 0$$

NB !

**Nontrivial hydrodynamics of coming through
the zone of anomalous thermodynamics
of entropic phase transition**

Нетривиальная гидродинамика прохождения сквозь зоны аномальной термодинамики энтропийного
фазового перехода

Outlook-I

Inventory of hypothetical terrestrial phase transitions in real and “numerical” experiments and in modeling constructions:

Path Integral + MC , Density Functional Theory + MD, Wave-Packets + MD,...

Hydrodynamic features for adiabatic flow in matter with anomalous thermodynamics ($Gr < 0, \dots$)

Topology of phase boundaries in meeting point of entropic phase transitions (*triple point, quadruple point etc.*)

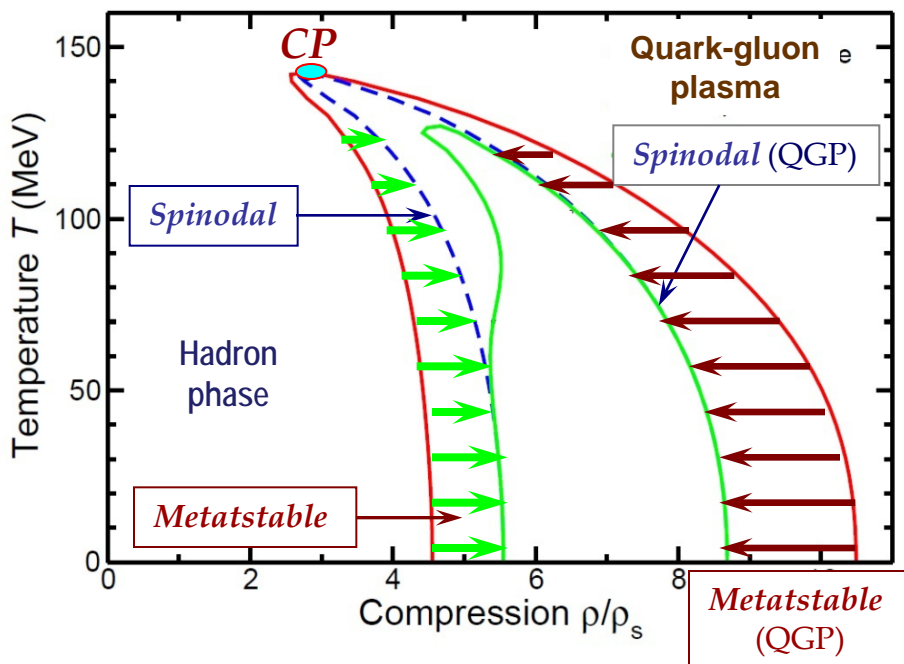
Entropic phase transitions at the “cold curve” (*isotherm $T = 0$*)

Non-congruentness and entropic phase transitions ?

Anomalous topology of binodals and spinodals in the two-phase region of entropic phase transition ($T-\rho$ diagram)

Model of Quark-Hadron Phase Transition

Jorgen Randrup, *Int. Conf. CPOD-2010* (Dubna)

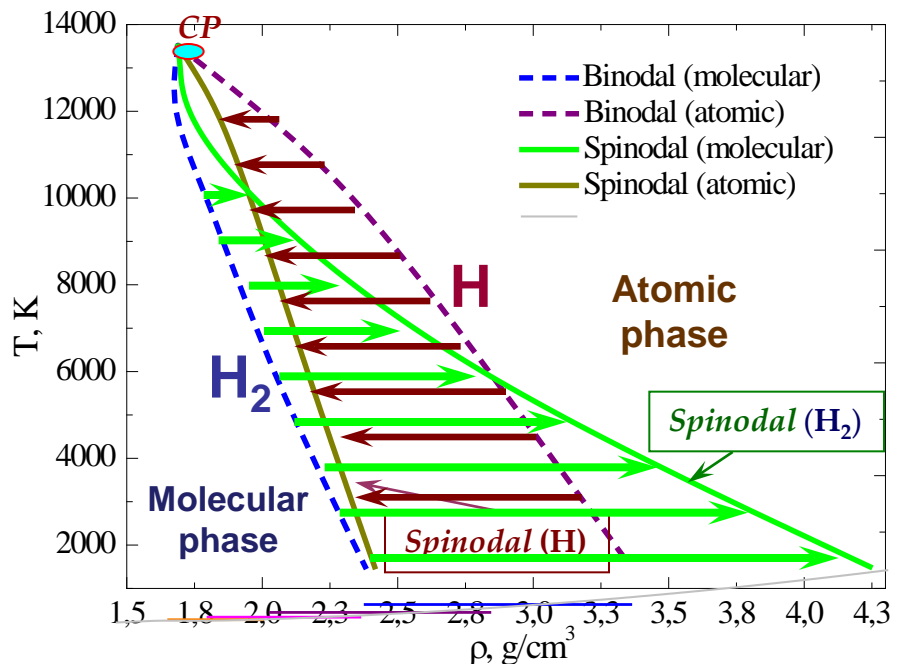


VdW-like structure of metastable zones

Dissociation-driven phase transition in hydrogen

Code SAHA-D

Gryaznov V., Iosilevskiy I. // *J. Phys. A*, 42 (2009)



"Night bat" structure of metastable "wings"

NB!

Two competing variants of structure of stable and metastable regions in quark-hadron phase transition

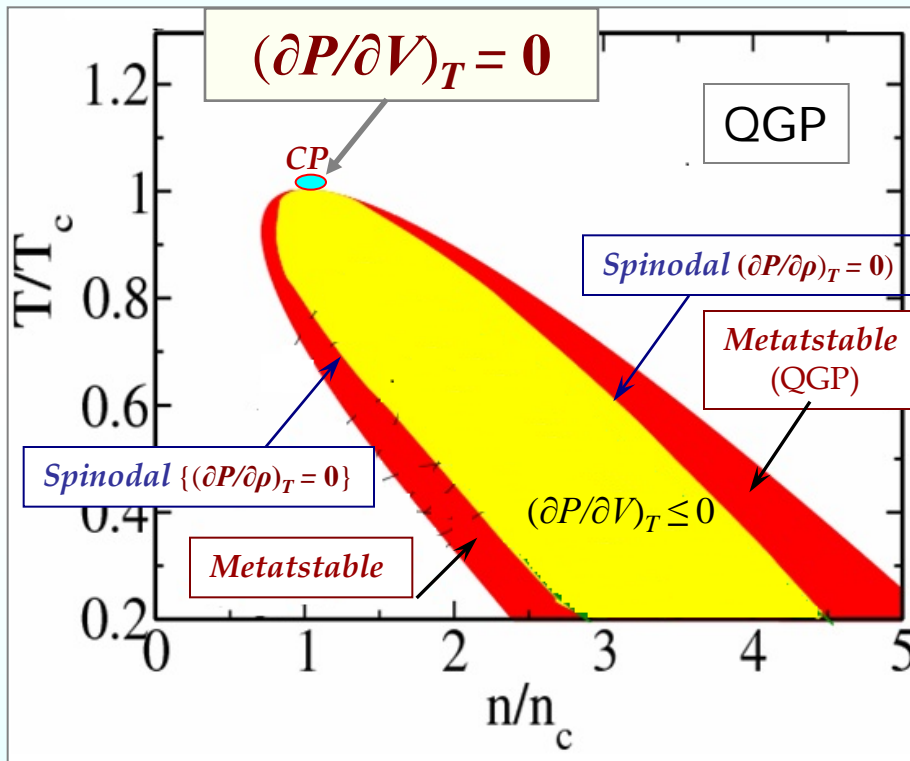
Anomalous features of entropic phase transition

(due to multi-layered structure of thermodynamic surfaces !)

($T - \rho$ diagram)

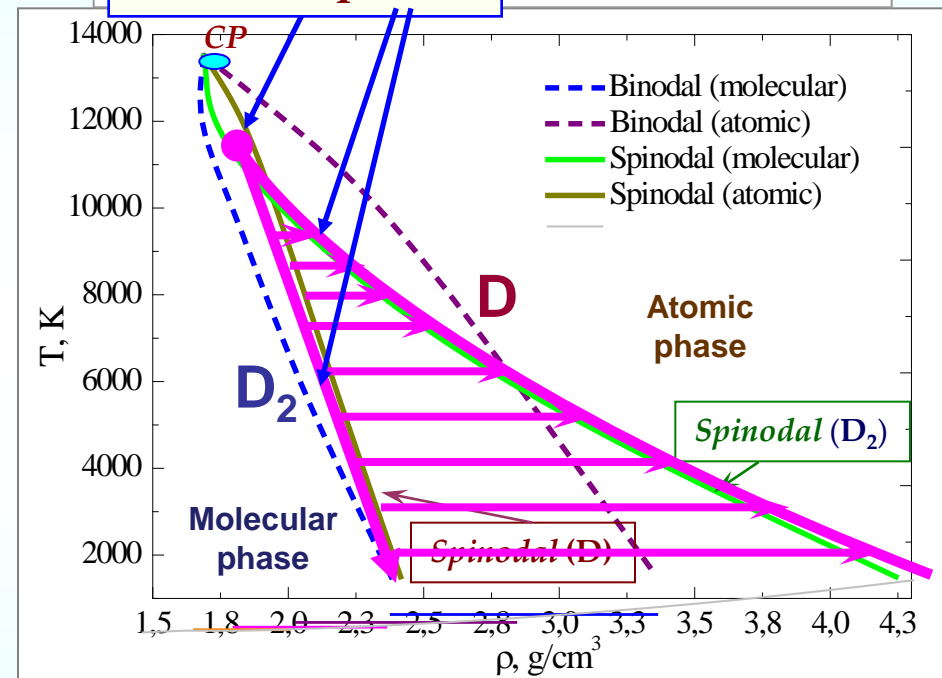
Quark-Hadron Phase Transition

After Vladimir Skokov, *Int. Conf. "Prerow-2009"*



Dissociation-driven Phase Transition

(MHA-D) // *J. Phys. A*, 42 (2009)
 $(\partial P/\partial V)_T = \infty$



NB !

New (additional) region of metastable state $\Leftrightarrow (\partial P/\partial V)_T \leq 0$

New (additional) singular point (no-named still) $\Leftrightarrow (\partial P/\partial V)_T = \infty !$

{ Iosilevskiy I. // (in preparation) }

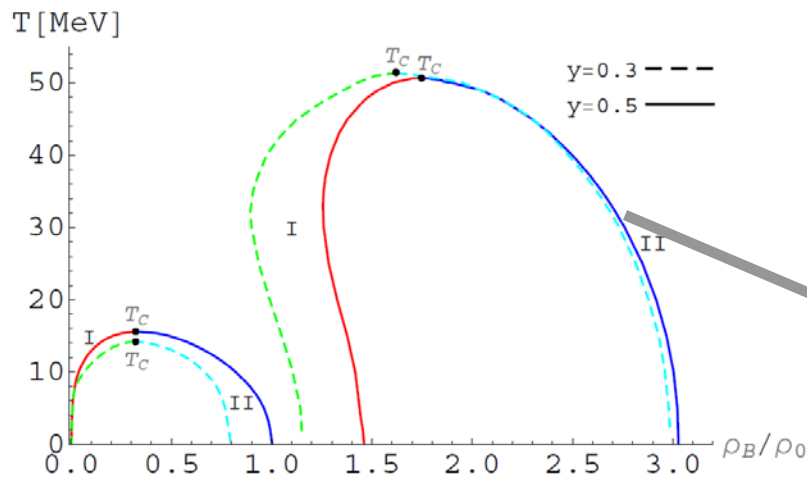
Outlook-I

Inventory of new phase transitions in simplified models

Example

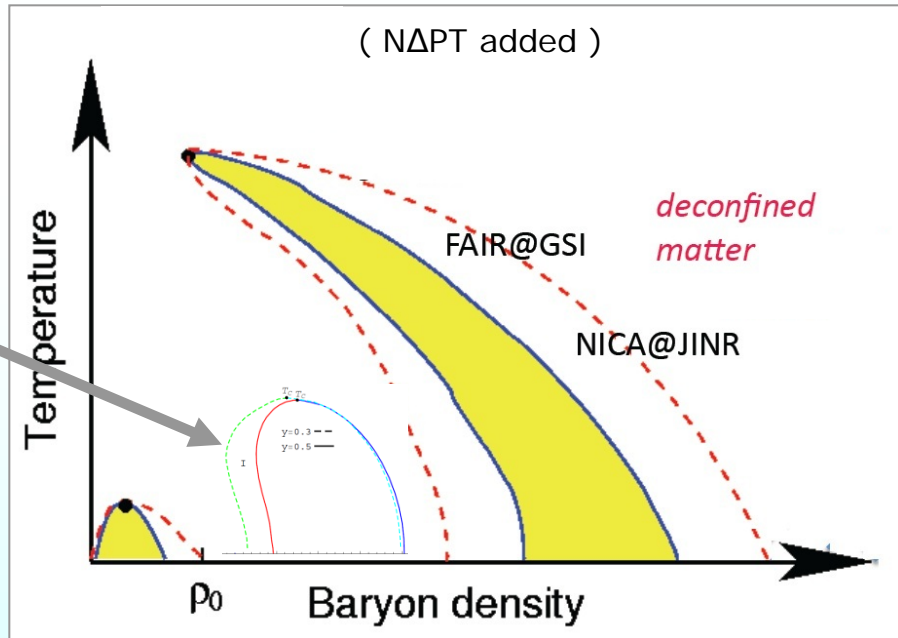
Liquid-gas and hypothetical nucleon \leftrightarrow Δ -matter phase transitions

Lavagno & Pigato // arXiv:1210.0400 (2012)



Phase diagram of the liquid-gas and the nucleon- Δ matter phase transition for $y = 0.3$ (dashed curves) and $y = 0.5$ (continuous curves).

Jorgen Randrup, *Int. Conf. "CPOD-2010 /Dubna, Russia*

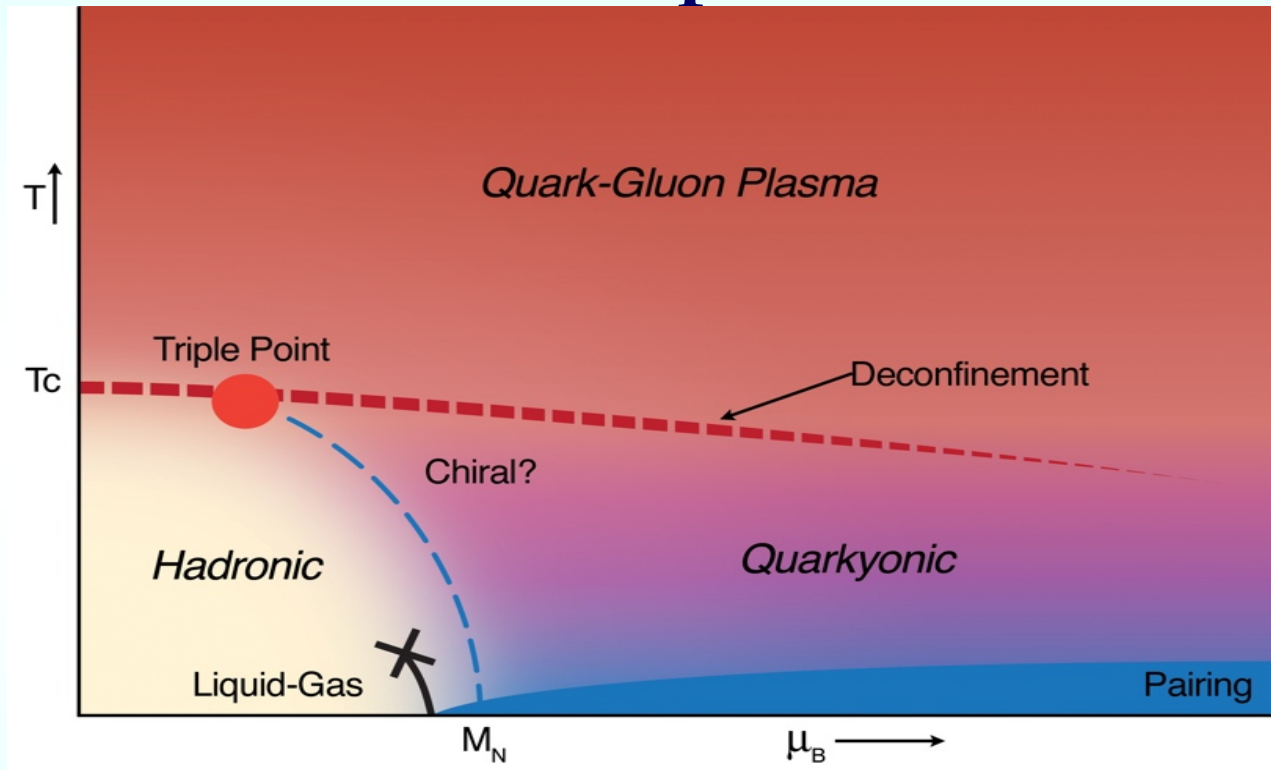


What is the type of this new phase transition: - enthalpic *or* entropic ?

Outlook-III

Inventory of new hypothetical phase transitions

Example-II



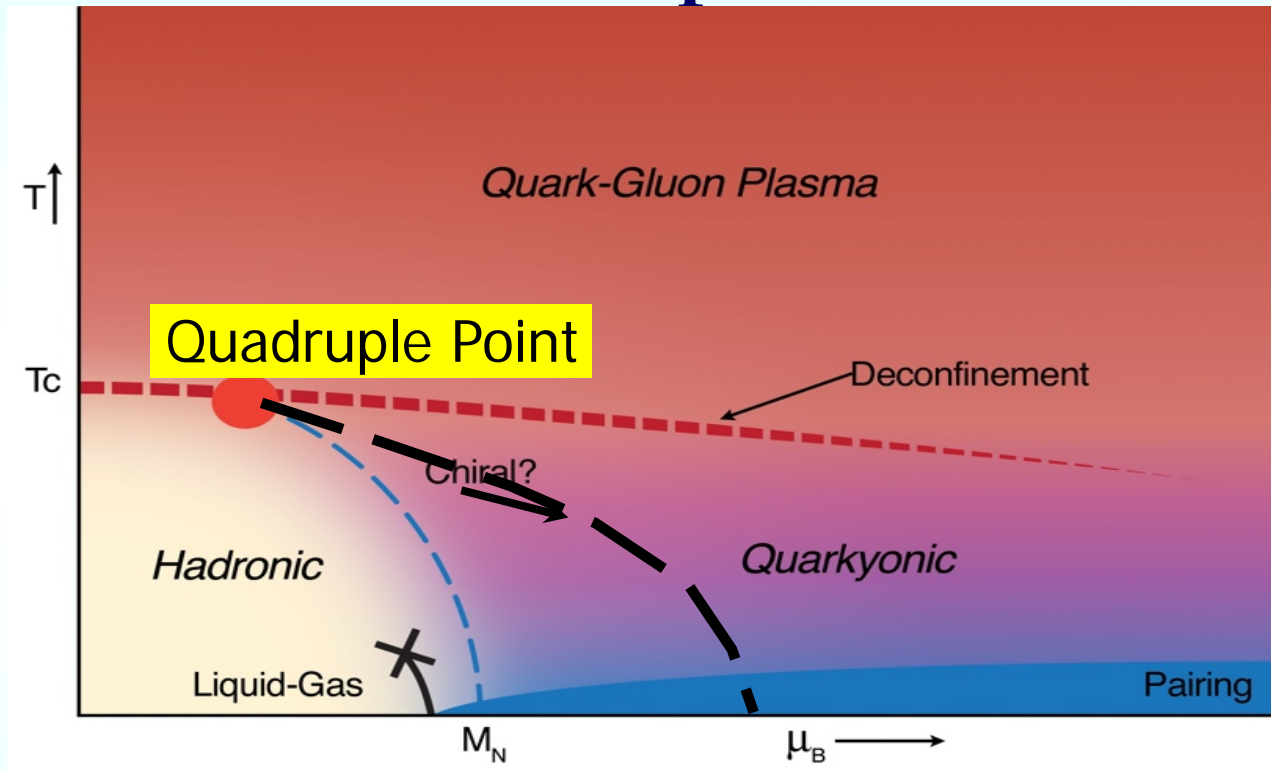
R.Pisarski & L.McLerran, EMMI (Wroclaw) /2009/, QCD (Bad Honnef) /2010/

**What is the type of all these hypothetical phase transitions:
- Are they enthalpic or entropic?**

Outlook-III

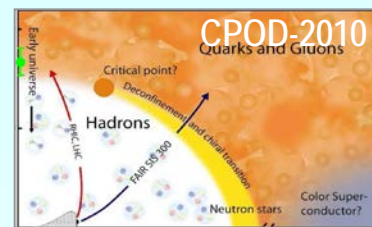
Inventory of new hypothetical phase transitions

Example-II



R.Pisarski & L.McLerran, EMMI-Wroclaw /2009/, QCD-Bad Honnef /2010/

**What is the type of all these hypothetical phase transitions:
- Are they enthalpic or entropic?**



Conclusions *and* perspectives

- **Visible equivalence** of **gas-liquid-like** and **quark-hadron phase transitions**
- in high energy density nuclear matter **is illusive**.
- Both phase transitions belong to **fundamentally different classes**:
- **Gas-Liquid PT** is **enthalpic**, while **Quark-Hadron PT** is **entropic**.
- **In spite of** many order **difference** in density and energy of **deconfinement-driven PT** and **ionization-driven PT** (dissociation-driven, polymerization-driven *etc.*) they have many **common features** because both are **entropic** PTs.
- **Properties** of **entropic PTs** differ **significantly** from those of **enthalpic PTs**.
- **Entropic phase transitions** are always accompanied with existence of region with **anomalous thermodynamic properties** $\{(\partial P/\partial T)_V < 0, V(\partial P/\partial U)_V < 0, (\partial P/\partial S)_V < 0, (\partial V/\partial T)_P < 0 \dots\}$
- **Anomalous** features of **entropic phase transition** are due to **multi-layered structure** of thermodynamic surfaces $\{U(p, V), T(p, V), S(p, V)\}$

What should we classify when we meet unexplored phase transition -?

1st *or* 2nd order ?

Isostructural *or* non-isostructural ?

Congruent *or* non-congruent ?

Enthalpic *or* entropic ?

Do we use **Coulomb-less approximation** *or* we take into account all consequences *of* long-range nature *of* **Coulomb** interaction ?

Scenario *of* phase transformation *in* two-phase region –
– Macro- *or* Mesoscopic ?

Неконгруэнтное испарение в U-O системе

(Совместное фазовое, ионизационное и химическое равновесие согласно условиям Гиббса – Гугенгейма)

Диаграмма давление - плотность

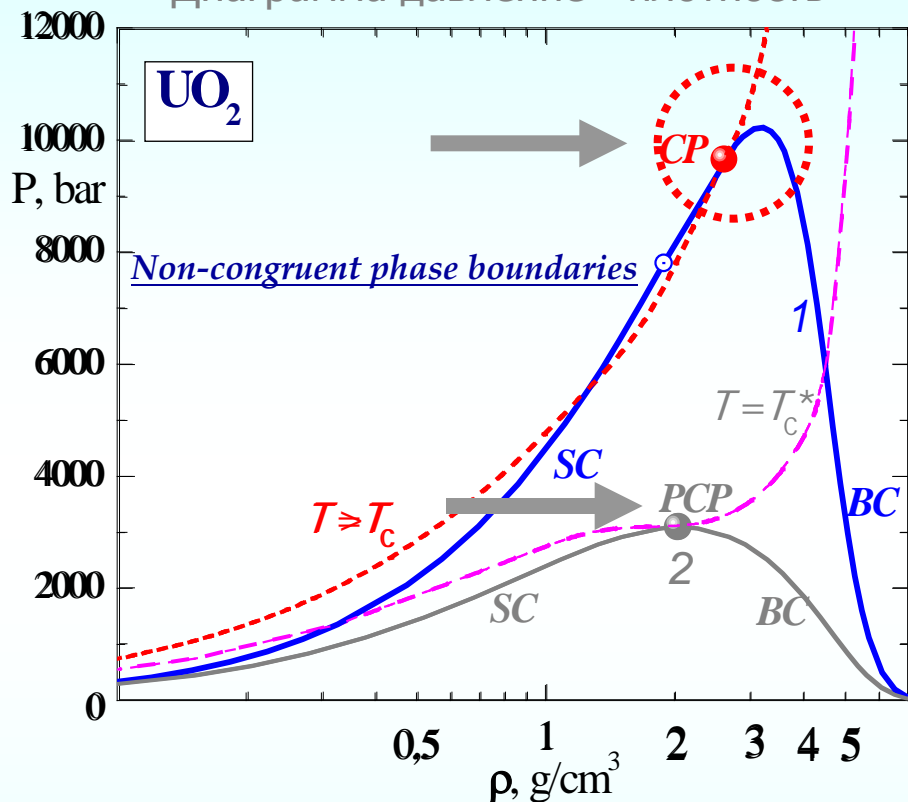
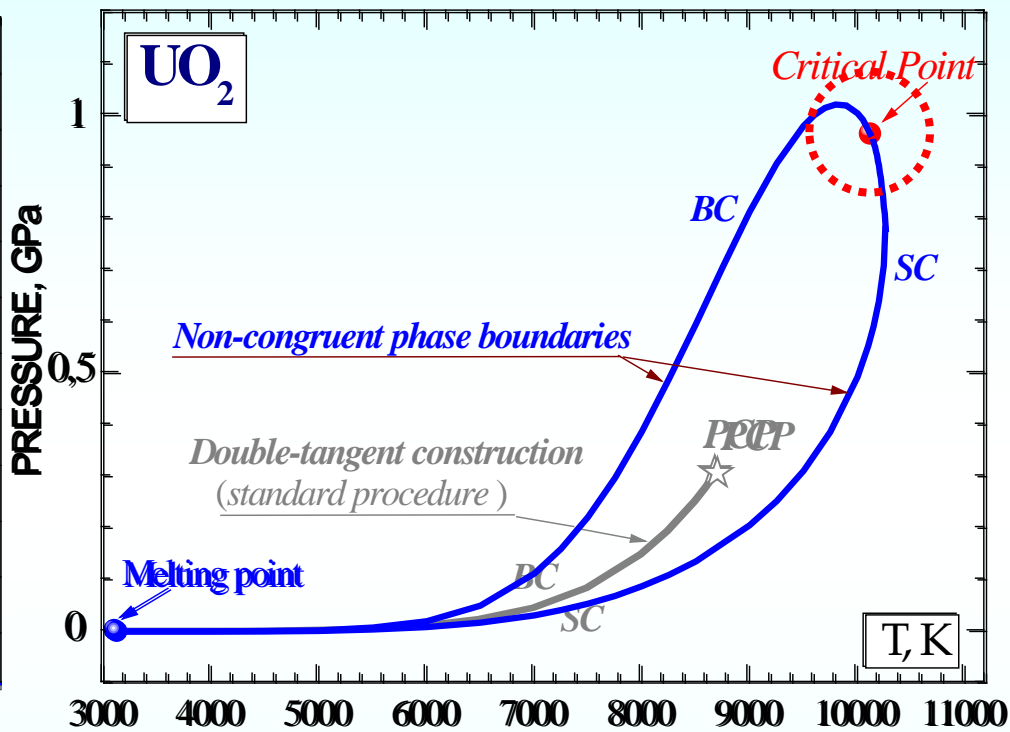


Диаграмма давление - температура



1 – Неконгруэнтное (полное) равновесие

2 – Принудительно-конгруэнтное равновесие

BC – Граница кипения жидкости

SC – Граница насыщения пара

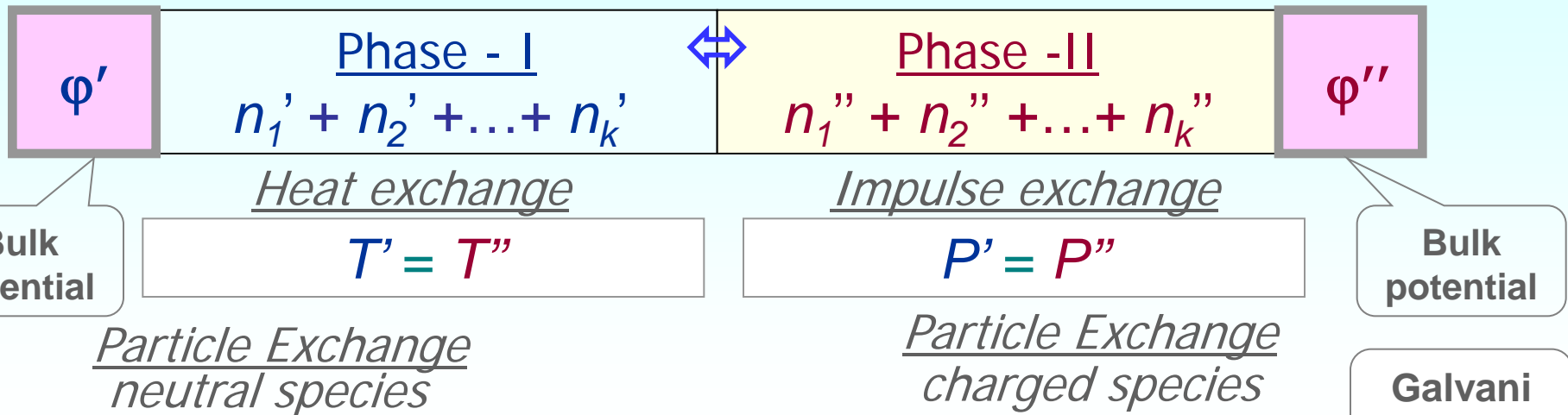
NB! 2-dimensional two-phase region instead of standard P - T saturation curve

NB! High pressure level of non-congruent phase decomposition

NB! Critical point should be of non-standard type: $(\partial P/\partial V)_T \neq 0$ $(\partial^2 P/\partial V^2)_T \neq 0$

It should be instead: $(O/U)_{\text{liquid}} = (O/U)_{\text{vapor}}$ and $\{ \partial \mu_i / \partial n_k \}_T \}_{CP} = 0$

Phase equilibrium in reacting **Coulomb** system (Gibbs – Guggenheim conditions)



$$\begin{aligned} \mu_1'(P,T, x') &= \mu_1''(P,T, x'') \\ \mu_2'(P,T, x') &= \mu_2''(P,T, x'') \\ &\dots\dots\dots \\ \mu_k'(P,T, x') &= \mu_k''(P,T, x'') \end{aligned}$$

Equilibrium reactions
 $ab \rightleftharpoons a + b$
(reduced number of basic units)

Uranium – Oxygen system

$$\begin{aligned} \mu_U'(P,T, x') &= \mu_U''(P,T, x'') \\ \mu_O'(P,T, x') &= \mu_O''(P,T, x'') \end{aligned}$$

NB! - Chemical potentials of charged are **not equal** (Guggenheim, 1929)
Electro-chemical potentials are equal

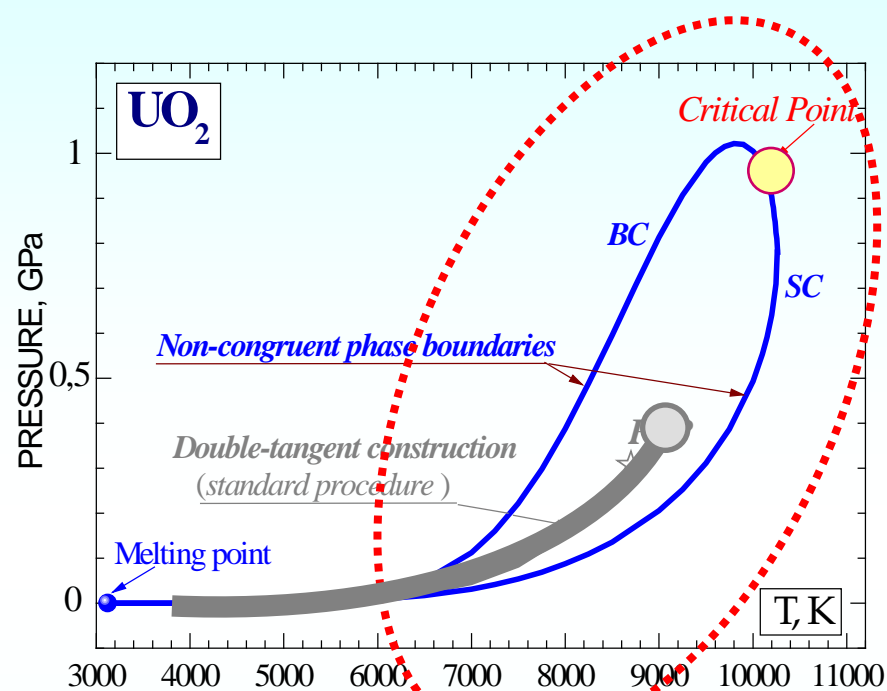
$$\mu_i' + Z_i e \phi' = \mu_i'' + Z_i e \phi'' \quad \Leftrightarrow \quad \Delta\phi(T)$$

Potential drop at mean-phase interface in equilibrium Coulomb system

$$\begin{aligned} \mu_1'(P,T, x') &= \mu_1''(P,T, x'') + Z_1 e \Delta\phi(T) \\ \mu_2'(P,T, x') &= \mu_2''(P,T, x'') + Z_2 e \Delta\phi(T) \\ &\dots\dots\dots \\ \mu_e'(P,T, x') &= \mu_e''(P,T, x'') - e \Delta\phi(T) \end{aligned}$$

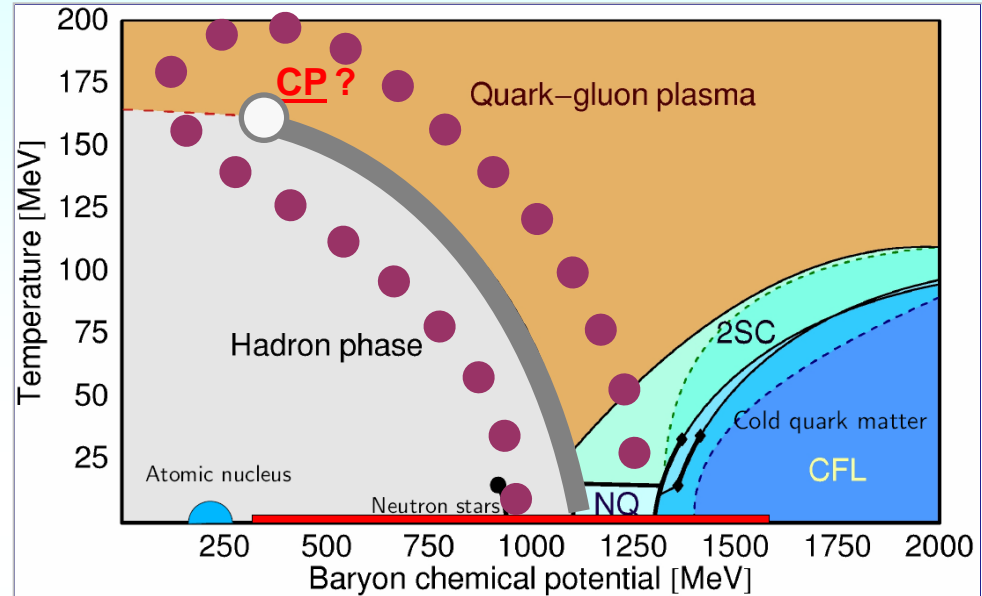
see for example : Iosilevskiy I., Encyclopedia on Low-T Plasmas. III-1 (Suppl) 2004

Hypothetical phase transitions in ultra-dense matter: are they CONGRUENT or NON-CONGRUENT ?



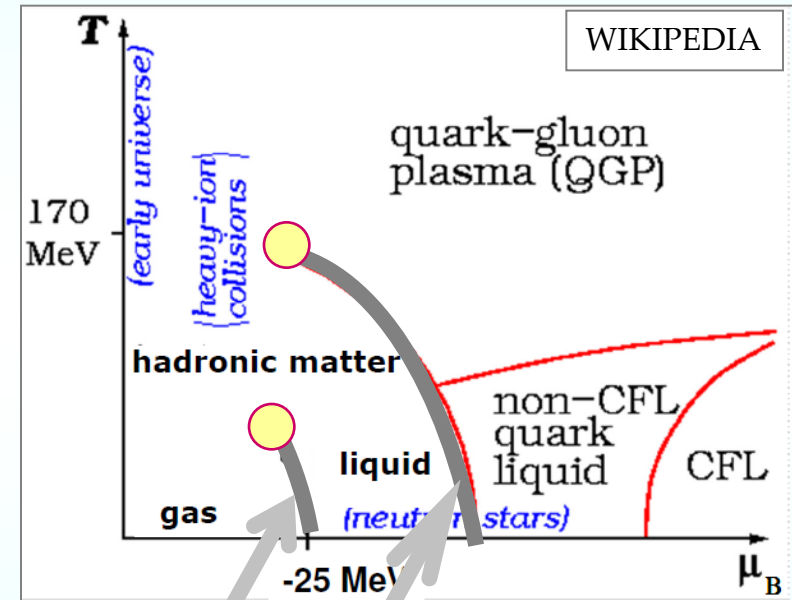
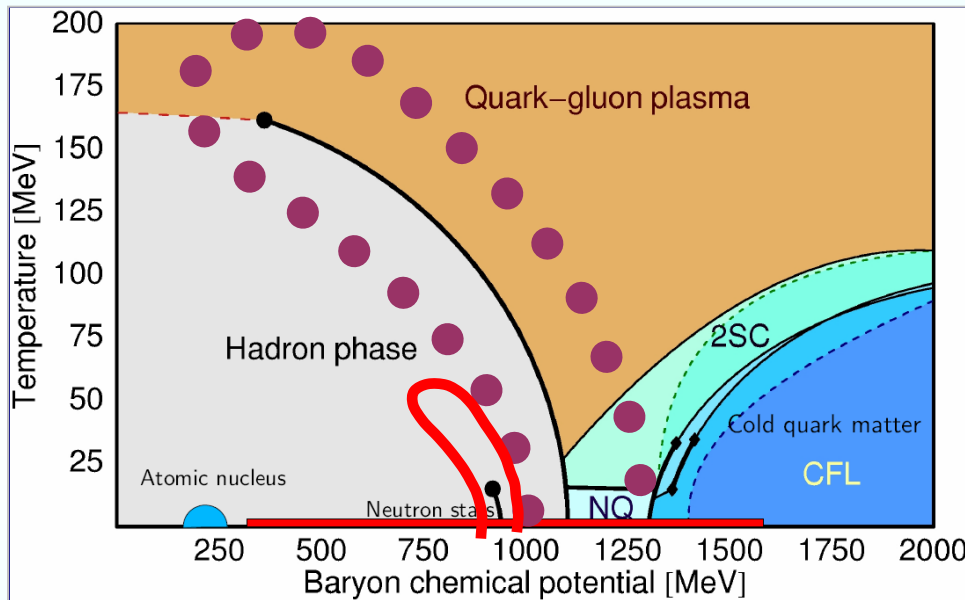
- Forced-congruent phase transition
- Non-congruent phase transition

Phase diagram of quark-hadron matter



Iosilevskiy I. / Int. Conf. "Physics of Neutron Stars", St.-Pb. Russia, 2008
 Int. Congress "Plasma Physics", Fukuoka, Japan, 2008
 Int. Conf. "Critical Point and Onset of Deconfinement", JINR, Dubna, Russia, (2009)
 Acta Phys. Polonica B (Proc. Suppl.) **3**, 589 (2010)

Non-congruent phase transitions in compact stars *and* supernova explosions

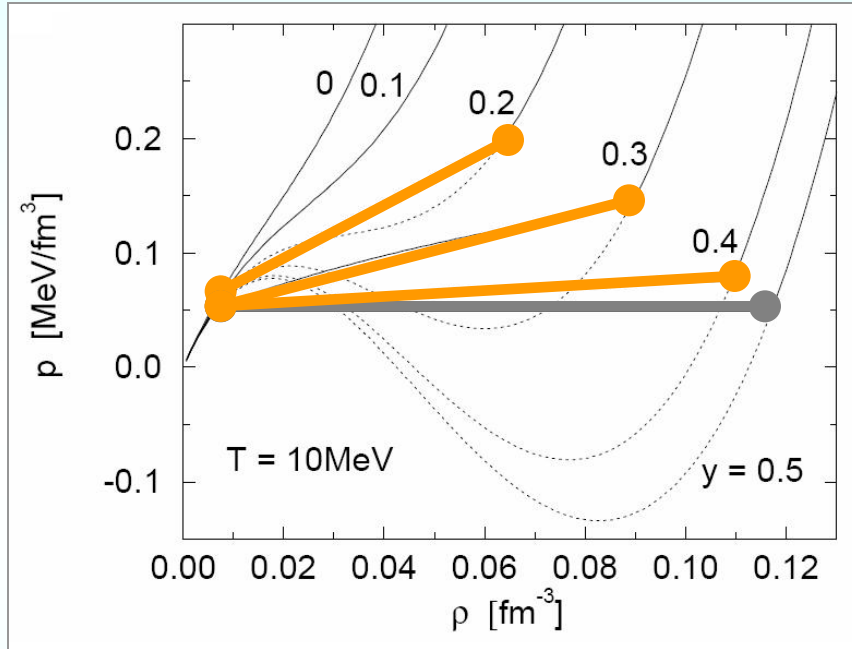


“Gas-liquid” phase transition in dense nuclear matter
{ $p, n, N(A, Z)$ }

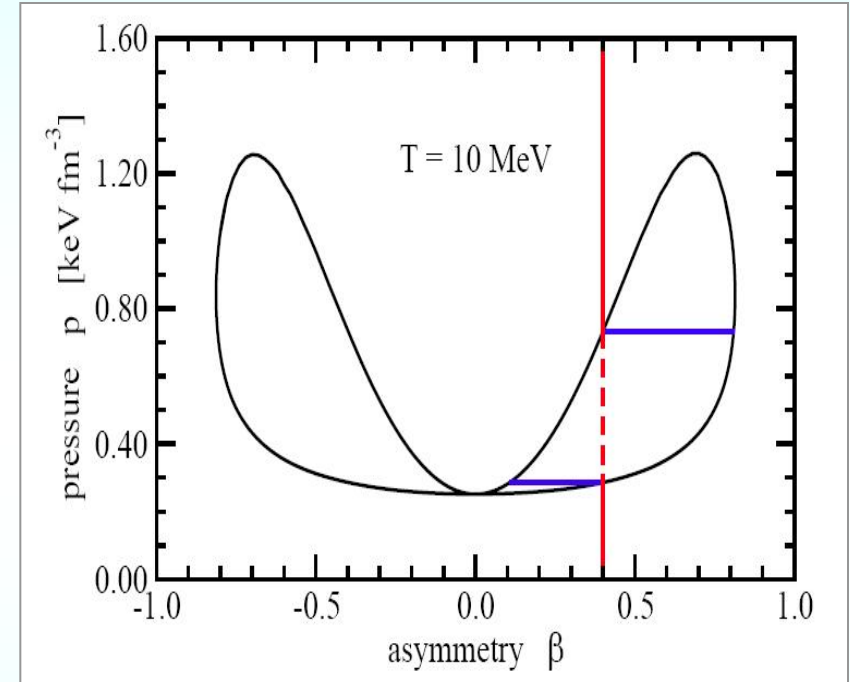
Quark-hadron phase transition /QHPT/

Typical features of non-congruency for “gas-liquid” phase transition in asymmetric nuclear matter of “low density” are well known

(see e.g. Muller & Serot /1995/)



Muller H., Serot B., *Phys. Rev. C* **52** (1995)
arXiv: nucl-th/9505013



(after S. Typel, HIC for FAIR, Prerow-2009)

Phase transition in **asymmetric** p - n - $N(A,Z)$ nuclear matter is **non-congruent** !

Phase transition in **symmetric** p - n - $N(A,Z)$ system is **congruent** (azeotropic) !

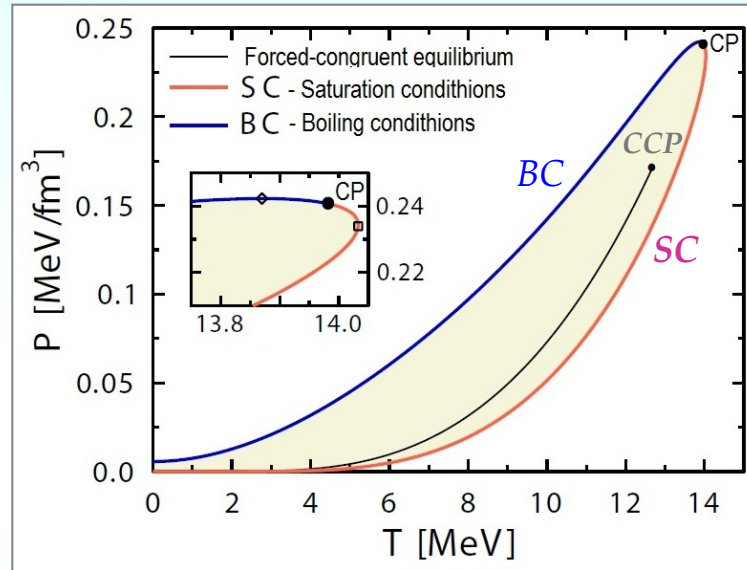
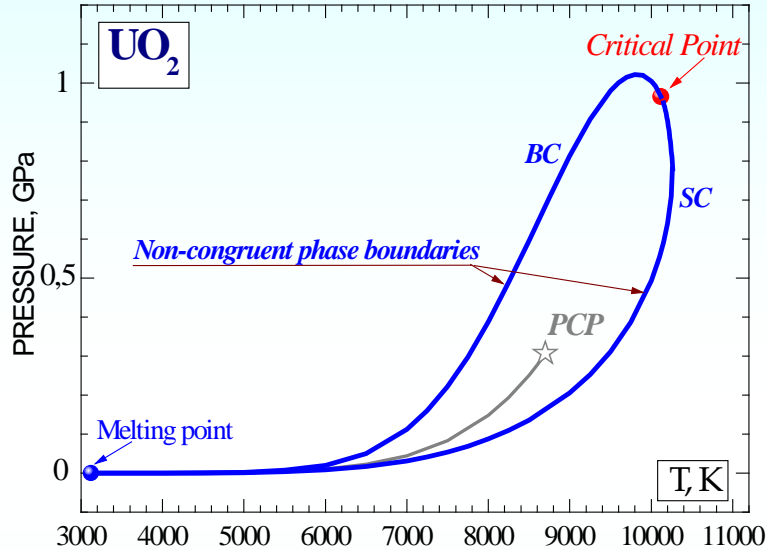
ILL, S. Typel M. Hempel *et al.* Non-congruence of “gas-liquid” phase transition in asymmetric nuclear matter (in progress)

(*) EOS – Typel S., Ropke G., Klahn T., Blaschke D. and Wolter H., *Phys. Rev. C*, **81**, 015803 (2010)

Non-congruent GLPT in asymmetric nuclear matter

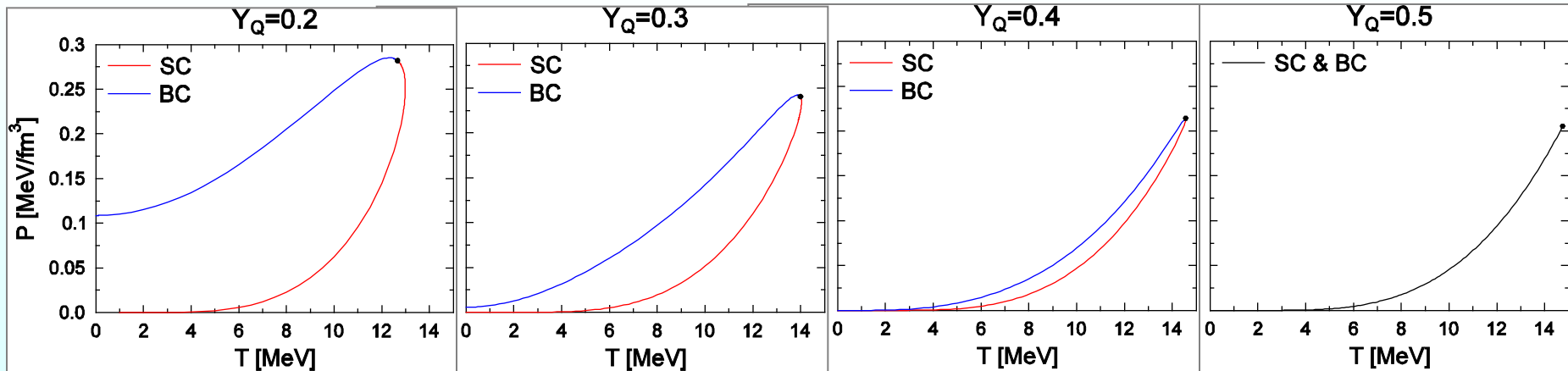
(banana-like pressure - temperature diagram)

Hempel M., Dexheimer V., Schramm S. and Iosilevskiy I.,
Phys. Rev. C **88** (2013)



$Y = 0.3$

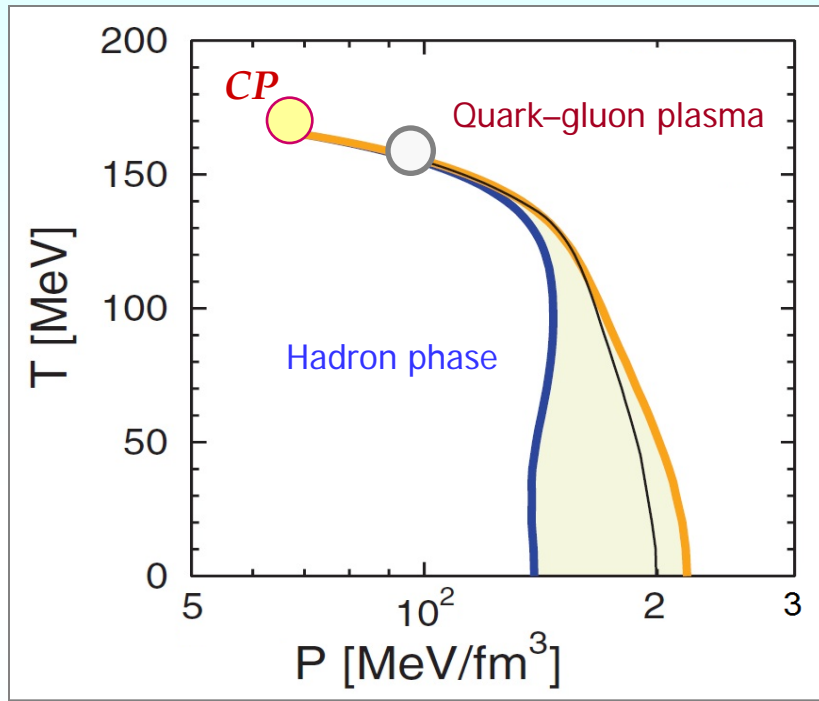
$Y \equiv$ proton fraction in
 $\{p, n, N(A, Z)\}$
system



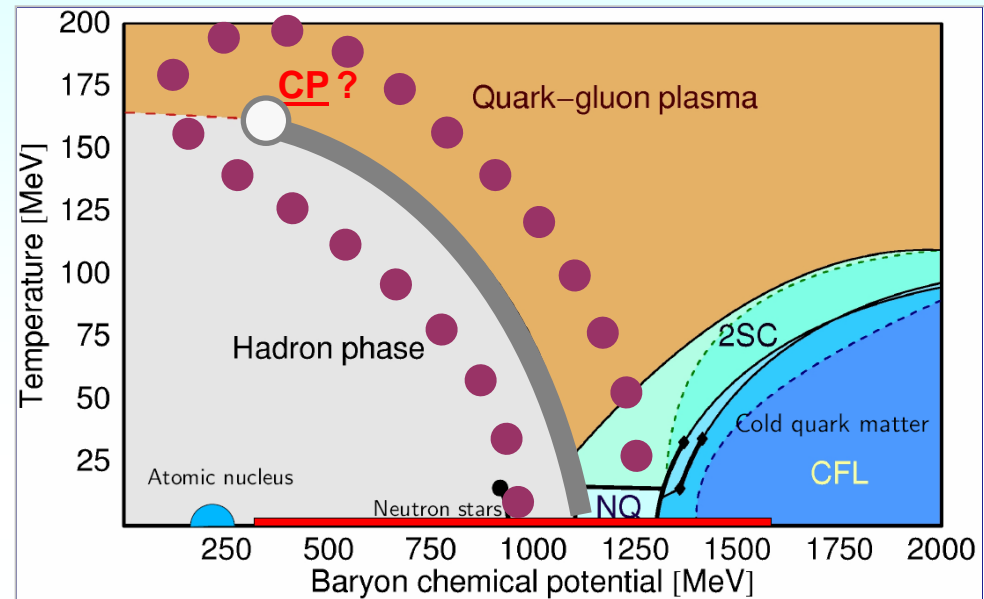
M. Hempel (supplement to: *Phys. Rev. C*, **88** (2013)) / [arXiv:1302.2835](https://arxiv.org/abs/1302.2835)

$Y = 0.5$ – azeotropic comp.



Hypothetical phase transitions in ultra-dense matter: are they CONGRUENT or NON-CONGRUENT ?



Phase diagram of quark-hadron matter



Yes

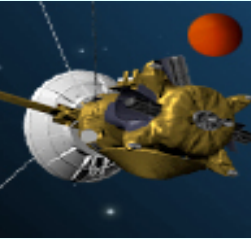
-  - Forced-congruent phase transition
-  - Non-congruent phase transition

Iosilevskiy I. / Int. Conf. *"Physics of Neutron Stars"*, St.-Pb. Russia, 2008 // Int. Conf. *"Critical Point and Onset of Deconfinement"*, JINR, Dubna, Russia, 2010 // *Acta Physica Polonica B (Proc. Suppl.)* **3**, 589 (2010)

Hempel M., Dexheimer V., Schramm S. and Iosilevskiy I. // *Non-congruence of the nuclear liquid-gas and the deconfinement phase transitions* // *Phys. Rev. C* **88**, 014906 (2013) // [arXiv:1302.2835](https://arxiv.org/abs/1302.2835)

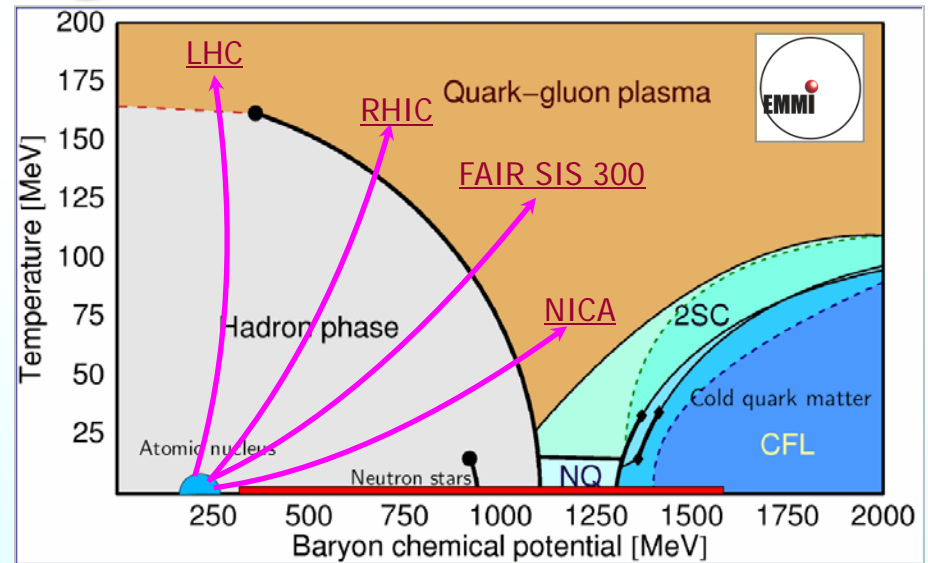
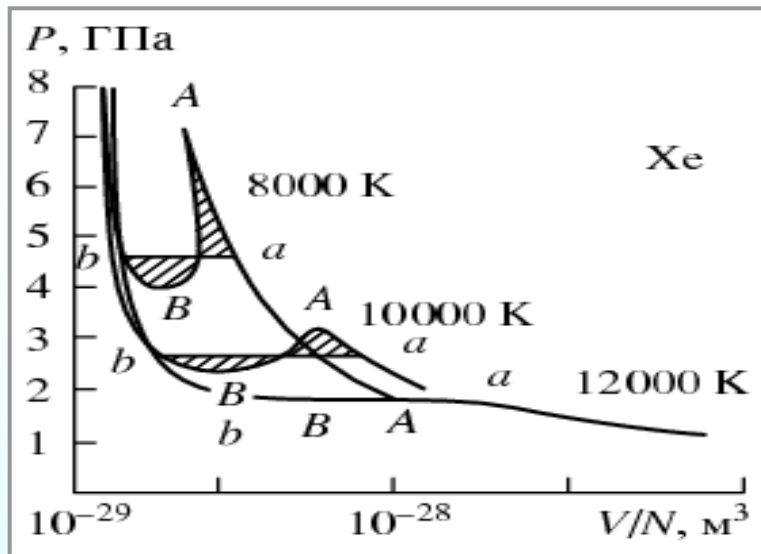
Cassini-Huygens

MISSION TO SATURN & TITAN



Features of entropic phase transitions in cosmic matter and in the laboratory

Thank you!



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RAS Scientific Program “Physics of Extreme States of Matter”
Extreme Matter Institute – EMMI

Acknowledgements to Victor Gryaznov for calculations of dissociation phase transition in hydrogen



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(01-06 March 2018)
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<http://www.ihed.ras.ru/Elbrus18>