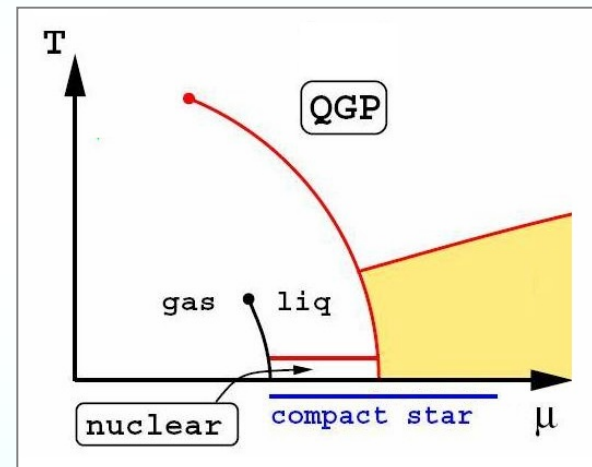
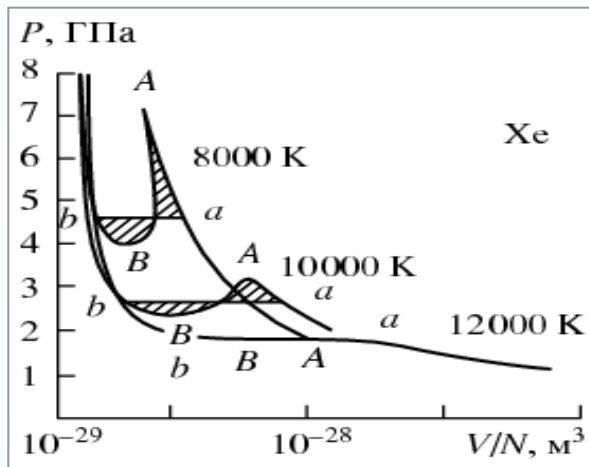


Entropic *and* Enthalpic Phase Transitions in high energy density matter



Igor Iosilevskiy

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

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 it in much more general context

The key feature

Enthalpic vs entropic PT

PT under isothermal compression

GLPT $\Leftrightarrow \Delta H < 0$

Enthalpic PT

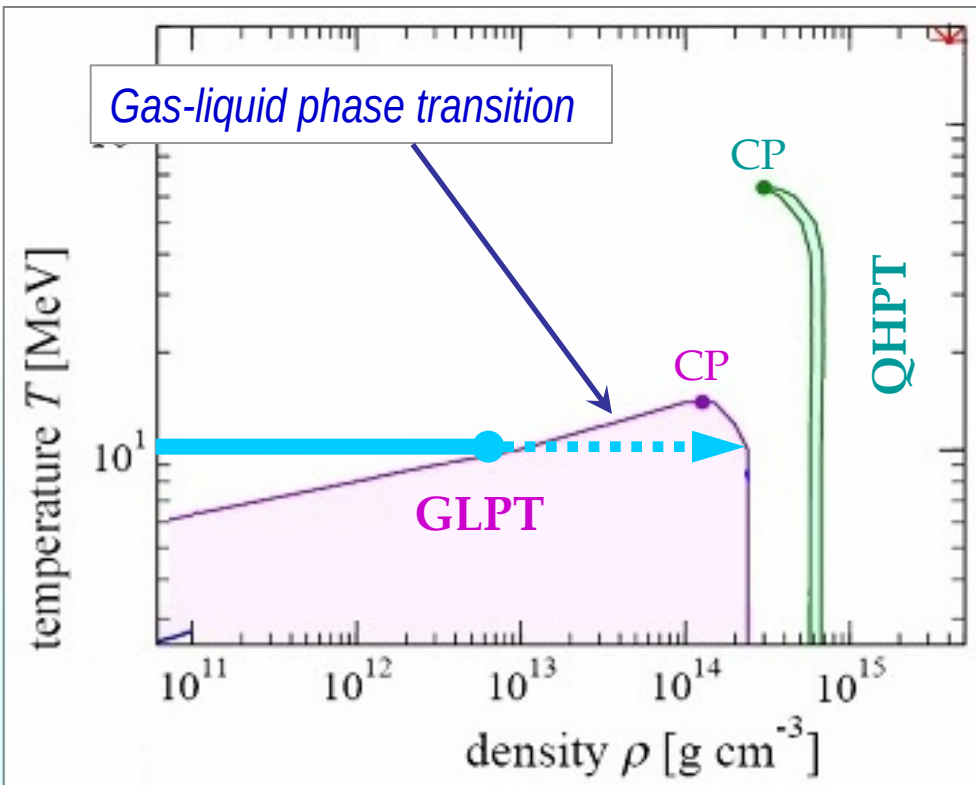


Figure after David Blaschke

The key feature

Enthalpic vs entropic PT

PT under isothermal compression

GLPT $\Leftrightarrow \Delta H < 0$

QHPT $\Leftrightarrow -T\Delta S < 0$

Enthalpic PT

Entropic PT

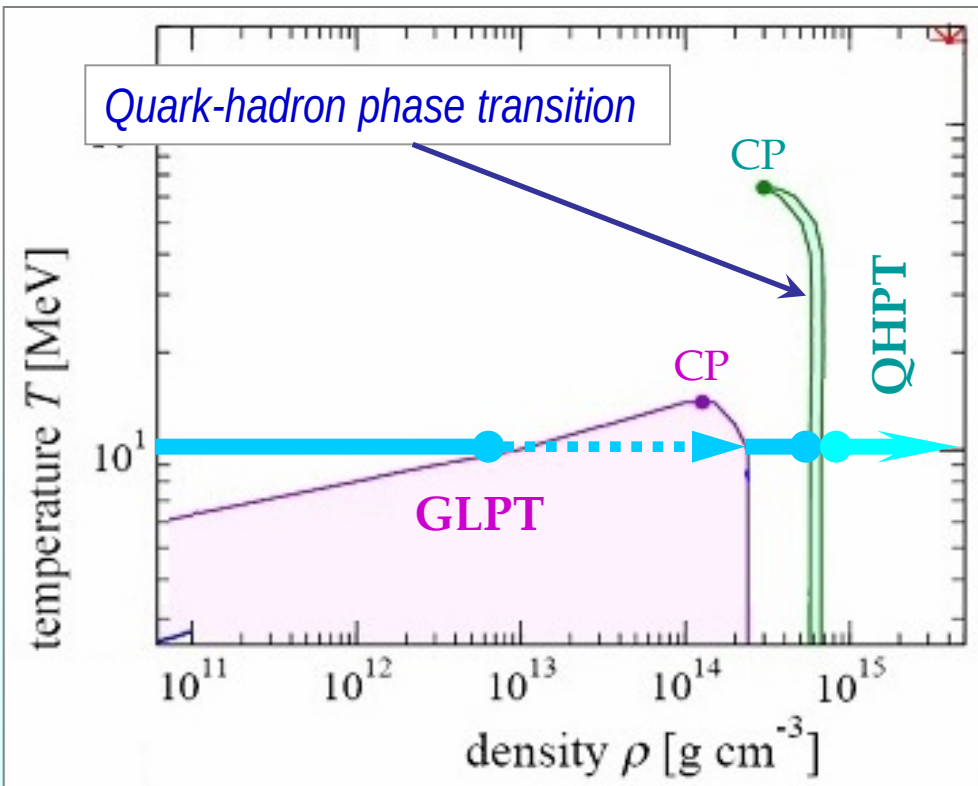
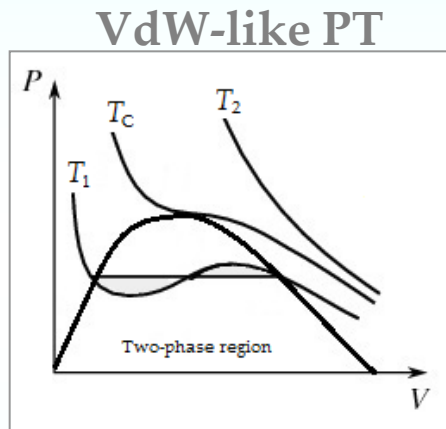


Figure after David Blaschke

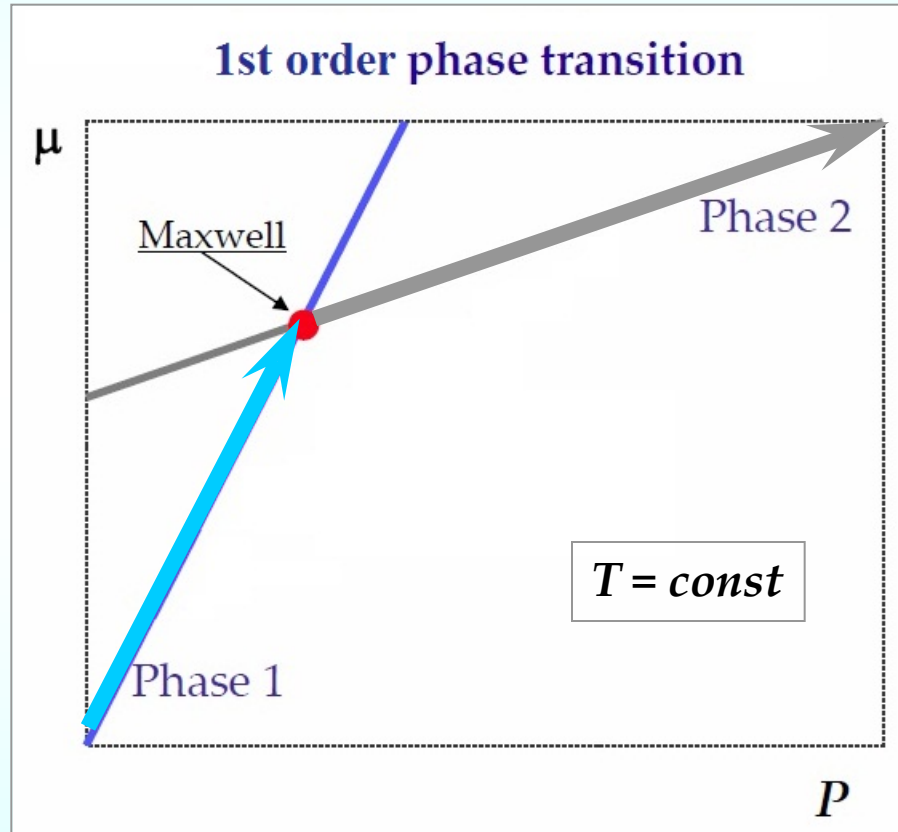
Definition

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

$$G = H - TS$$

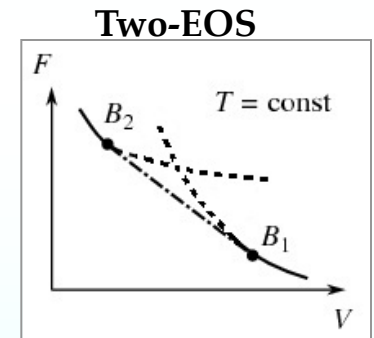
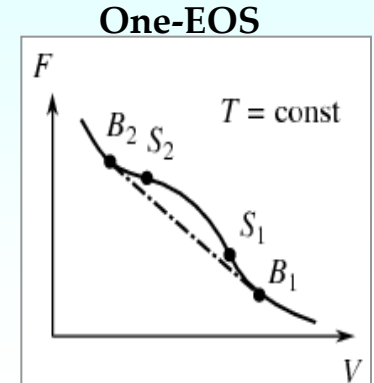


Maxwell "Equal squares"



Iso- T compression

$$\Delta G = 0 \quad \Leftrightarrow \quad \Delta H = T\Delta S$$



"Double tangent"

Enthalpic PT

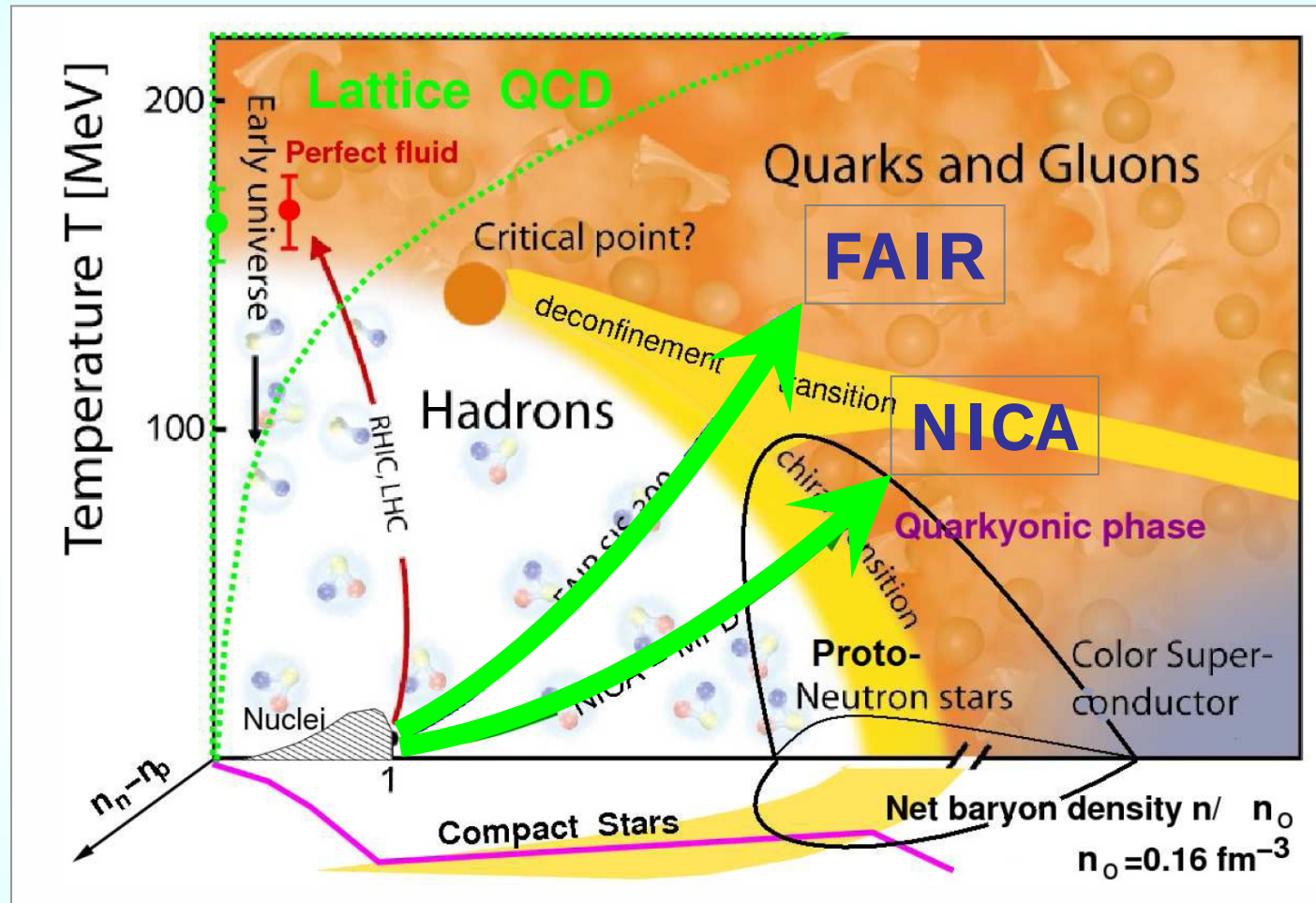
$$\Delta H = T\Delta S < 0$$

Entropic PT

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

Motivation

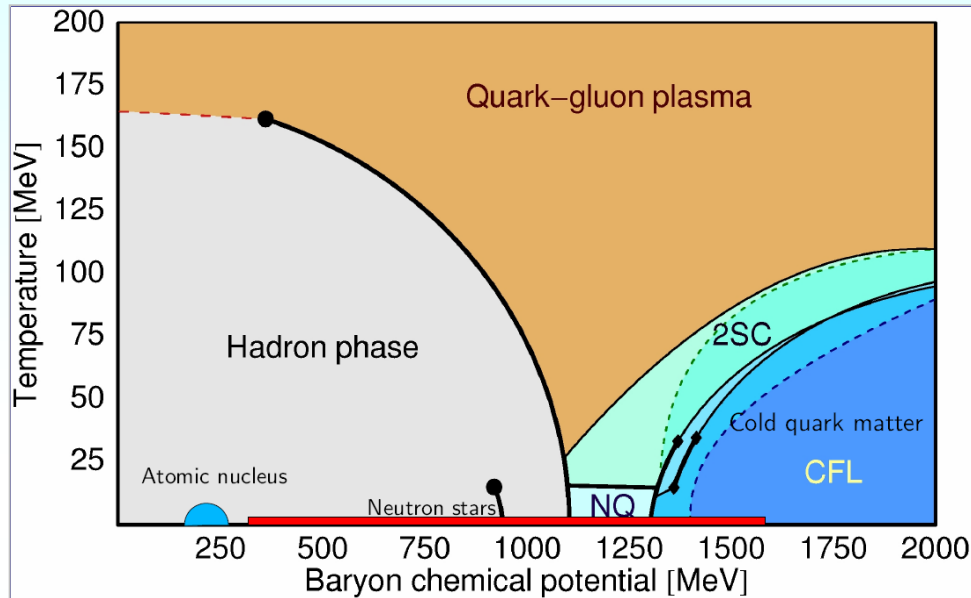
Phase diagram of matter *in* ultra-high energy *and* density



NICA White Book

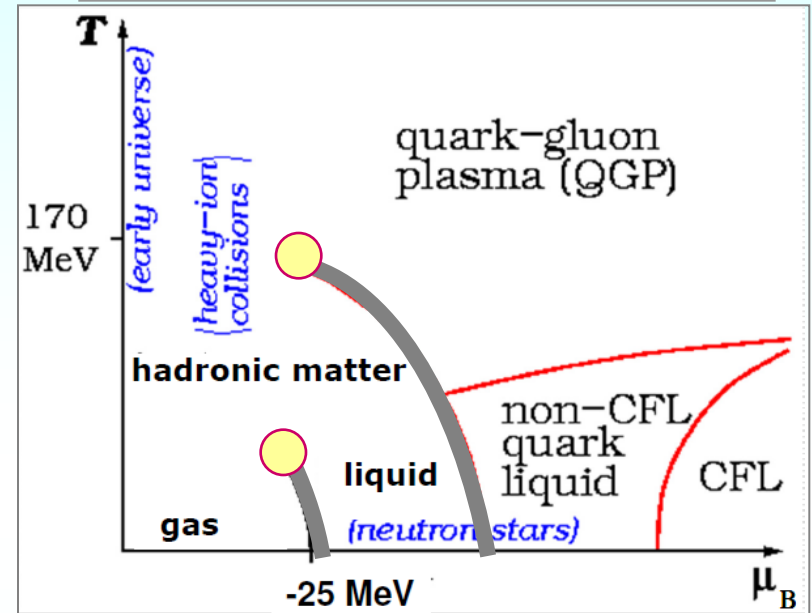
After David Blaschke, NICA Workshop, Dubna, 2009

Phase diagram of matter in ultra-high energy and density



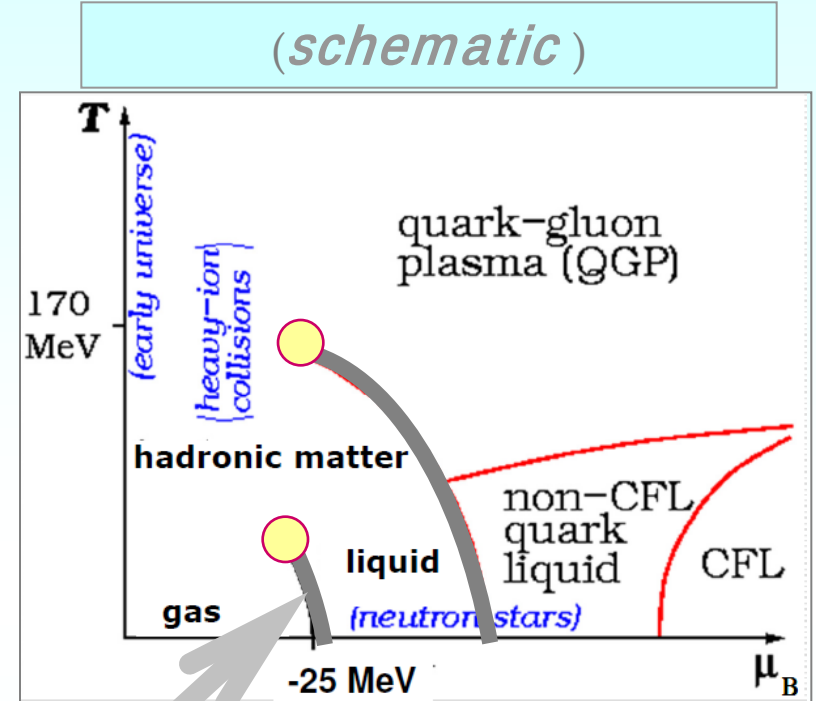
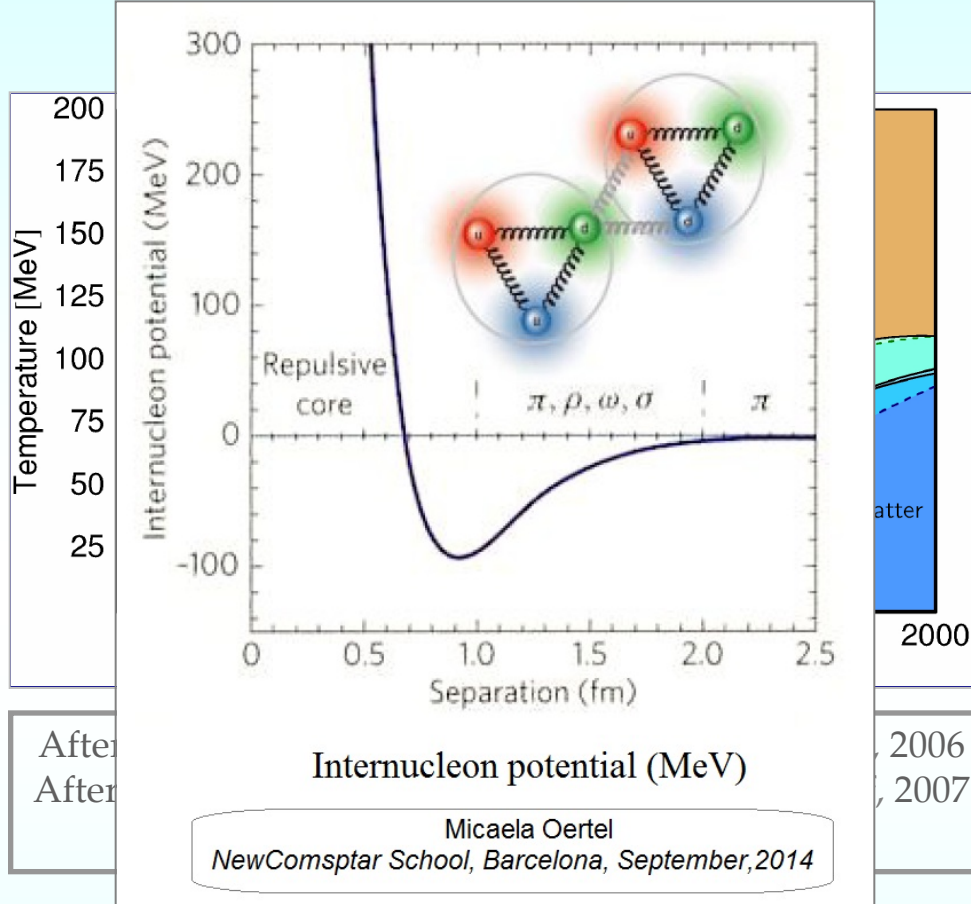
After Fridolin Weber, WEHS Seminar, Bad Honnef, 2006
After David Blaschke, WEHS Seminar, Bad Honnef, 2007

(*schematic*)



Source: WIKIPEDIA

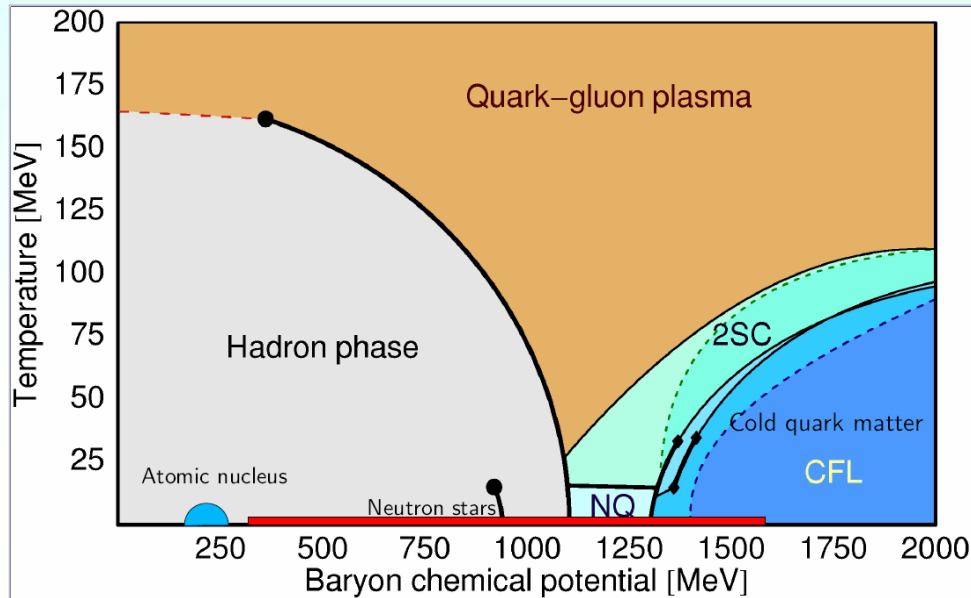
Phase diagram of matter in ultra-high energy and density



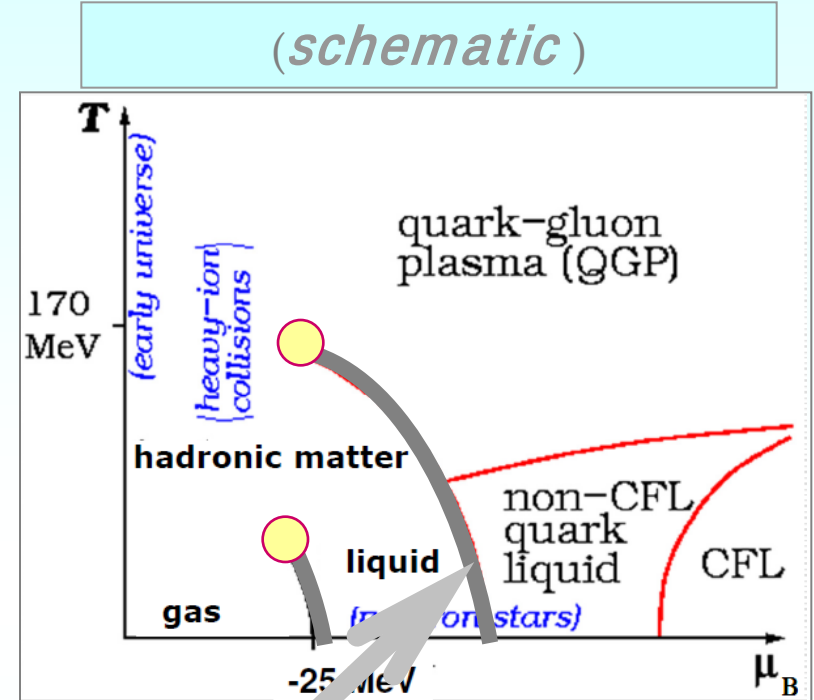
Source: WIKIPEDIA

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

Phase diagram of matter in ultra-high energy and density



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



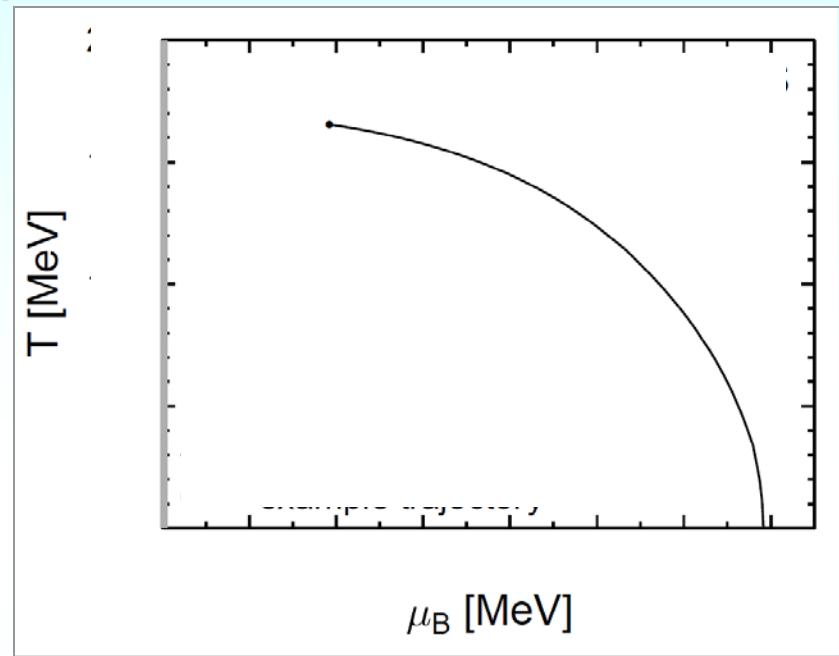
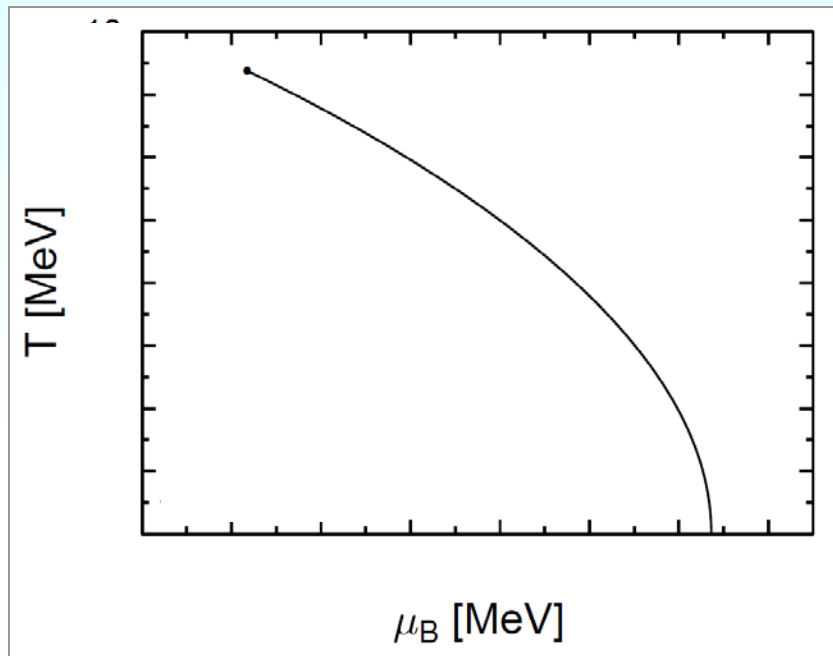
Source: WIKIPEDIA

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

Quark-Hadron phase transition
/ QHPT /

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!

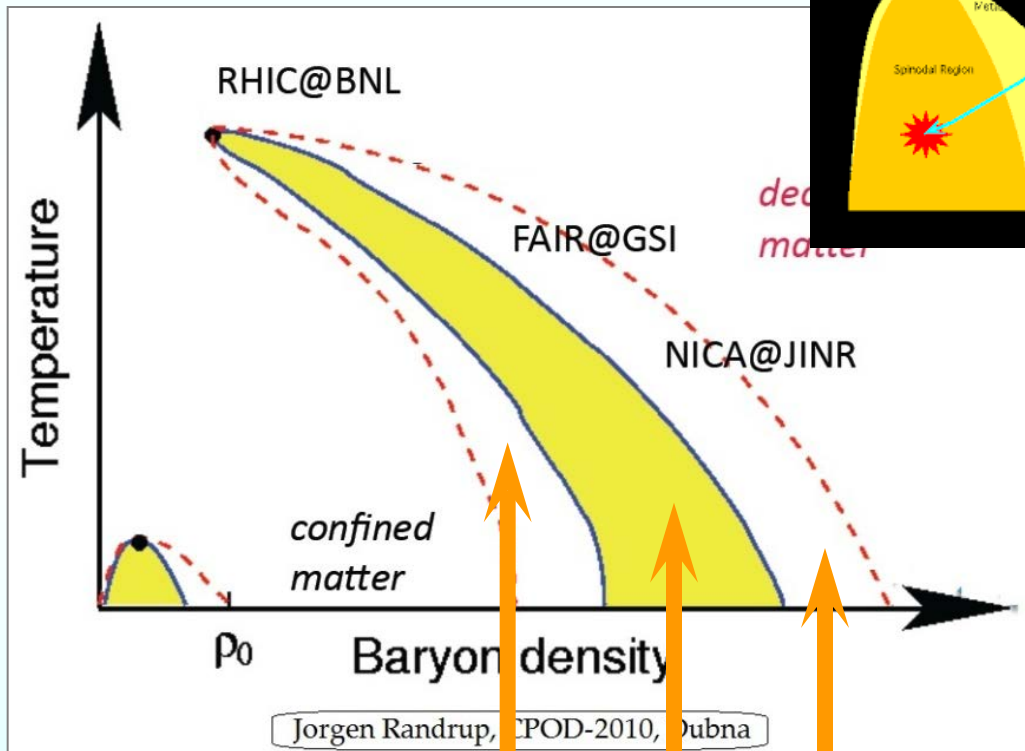
One could not distinguish GLPT vs. QHPT in T - μ plane

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

Prerow 2009

"Critical Point and Onset of Deconfinement"
Dubna, Russia, 2009

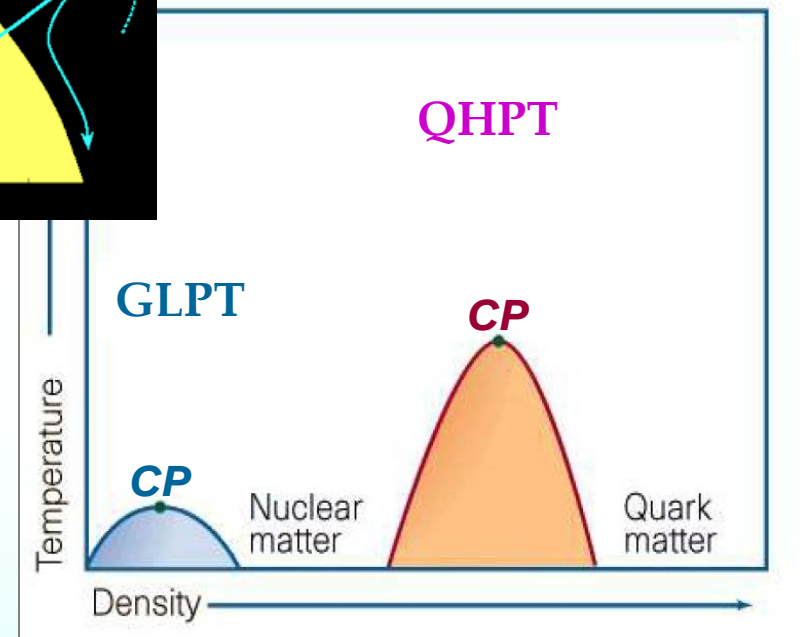
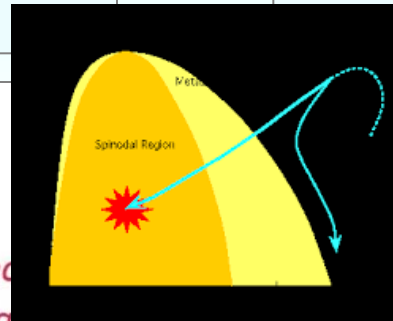
"Critical Point and Onset of Deconfinement"
Napa, USA, 2013



Metastable

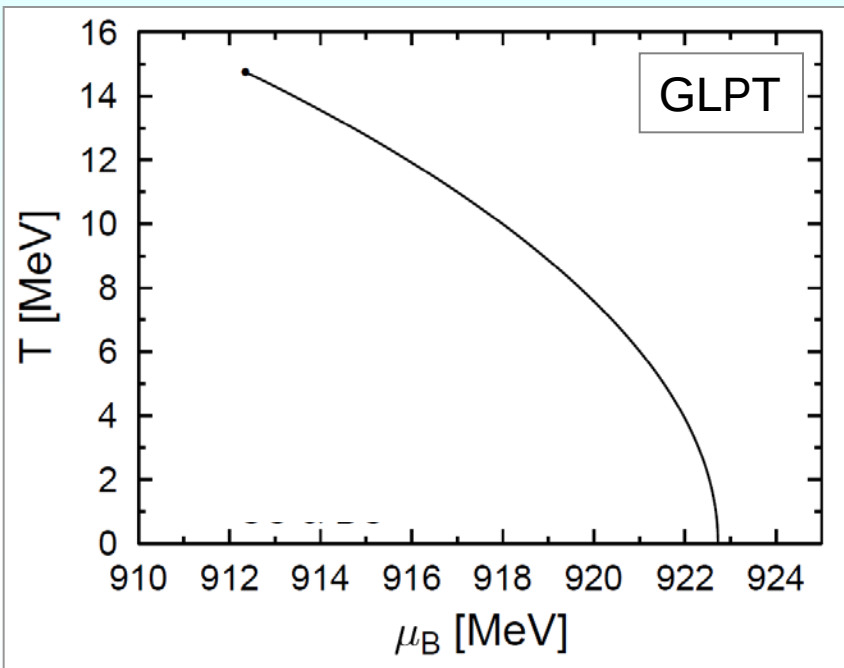
Spinodal
region

Metastable



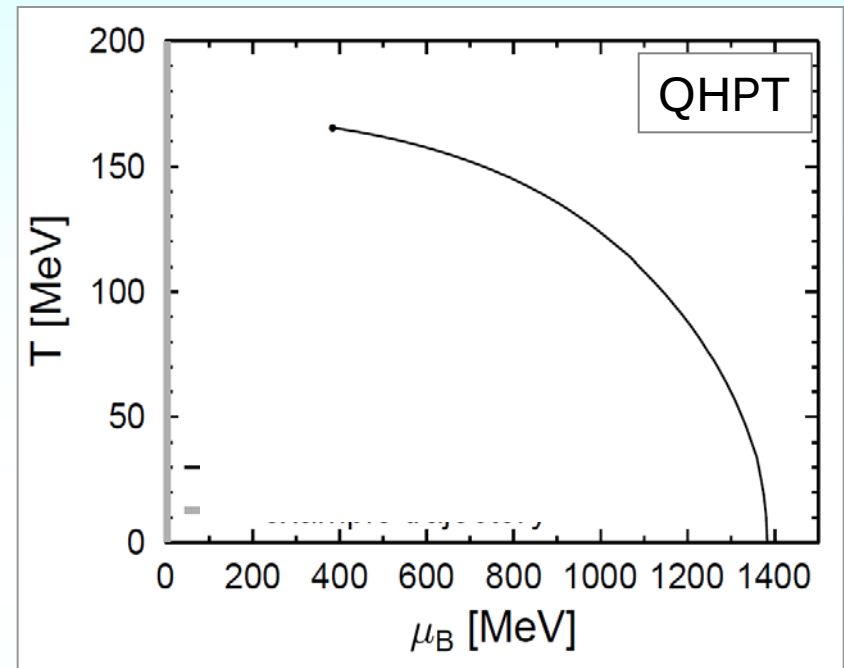
J. Steinheimer & J. Randrup, CPOD-2013

GLPT *and* QHPT look *like* equivalent *in* T - μ 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)

[arXiv:1302.2835](https://arxiv.org/abs/1302.2835)

No!

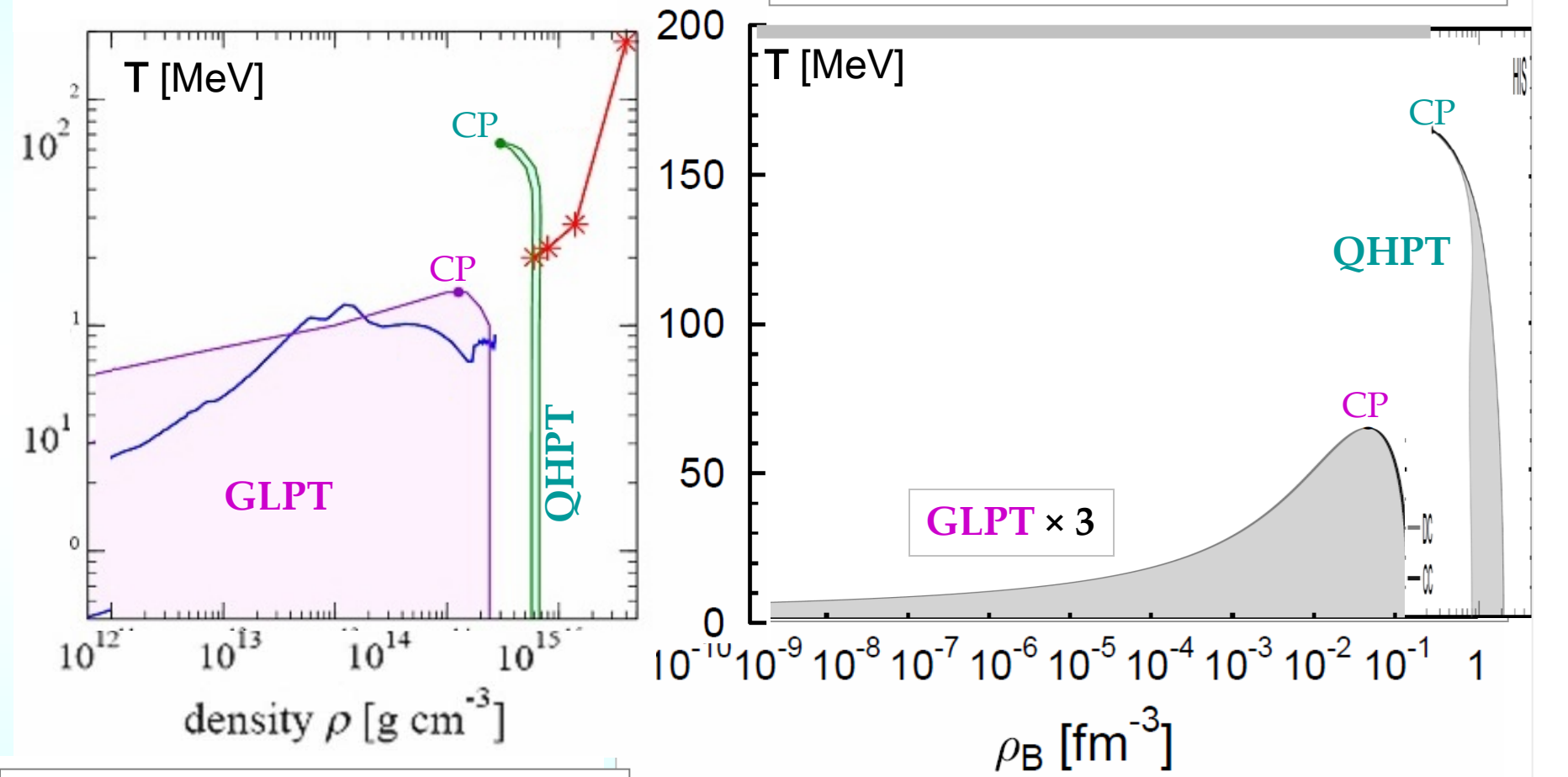
Enthalpic PT

$\neq$

Entropic PT

T - ρ phase diagram of symmetric Coulomb-less 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)

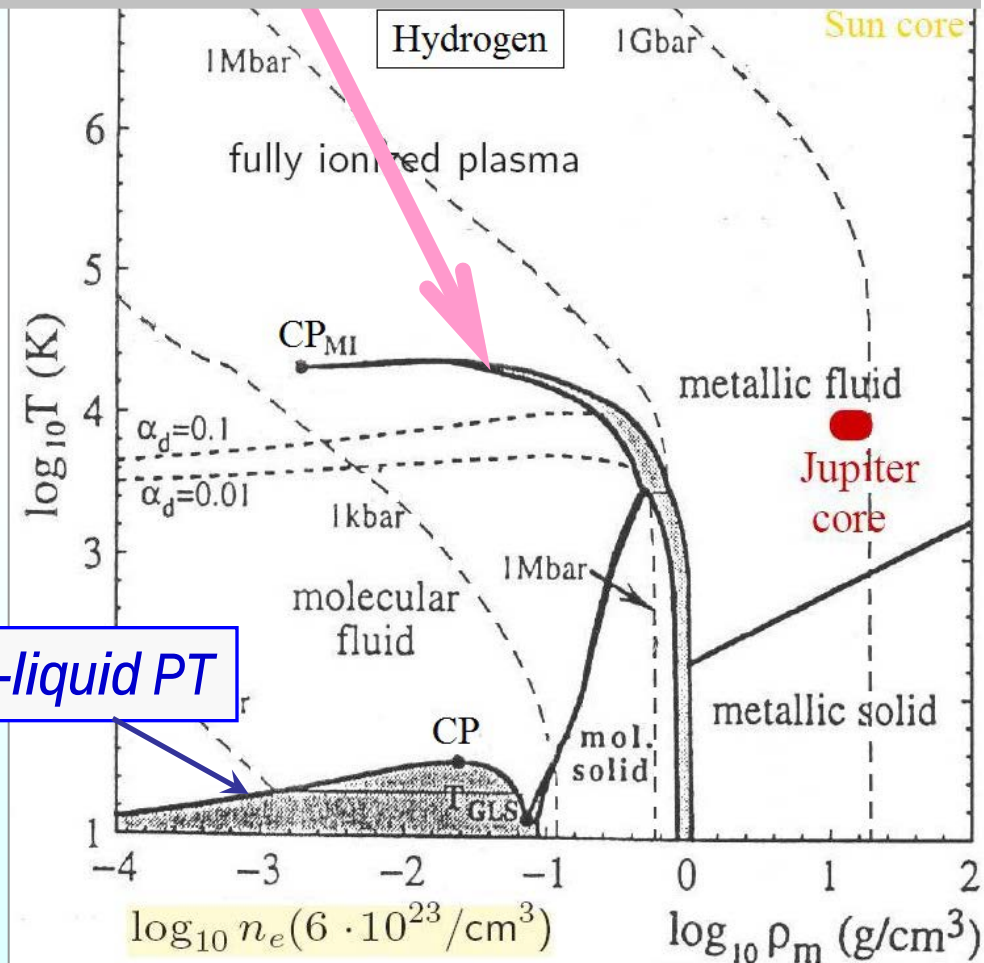
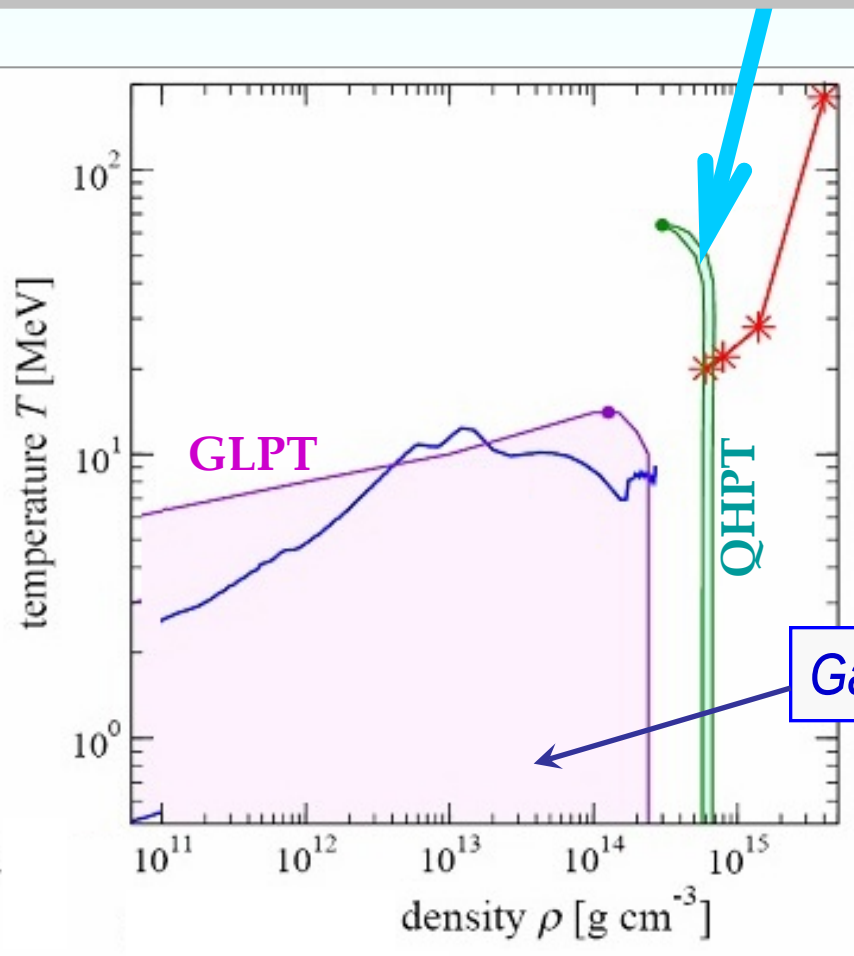
GLPT

QHPT

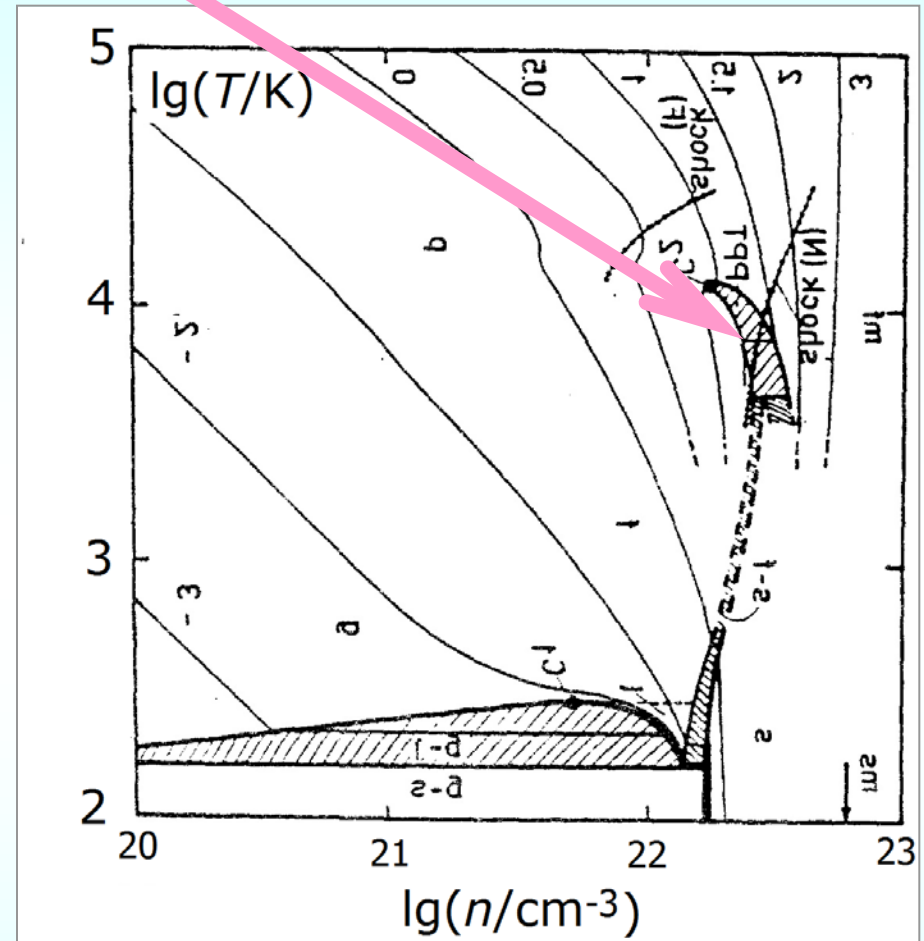
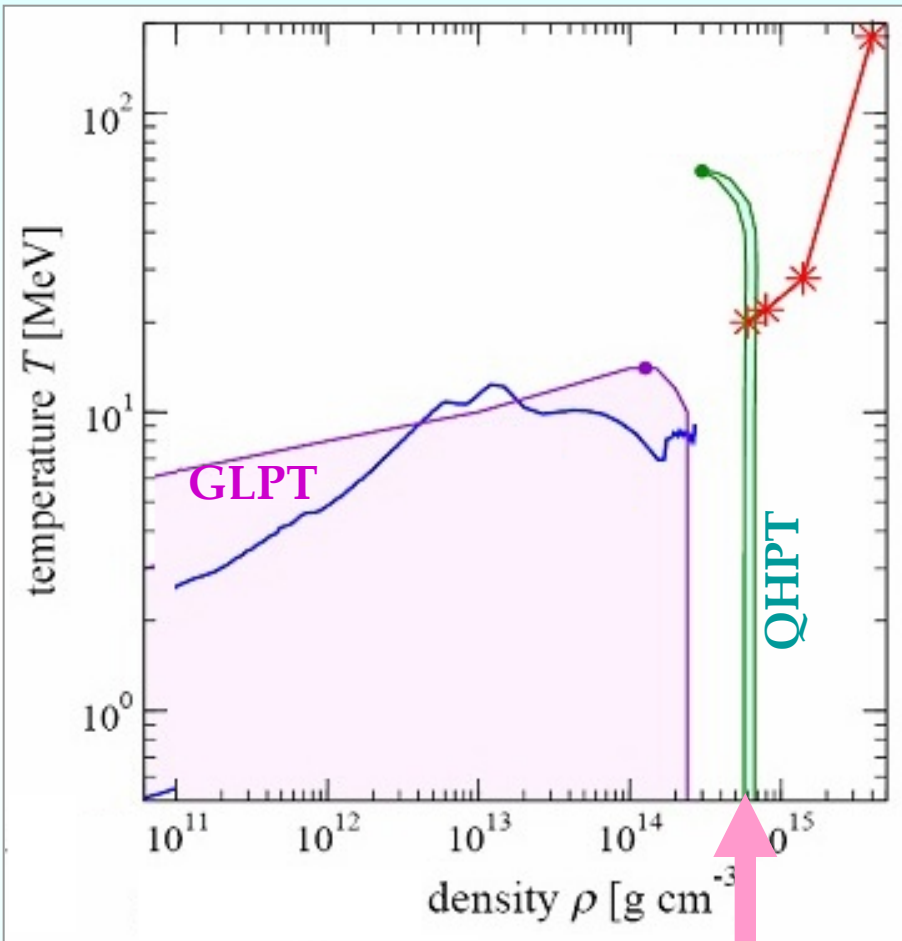
Ionization-driven (*entropic*) phase transition *in* hydrogen

Deconfinement-driven (*entropic*) phase transition *in* QCD

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



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



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

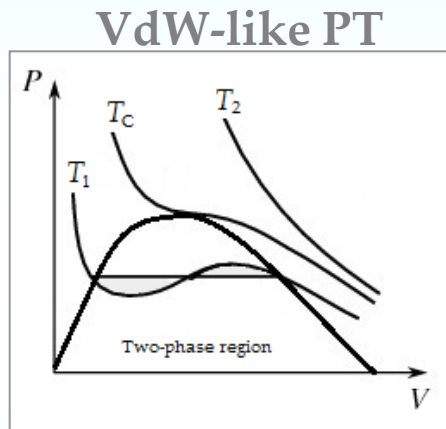
Gas-liquid *and* **deconfinement-driven** PT *in* dense nuclear matter

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

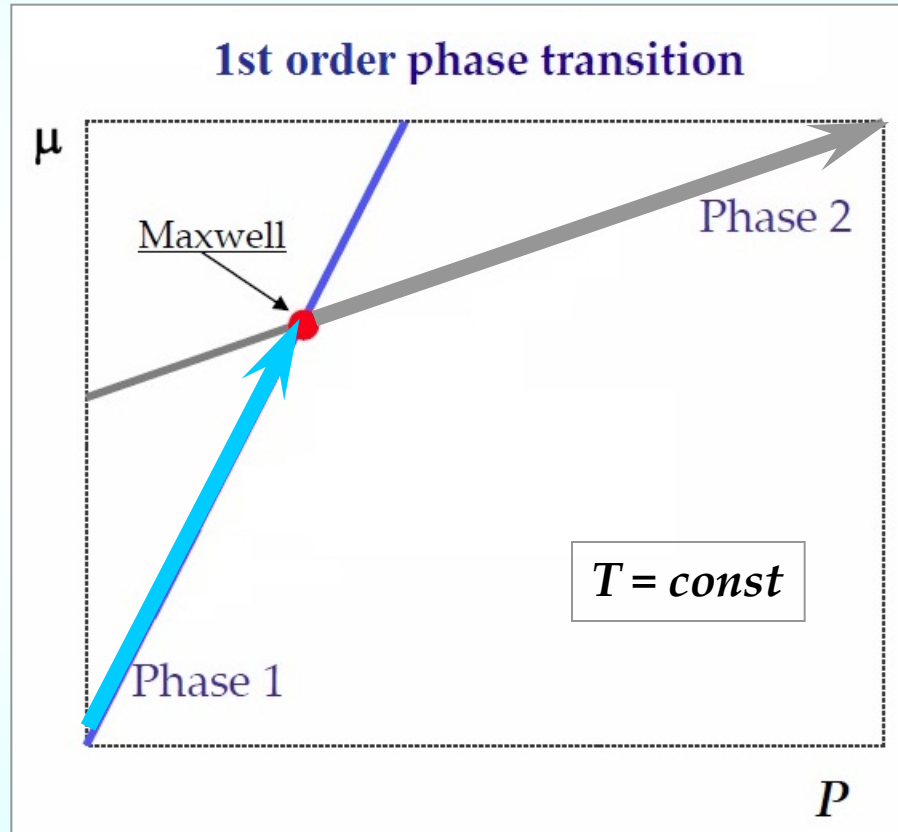
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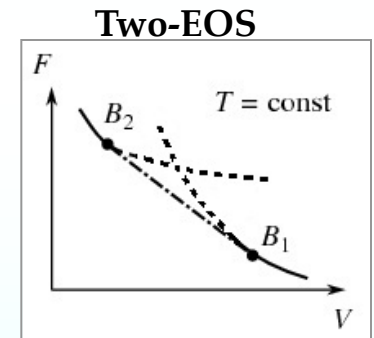
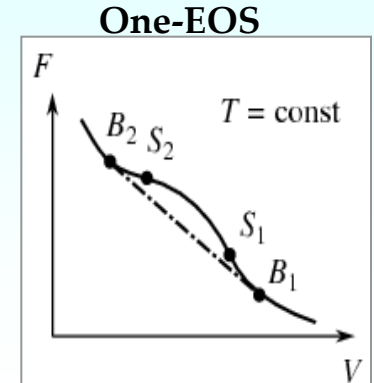


Maxwell “Equal squares”



Iso- T compression

$$\Delta G = 0 \Leftrightarrow \Delta H = T\Delta S$$



“Double tangent”

Enthalpic PT

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

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

Entropic PT

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

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

Enthalpic vs Entropic PTs

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

GLPT – *gas-liquid phase transition*

Enthalpic PT

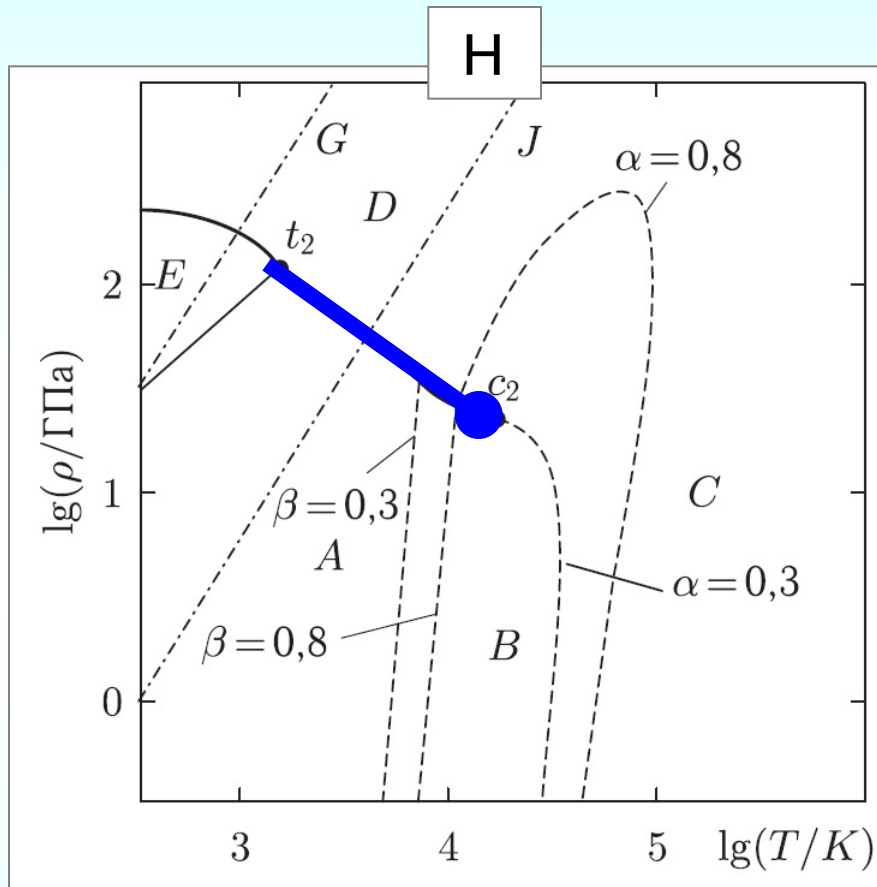
$$(dP/dT)_{\text{binodal}} > 0$$

PPT – *plasma phase transition*

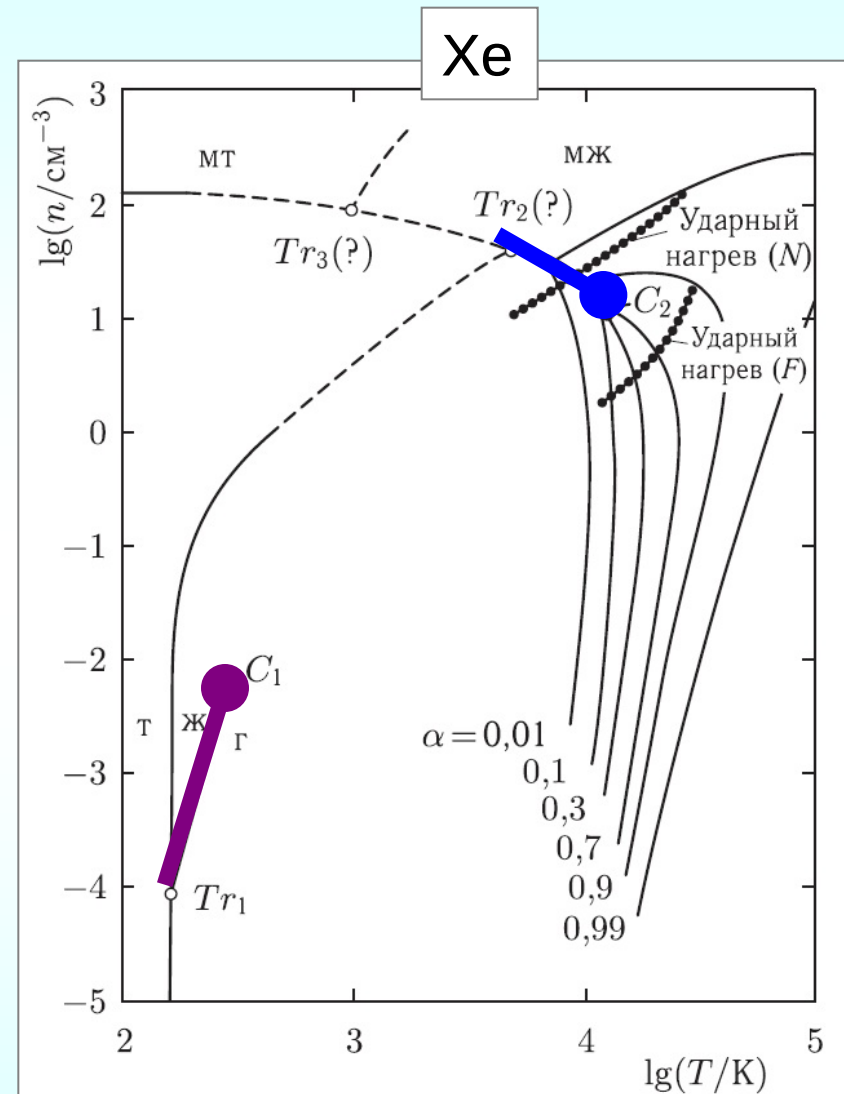
Entropic PT

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

P - T diagram of plasma phase transition



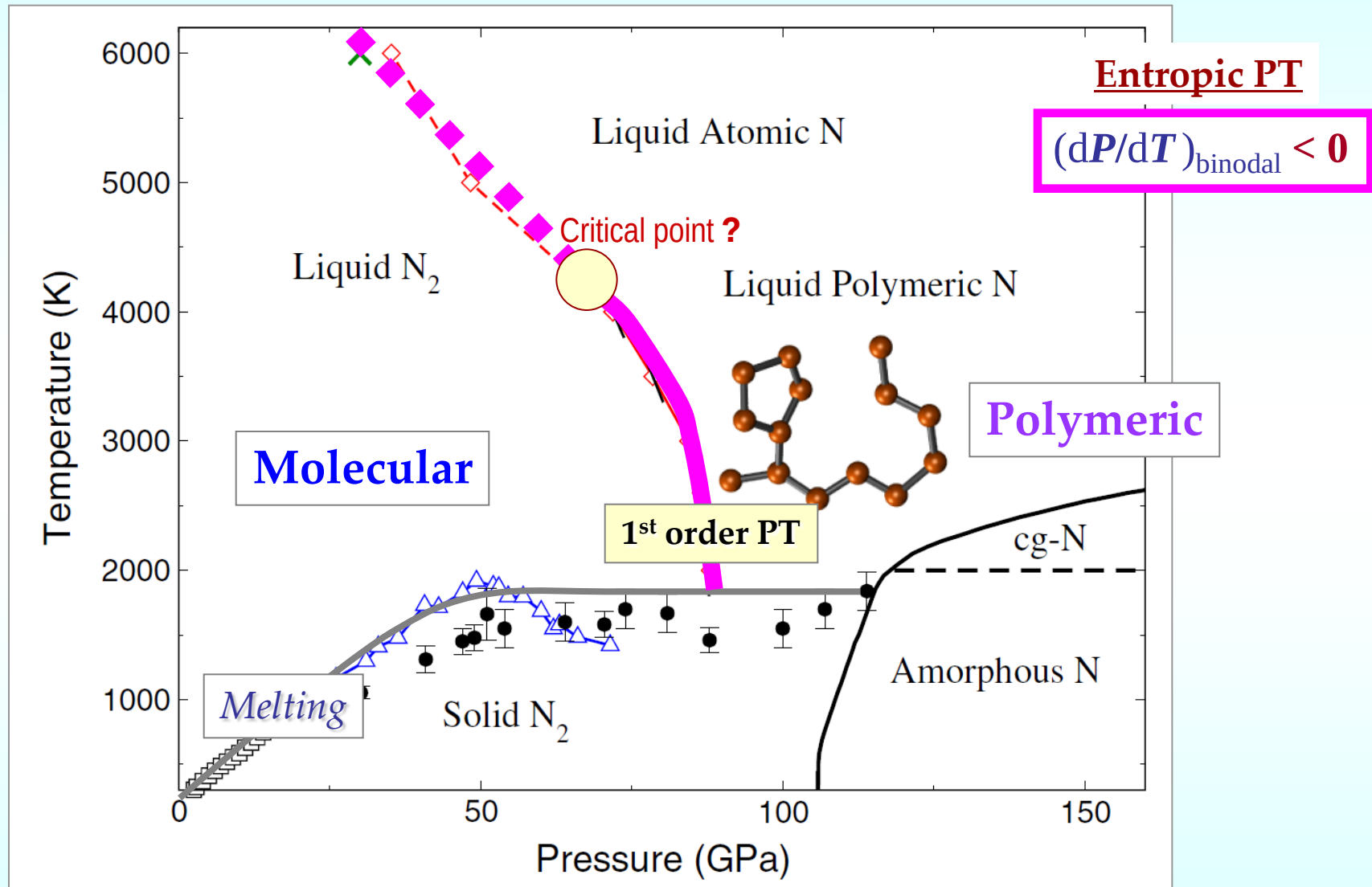
Ebeling W., Reichert W.
Phys. Lett. A, **80** (1985)



Ebeling W., Foerster A., Reichert W.

Gas-liquid phase transition

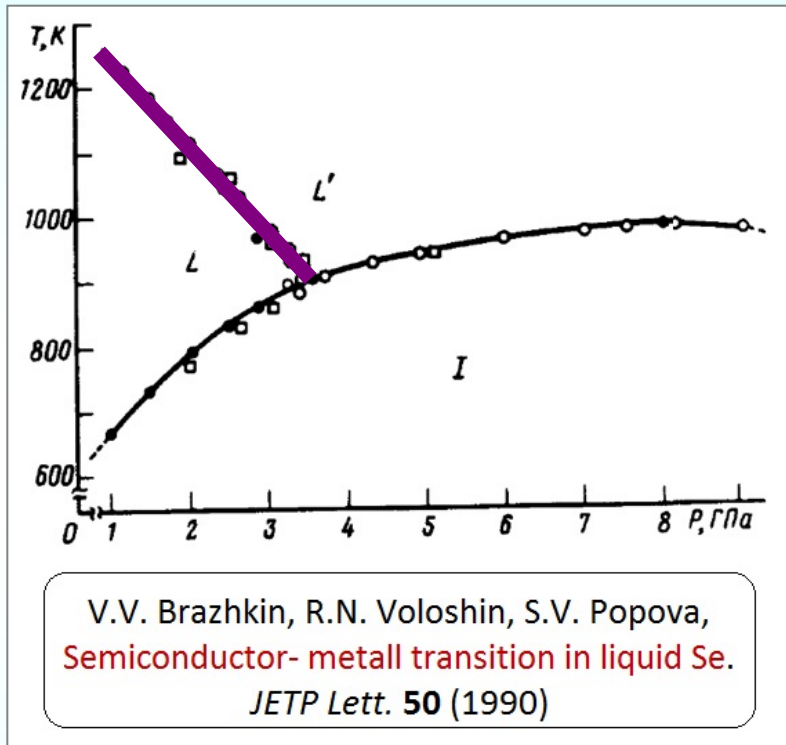
Entropy-driven fluid-fluid phase transitions (N_2)



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

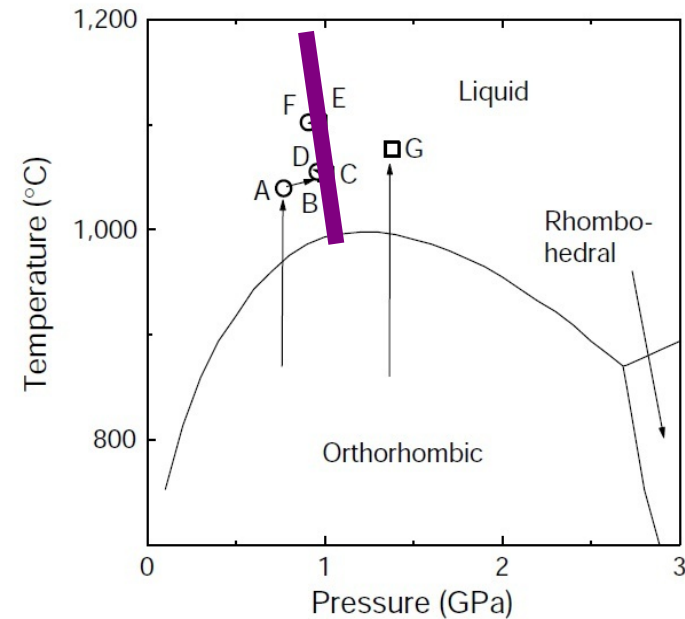
Entropy-driven fluid-fluid phase transitions

Selenium



Experiment

Phosphor



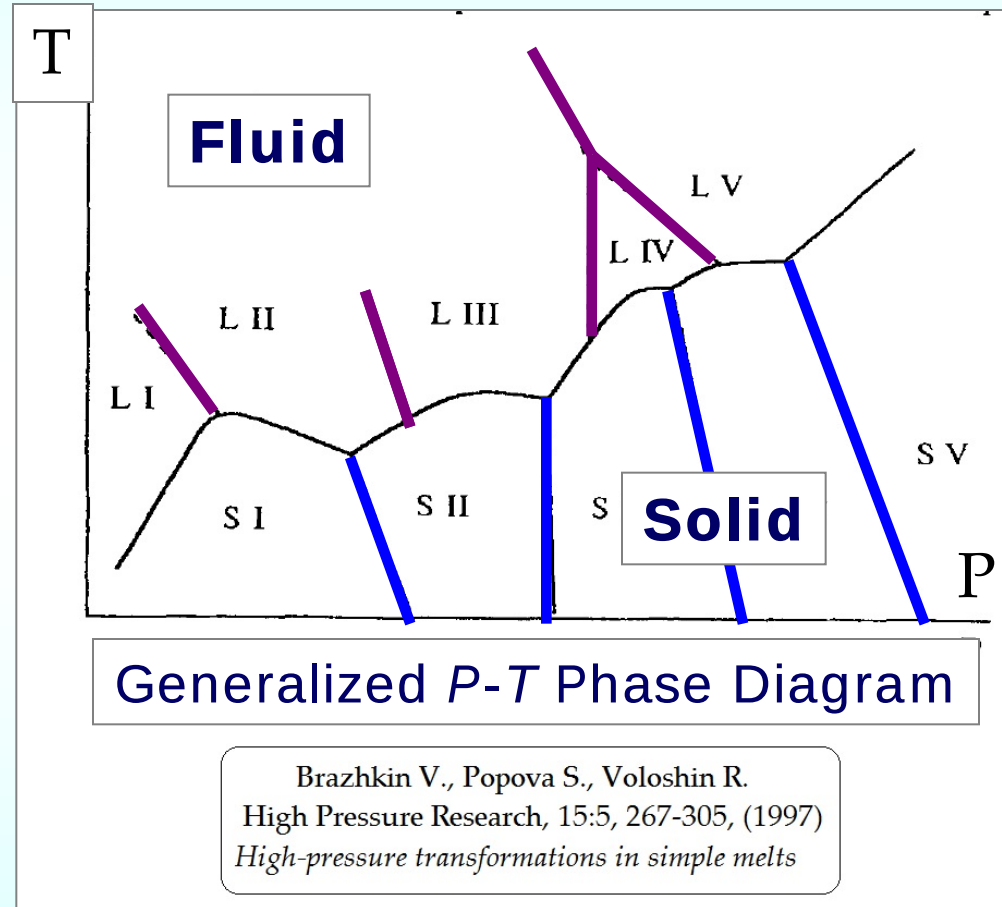
Katayama Y., Mizutani T. *et al.* (*Nature* **403**, 170 (2000))

Experiment

Enthalpic and Entropic Phase Transitions ?

Generalized P - T Phase Diagram

V. Brazhkin
(1997)



All polymorphic and fluid-fluid PTs are Entropic !

Enthalpic vs Entropic PTs

P - T phase diagram of GLPT and QHPT

GLPT – *gas-liquid phase transition*

Enthalpic PT

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

QHPT – *quark-hadron phase transition*

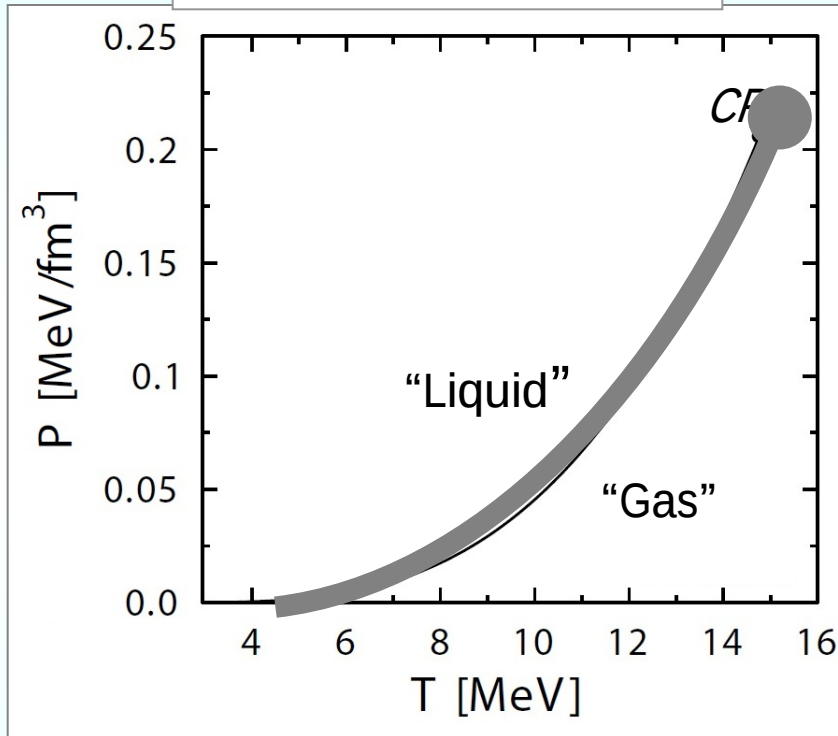
Entropic PT

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

$P - T$ phase diagram of symmetric Coulombless GLPT and QHPT

One-EOS approach (*critical point*)

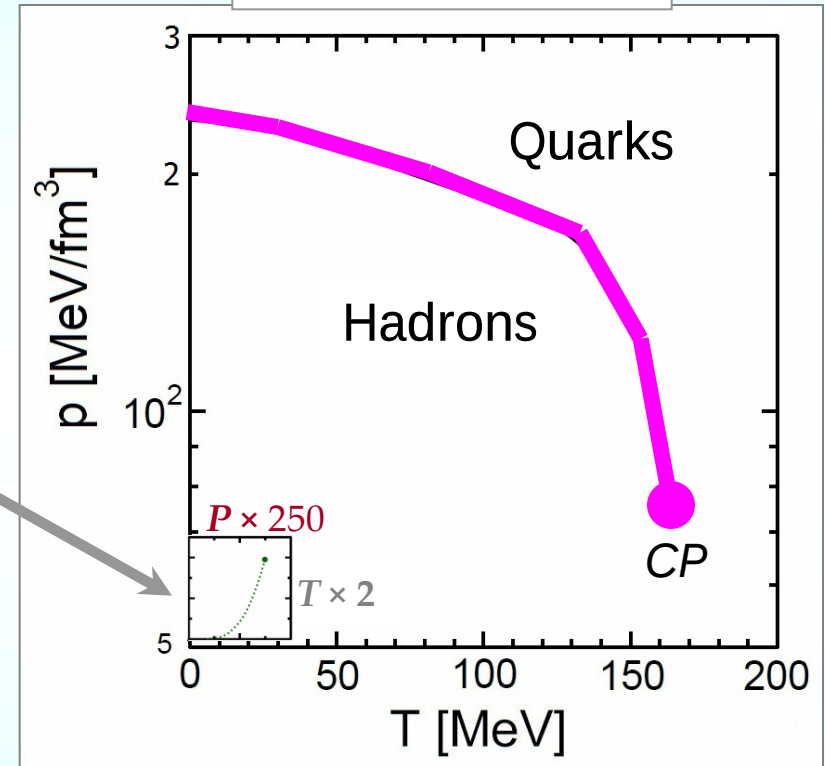
Nuclear Gas-Liquid PT



Standard VdW-like behavior

(*enthalpic PT*)

Quark-Hadron PT



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

(*entropic PT*)

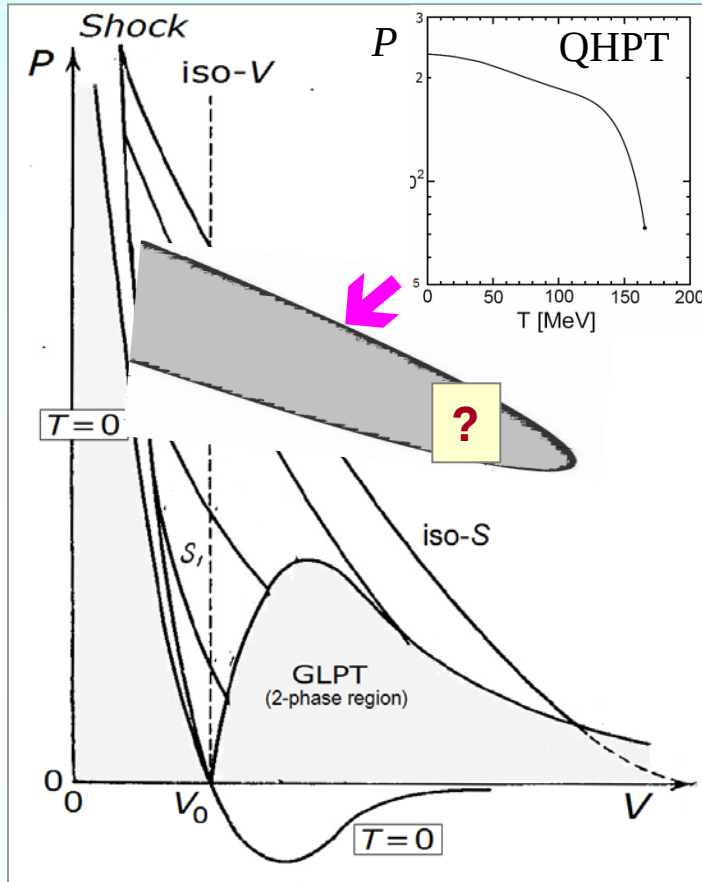
Non-congruence of the nuclear liquid-gas and the deconfinement phase transitions

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

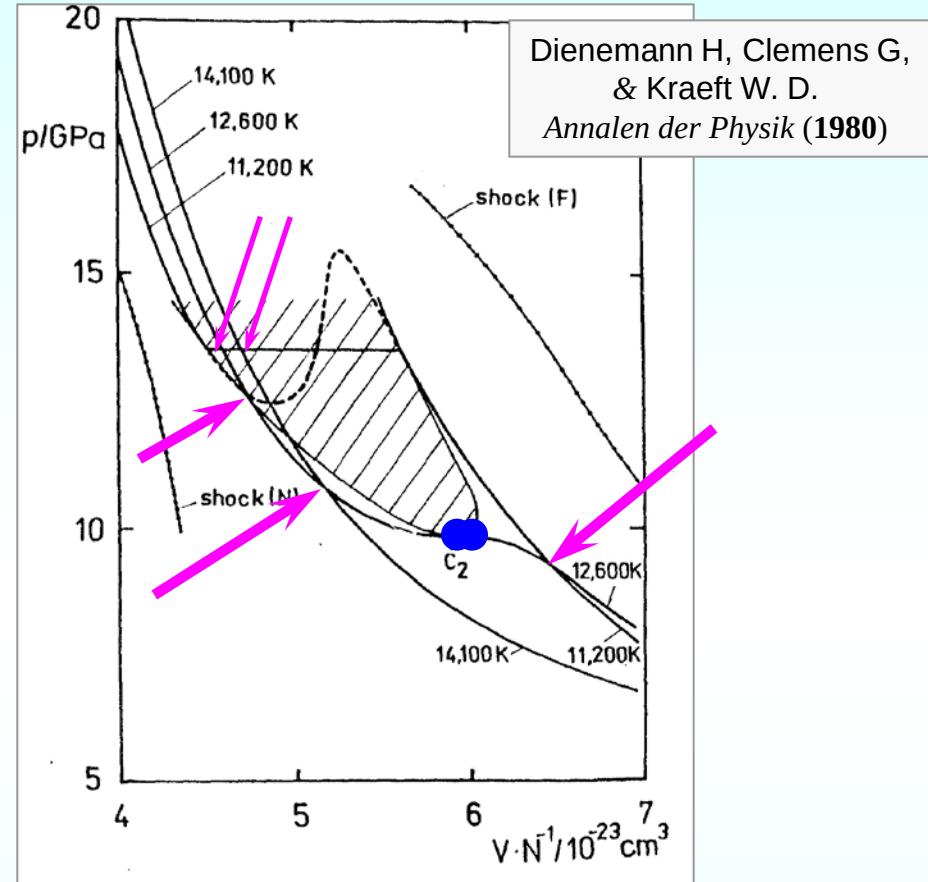
Enthalpic *vs.* Entropic phase transitions

***P-V* phase diagram !**

Ionization-driven (entropic) phase transition



$P(V)$



Enthalpic (gas-liquid) phase transition

Entropic (ionization-driven) phase transition in Xe

NB!

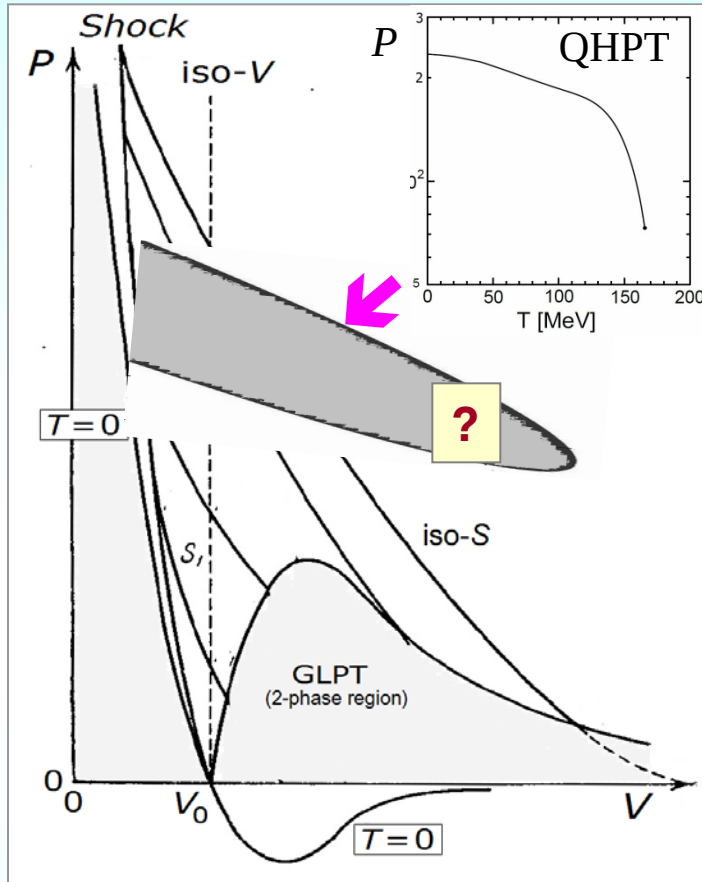
Abnormal order and crossing of isotherms !

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

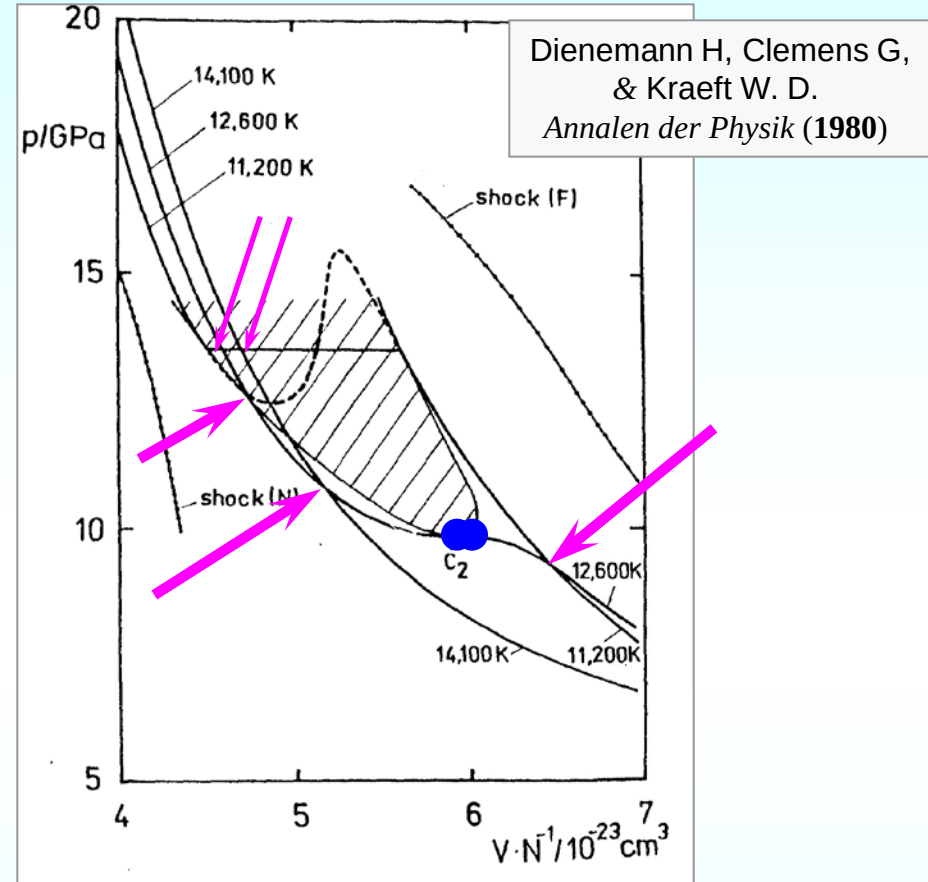
In the **vicinity** of **entropic PT** one meets **abnormal thermodynamics !**

(e.g.: Iosilevskiy I. & Starostin A., *Encyclopedia on Low-T Plasmas*, V.I, Ch. III-1, 2000, P.327-339) // V.III-1 (suppl) 2004, P. 349)

Ionization-driven (“plasma”) phase transition



$P(V)$



Enthalpic (gas-liquid) phase transition

Entropic (ionization-driven) phase transition in Xe

NB !

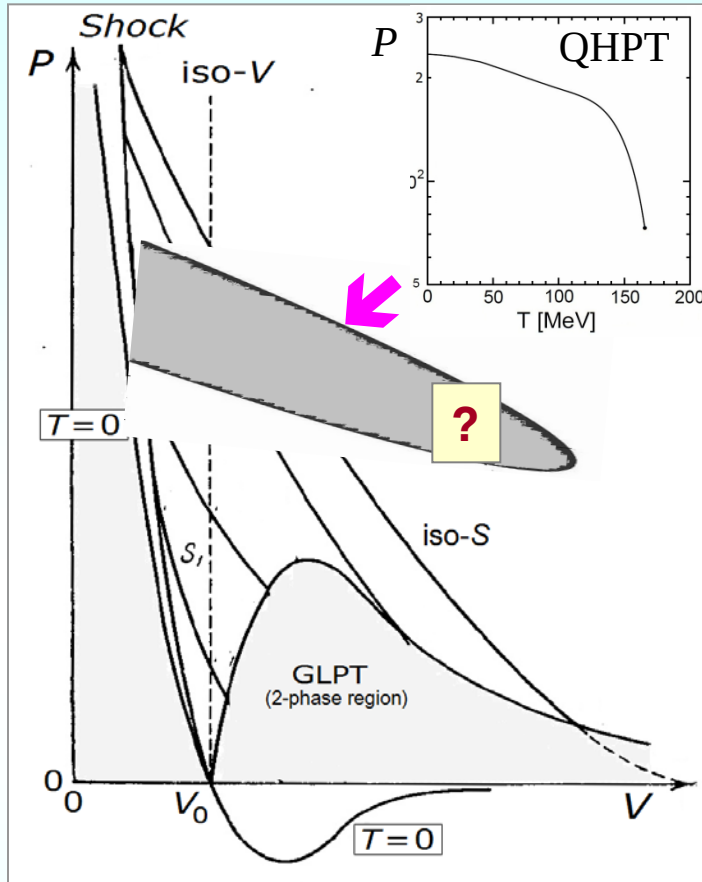
Abnormal order and crossing of isotherms !

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

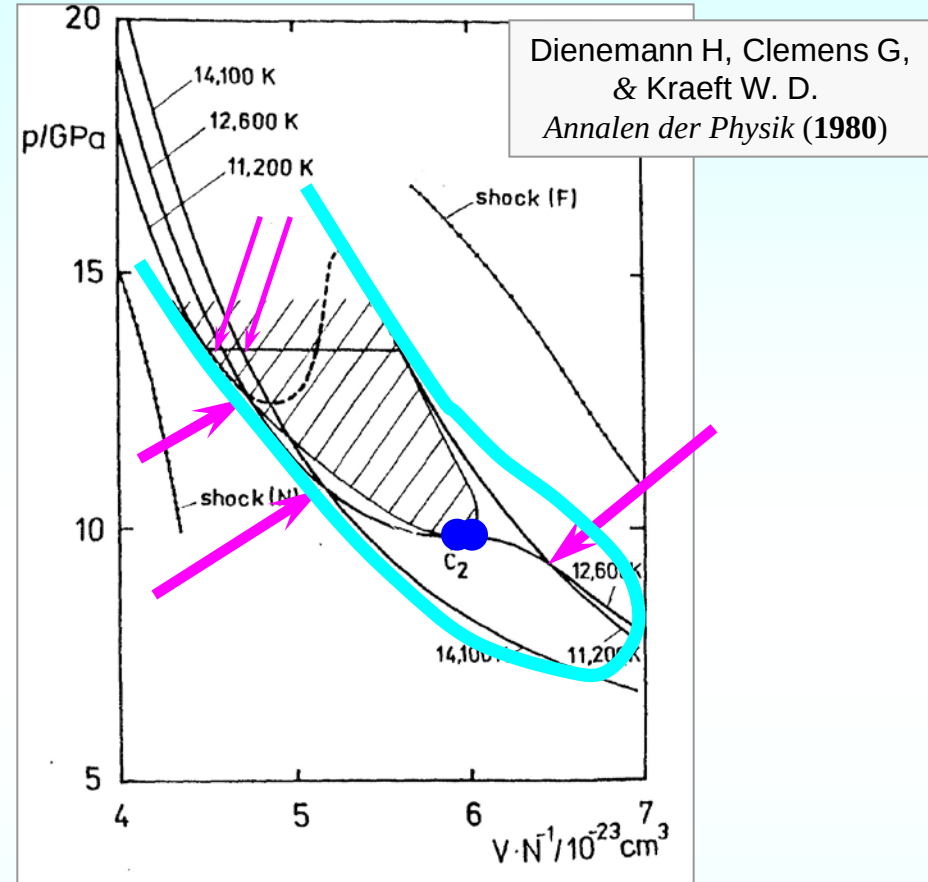
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Ionization-driven (“plasma”) phase transition



$P(V)$



Enthalpic (gas-liquid) phase transition

Entropic (ionization-driven) phase transition in Xe

NB !

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

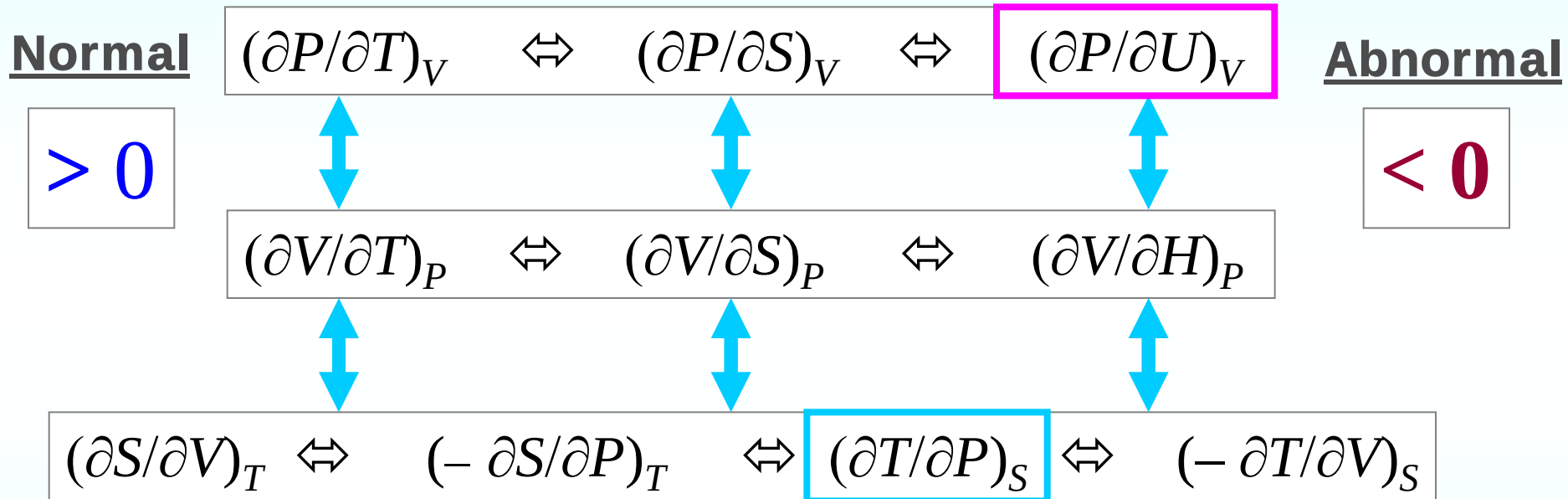
$$(\partial P / \partial T)_V < 0 \rightarrow V(\partial P / \partial U)_V < 0 \Leftrightarrow (\partial V / \partial T)_P < 0 \Leftrightarrow (\partial T / \partial P)_S < 0$$

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

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

Abnormal Thermodynamics Region - *ATR*

**Normally positive second cross derivatives became
*negative simultaneously !***



$Gr \equiv V(\partial P/\partial U)_V < 0$ – **Negative** Gruneisen parameter !

$(\partial T/\partial P)_S < 0$ – temperature **fall** under isentropic compression !

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

Abnormal 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) !**

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



**Abnormal decreasing temperature
under isentropic compression !**

$$(\partial S / \partial V)_T < 0$$



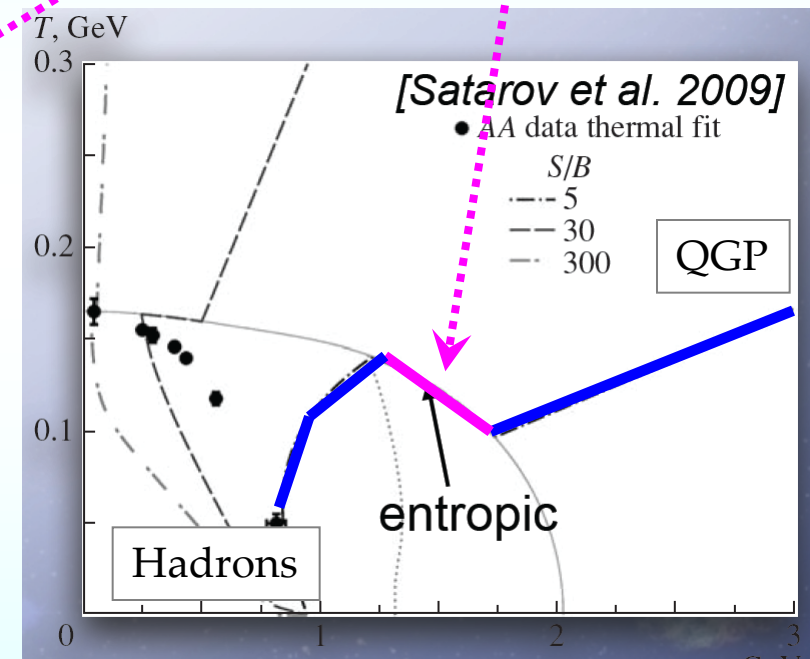
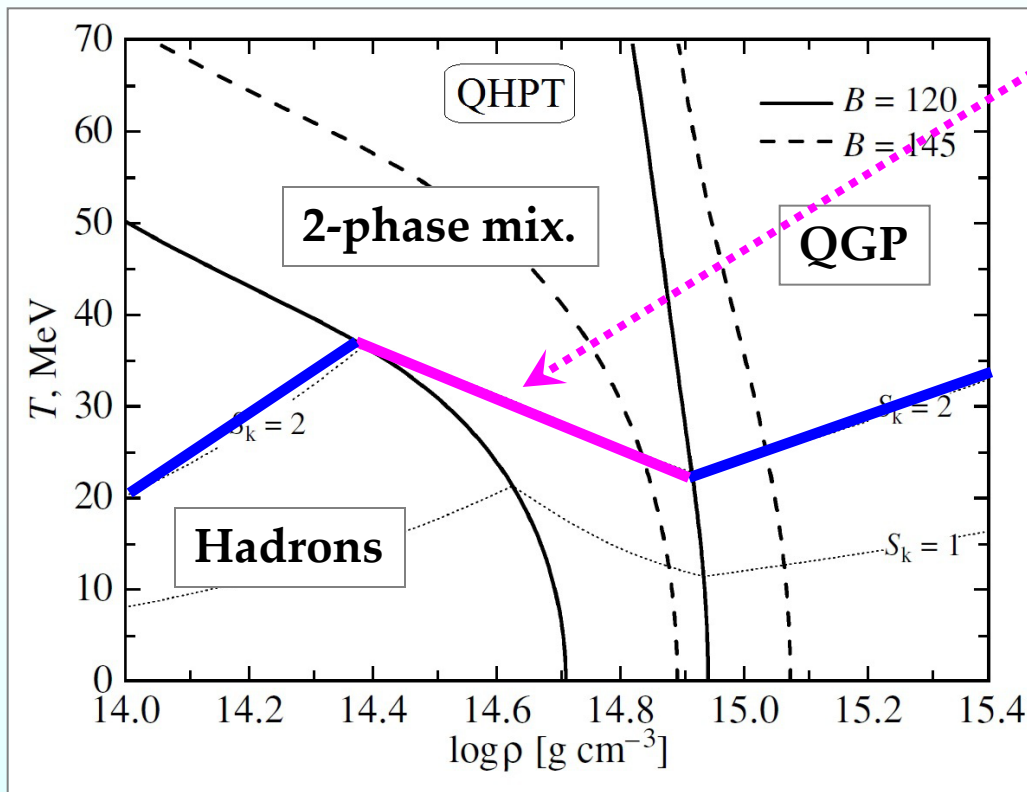
**Abnormal decreasing (increasing) entropy
under isothermal expansion (compression) !**

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

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



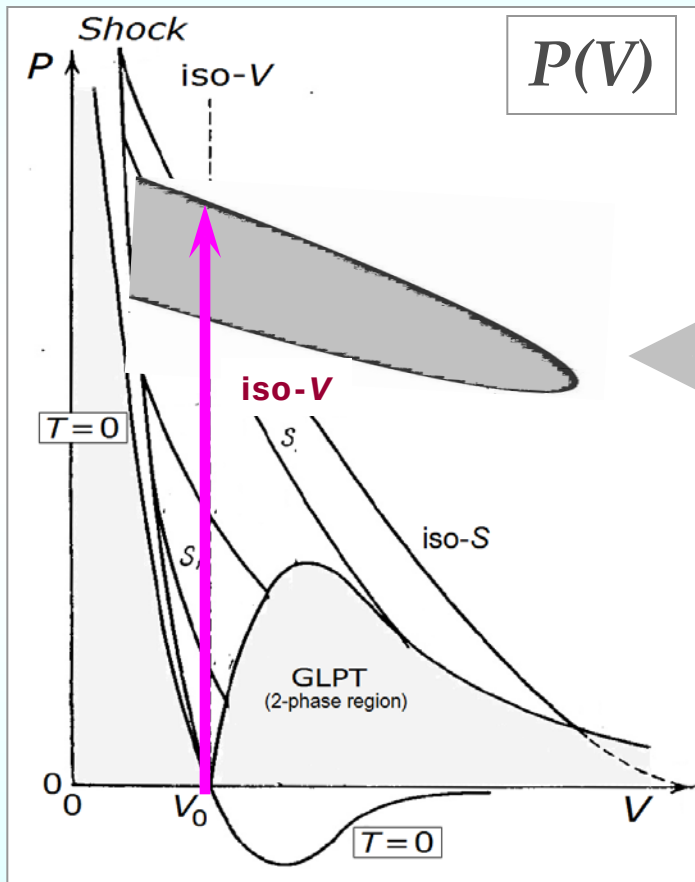
Matthias Hempel
Istanbul, 25.04.2016

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

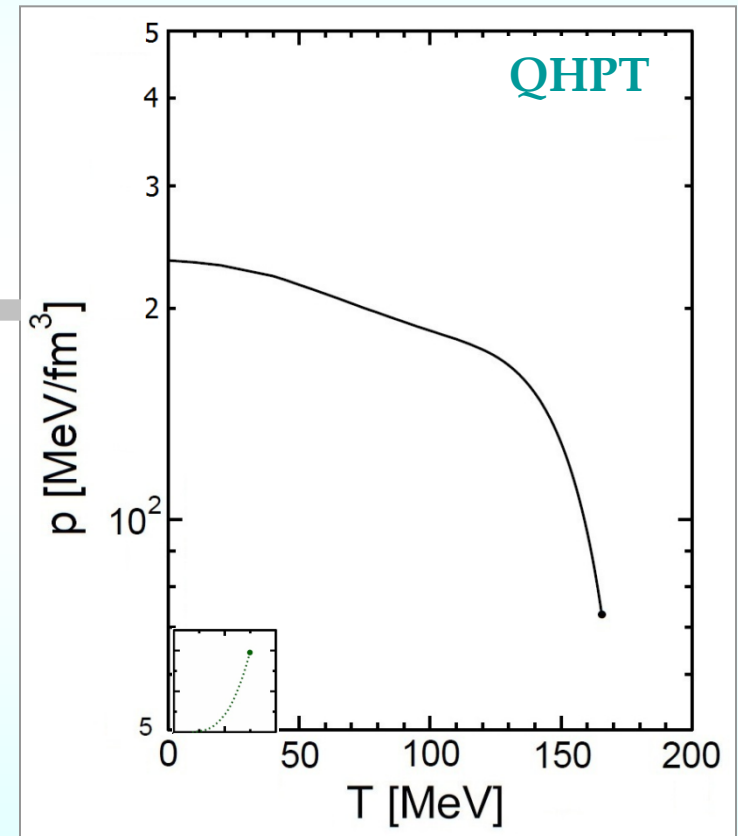
Multi-layered structure *of* thermodynamic surfaces

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

for entropic phase transitions



Gas-liquid phase transition
(*Van-der-Waals-like*)

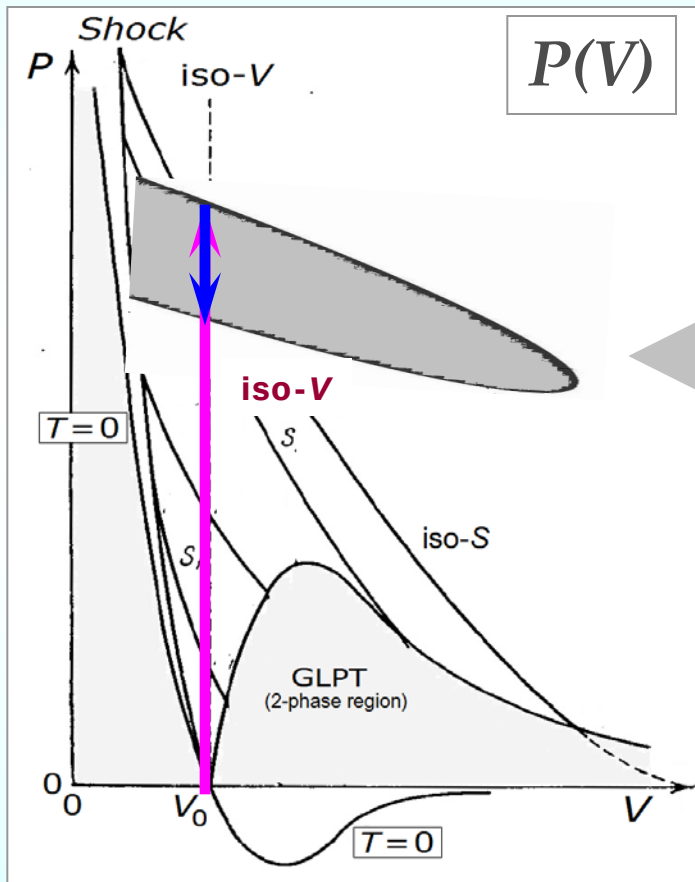


Entropic (*deconfinement-driven*) phase transition
SU(3) model (Veronica Dexheimer & Stefen Schramm)

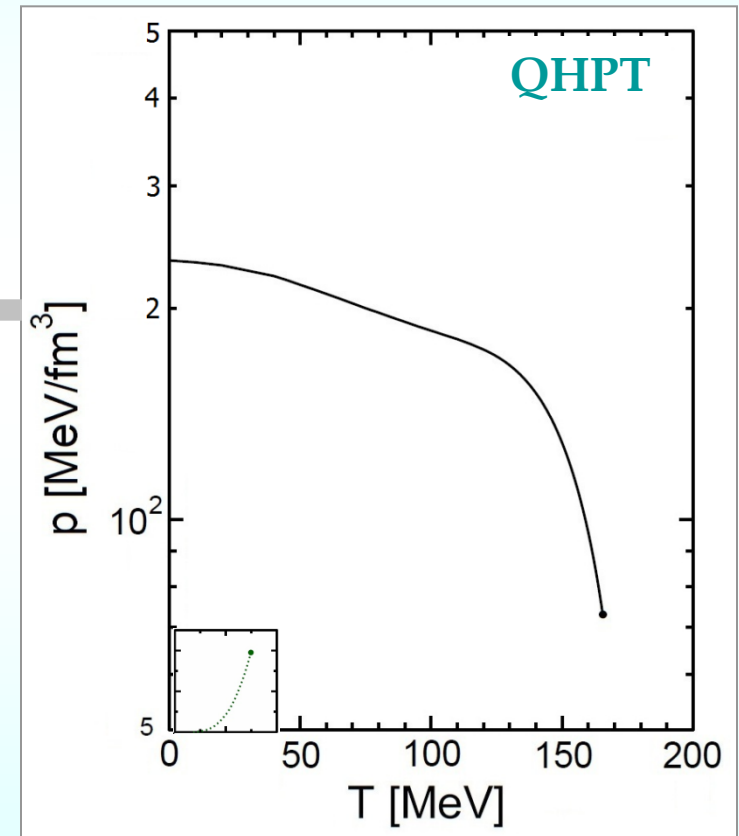
Multi-layered structure *of* thermodynamic surfaces

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

for entropic phase transitions

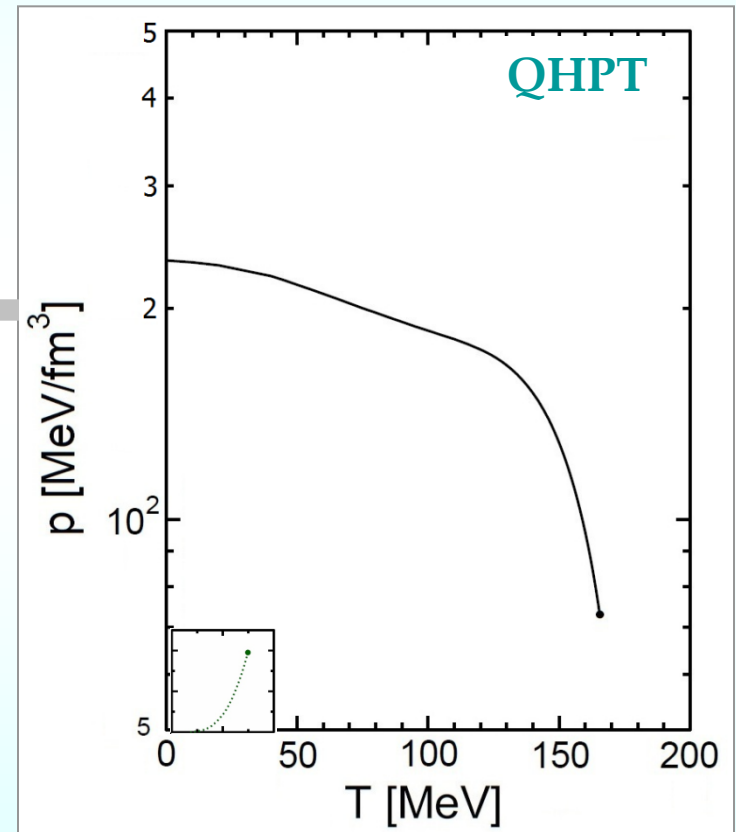
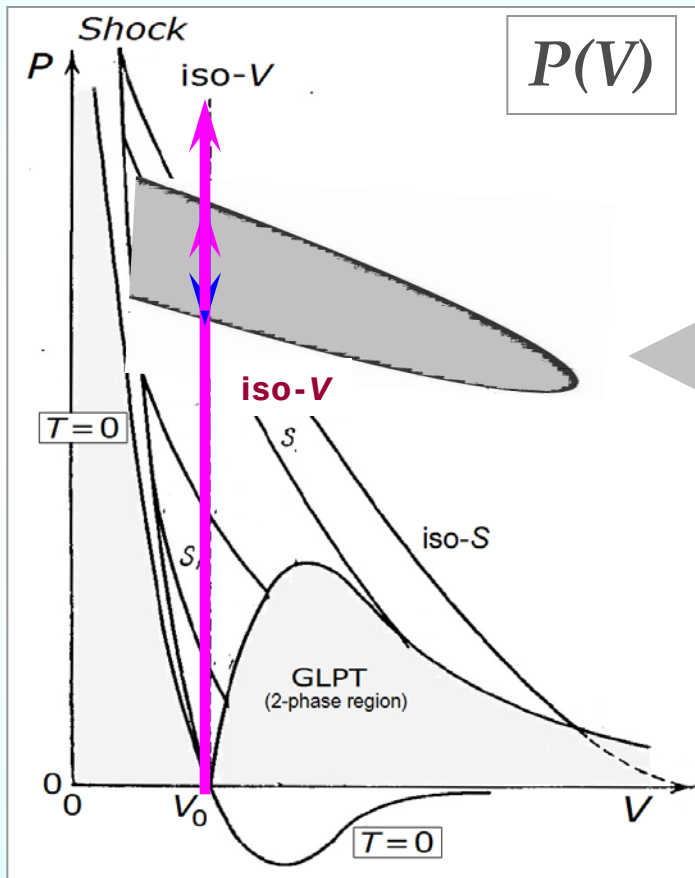


Gas-liquid phase transition
(*Van-der-Waals-like*)



Entropic (*deconfinement-driven*) phase transition
SU(3) model (Veronica Dexheimer & Stefen Schramm)

Multi-layered structure *of* thermodynamic surfaces $T(p,V)$, $U(p,V)$, $S(p,V)$... *for* entropic phase transitions



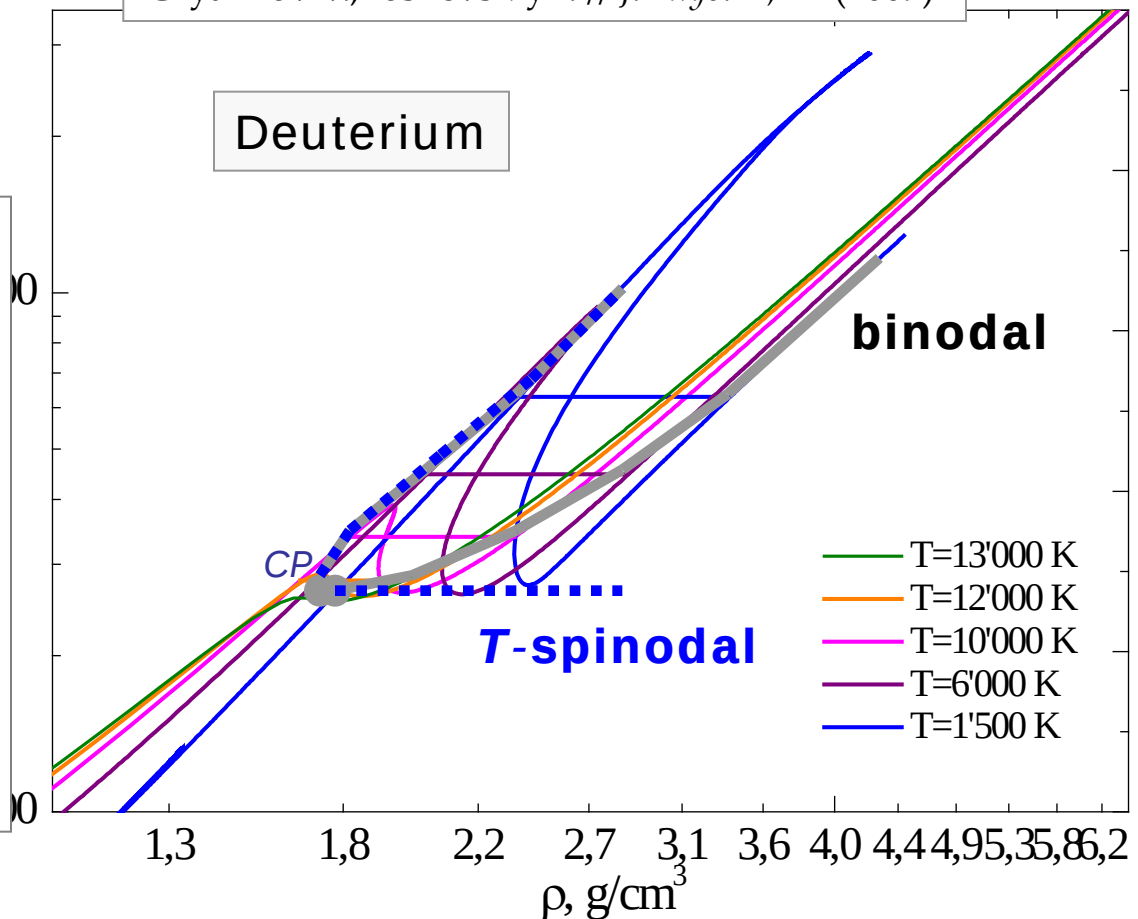
One comes *under*.., then *through*.., then *over* two-phase region
 during isochoric heating $\Longleftrightarrow (\partial P / \partial T)_V < 0$

Hypothetical dissociation-driven (*entropic*) PT

Code SAHA-D

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

Deuterium

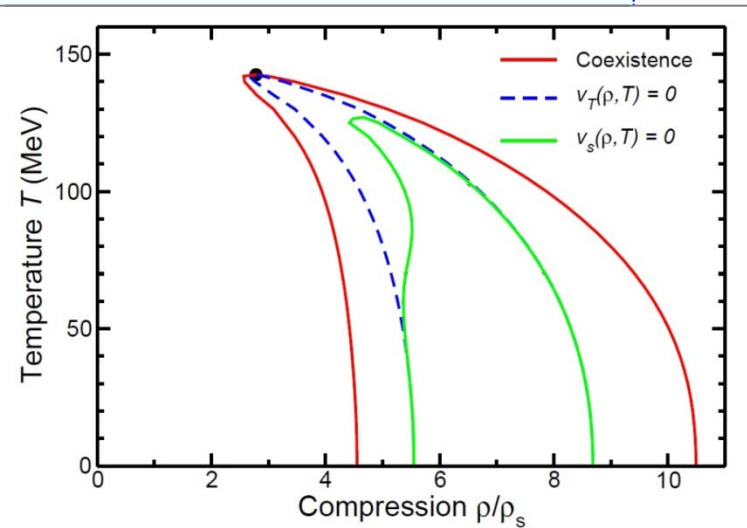


CP

Binodal

T-spinodal

S-spinodal



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

Spinodal phase separation in relativistic nuclear

phase transition

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** !

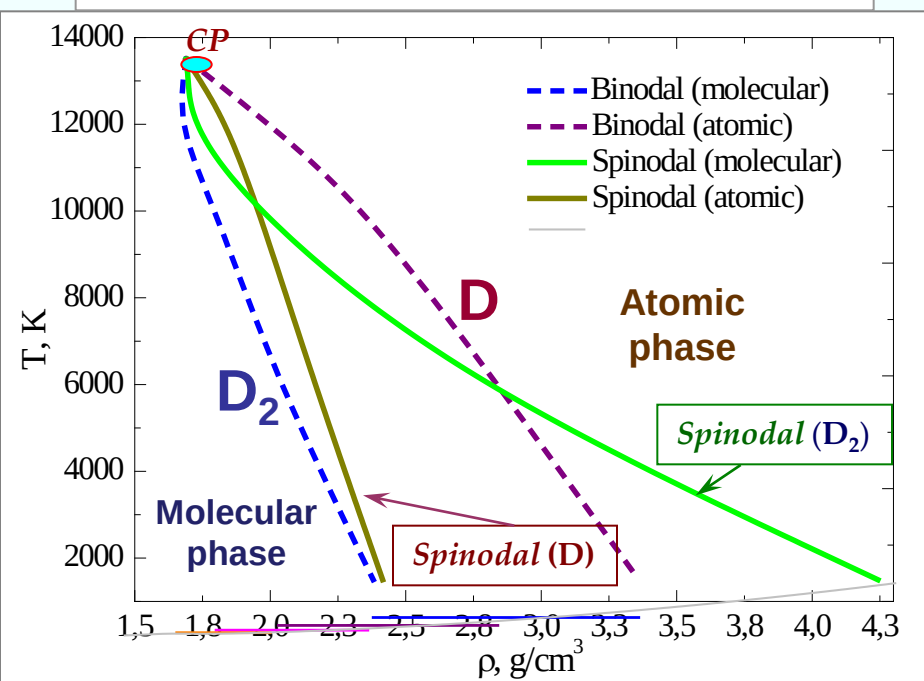
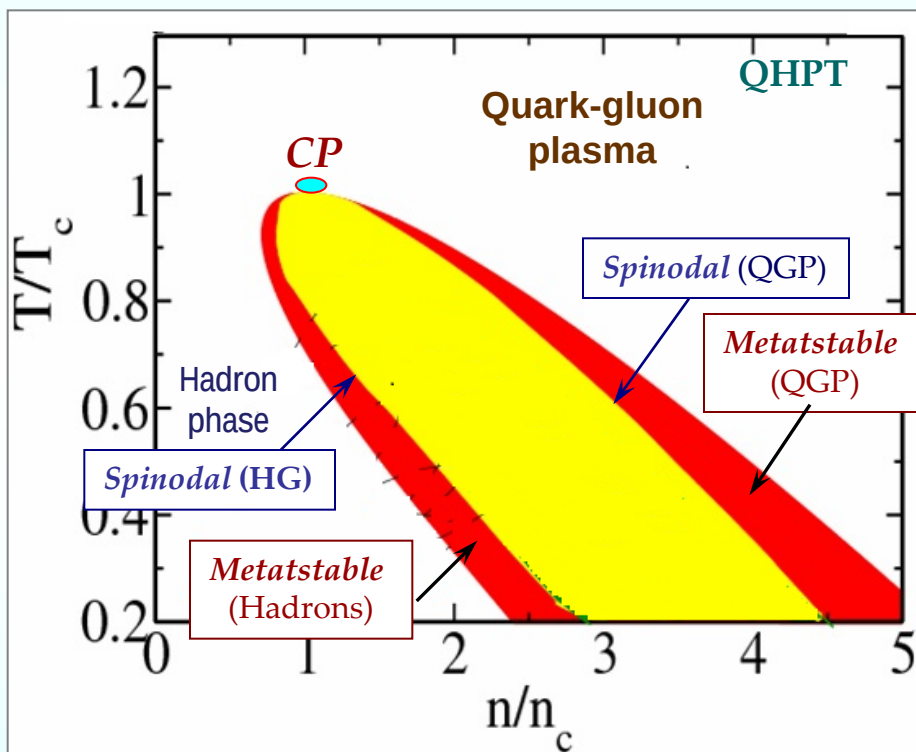
Abnomal topology *of* binodals *and* spinodals

in the region of **entropic phase transition**
(T - ρ diagram)

Vladimir Skokov, *Int. Conference "Prerow-2009"*

Code SAHA-D

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



“**Night bat**” structure of metastable “**wings**”

NB !

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

Abnomal topology *of* binodals *and* spinodals

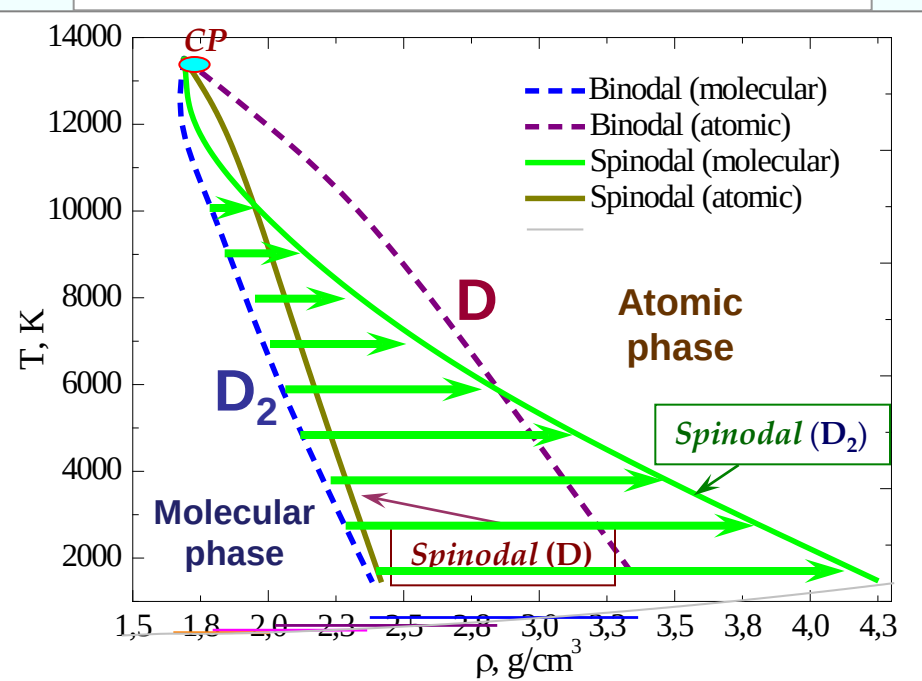
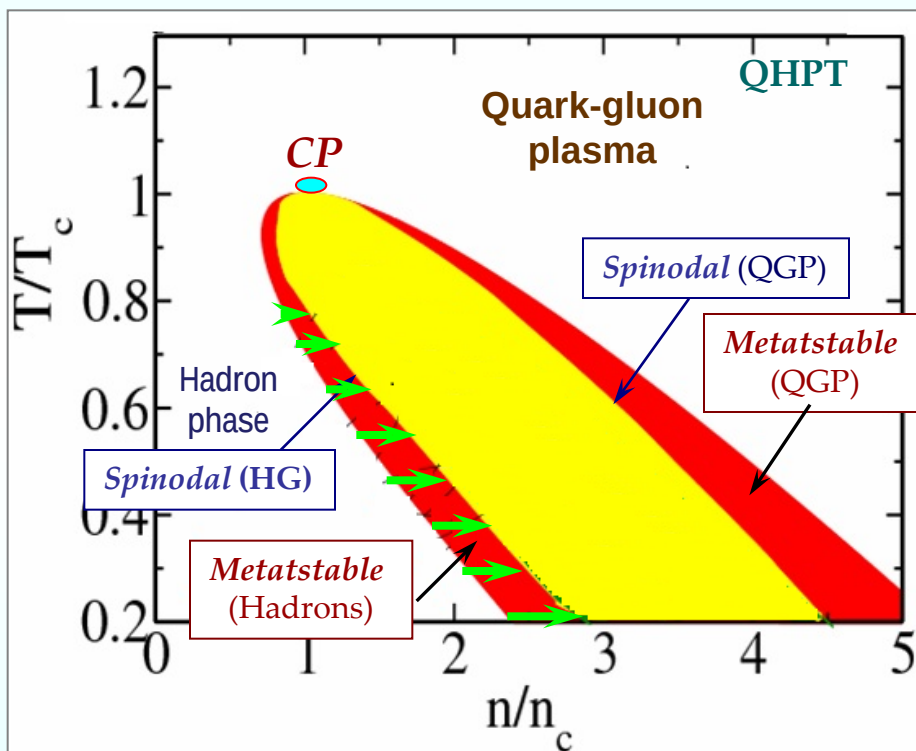
in the region of entropic phase transition

(T - ρ diagram)

Vladimir Skokov, *Int. Conference "Prerow-2009"*

Code SAHA-D

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



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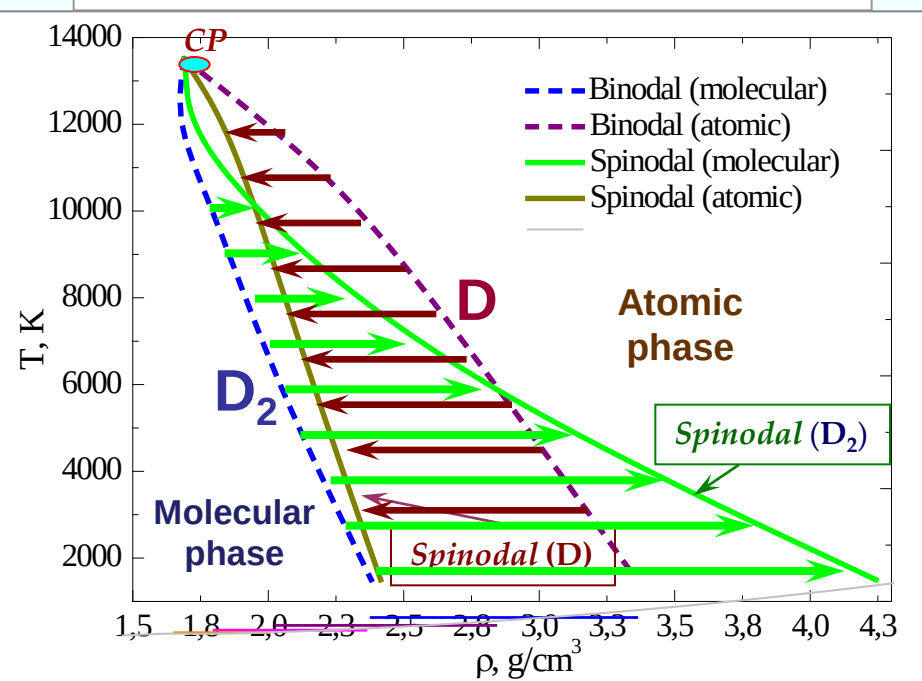
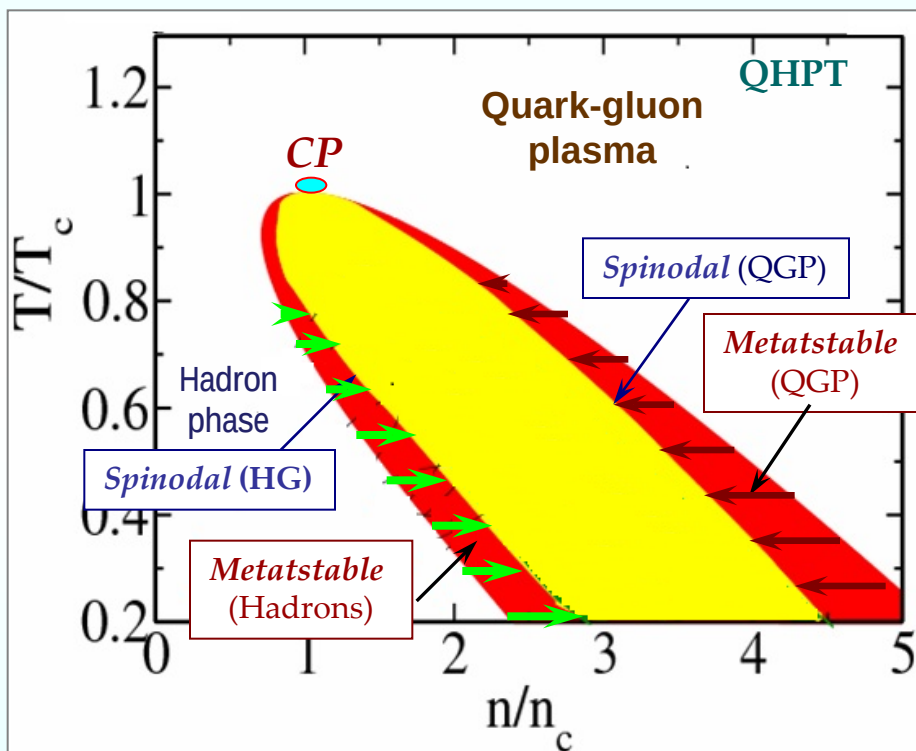
in the region of entropic phase transition

($T - \rho$ diagram)

Vladimir Skokov, *Int. Conference "Prerow-2009"*

Code SAHA-D

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



“**Night bat**” structure of metastable “**wings**”

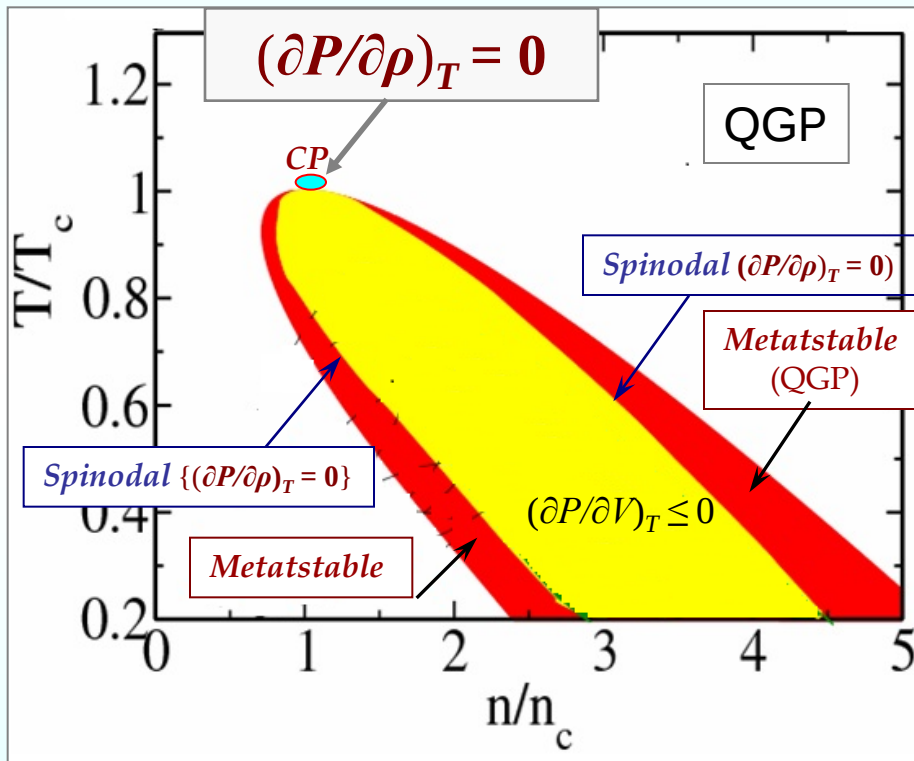
NB!

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

Abnomal features of entropic phase transition (due to multi-layered structure of thermodynamic surfaces !) (T - ρ diagram)

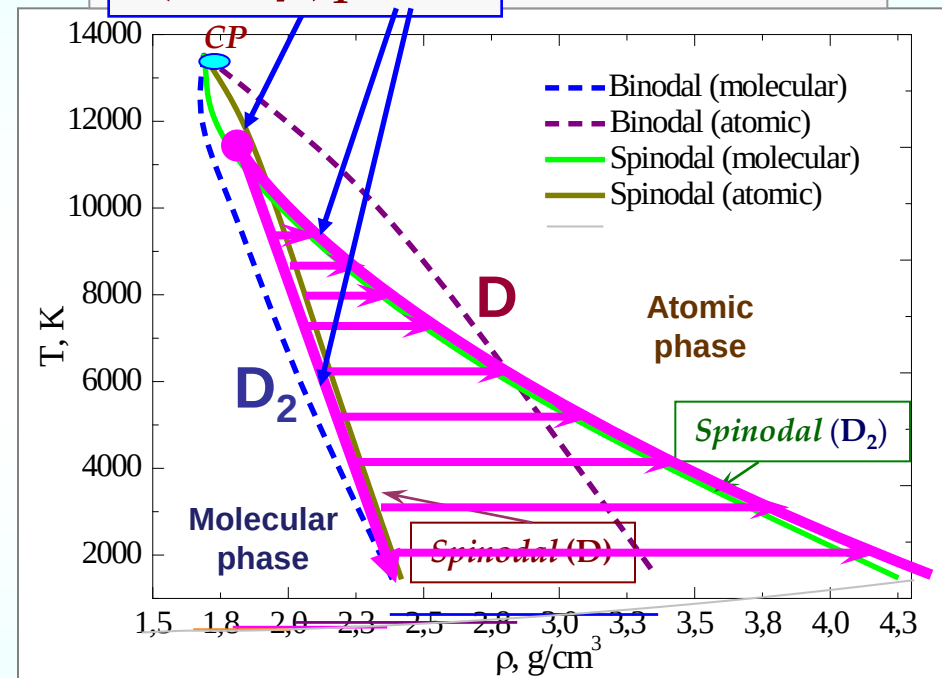
QHPT

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



QHPT

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



NB !

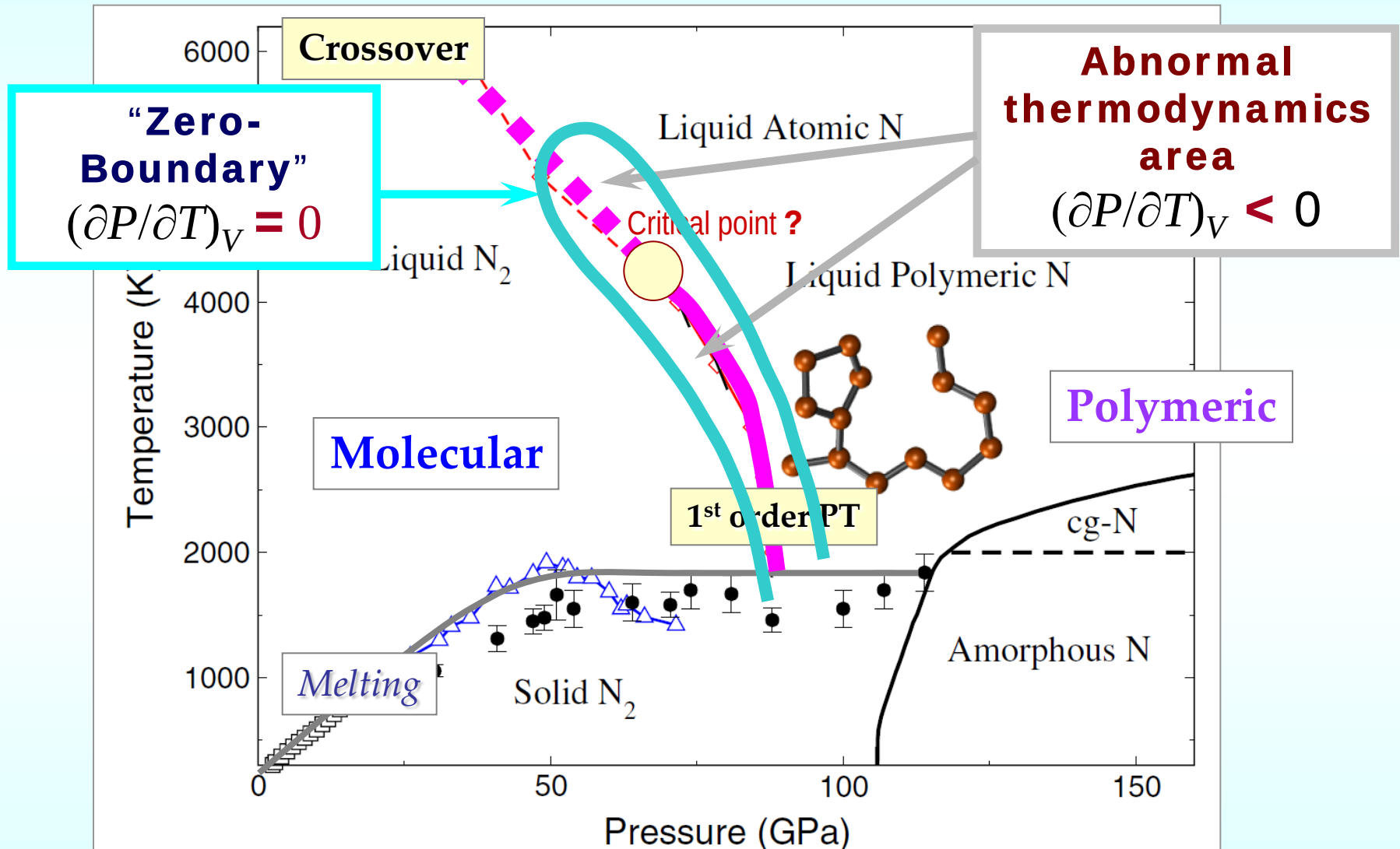
New (additional) region of metastable state $\Leftrightarrow (\partial P/\partial \rho)_T \geq 0$

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

{ Iosilevskiy I. // (in preparation) }

Entropy-driven fluid-fluid phase transitions (N_2)

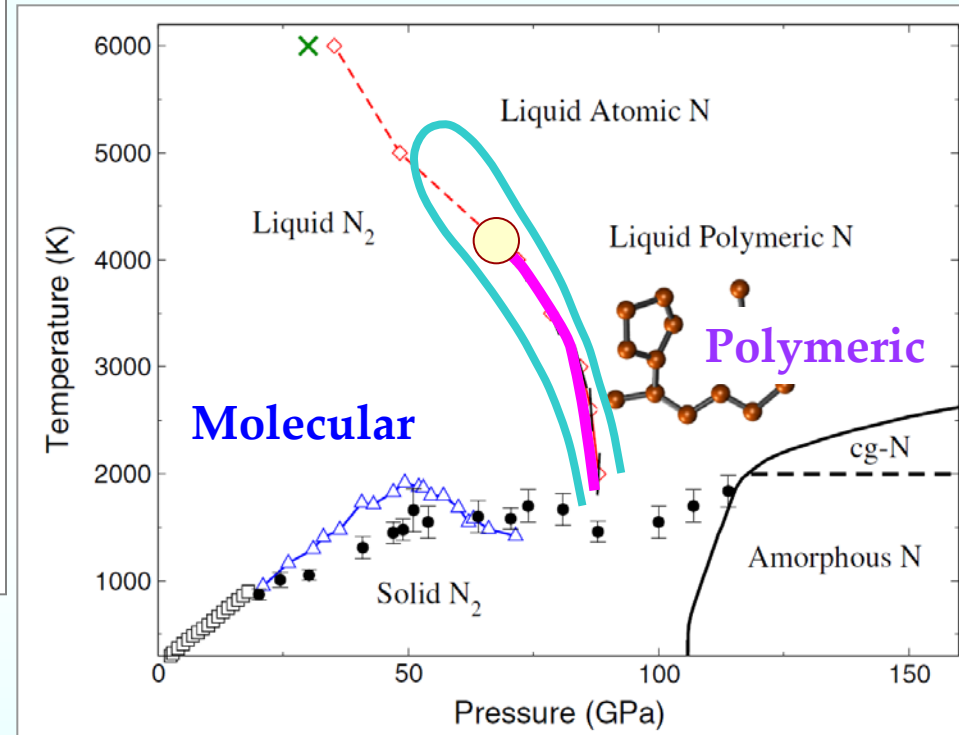
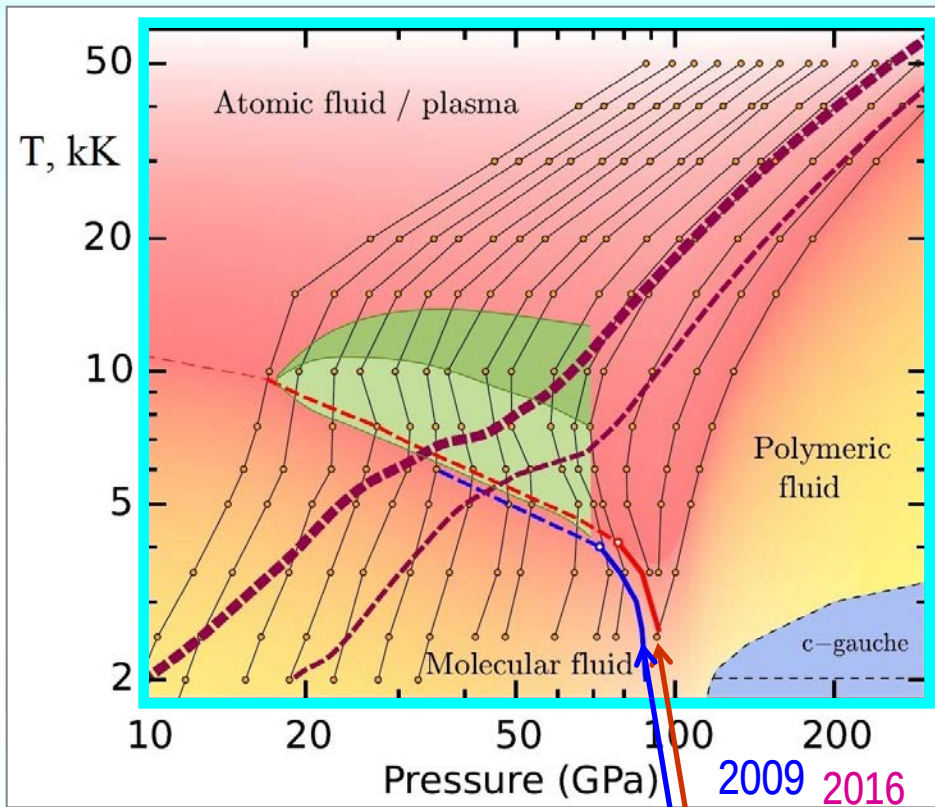
Boates B., Bonev S. *Phys. Rev. Lett.* **102** (2009)/ Quantum Molecular Dynamics



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

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

Phase Diagram of Warm Dense Nitrogen (*abnormal thermo- and hydrodynamics*)



(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

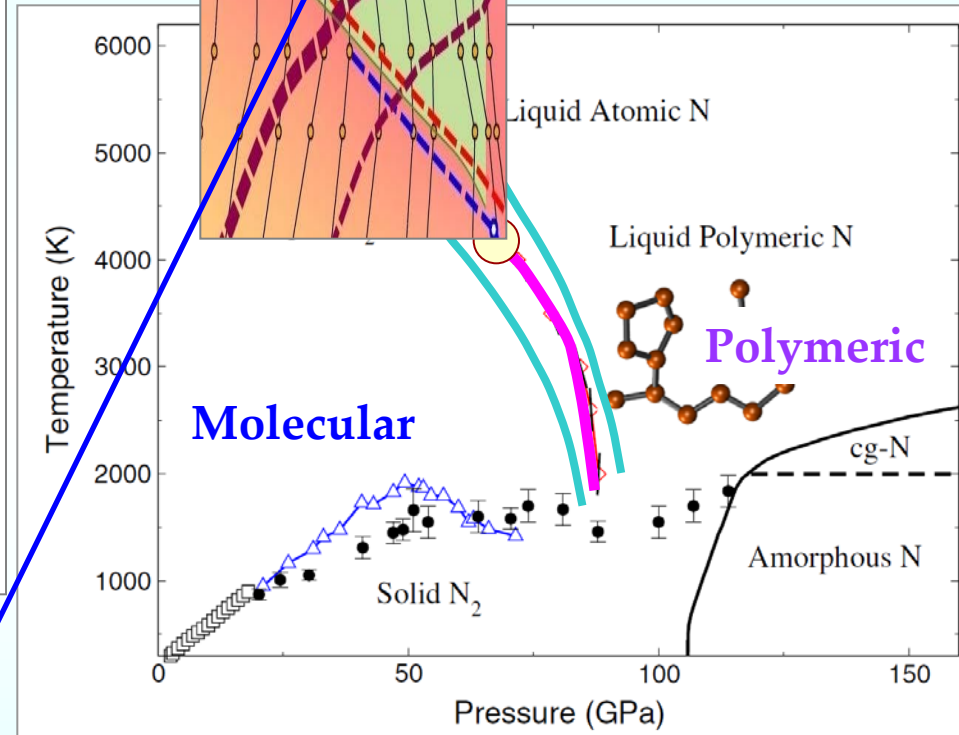
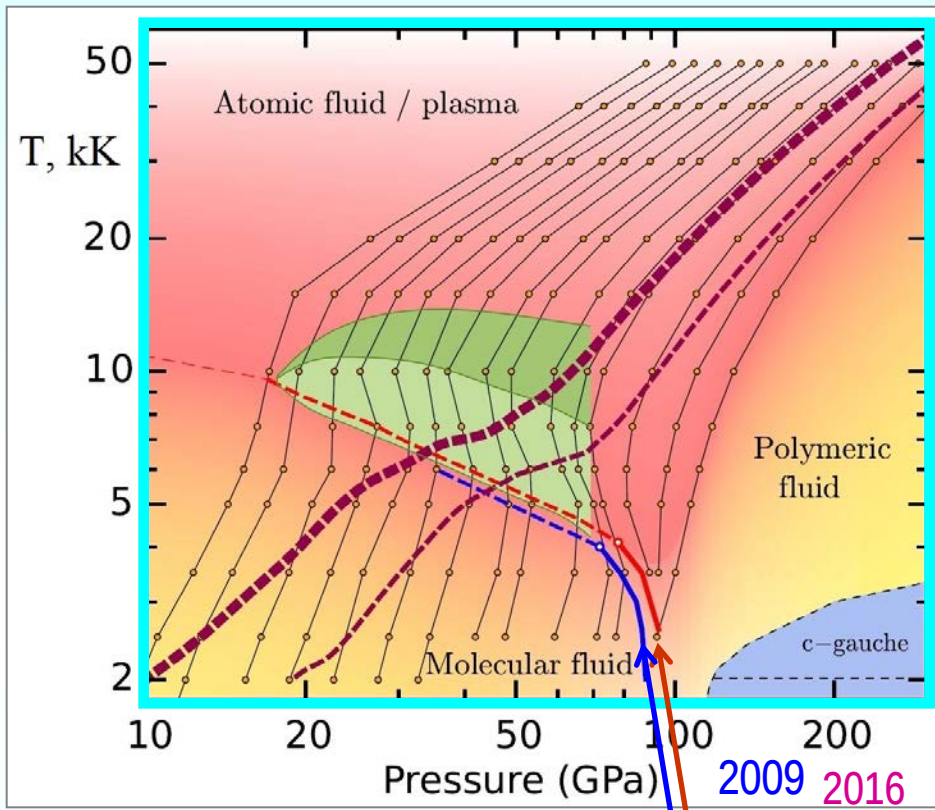
Driver K.P. & Militzer B., *Phys. Rev. B*, 93 (2016)
Principles Equation of State of Warm Dense Nitrogen

■ ■ ■ ■ ■ Liquid Hugoniot ($\rho_0 = 0.808$ g/cc)

..... Solid Hugoniot ($\rho_0 = 1.035$ g/cc)

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

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



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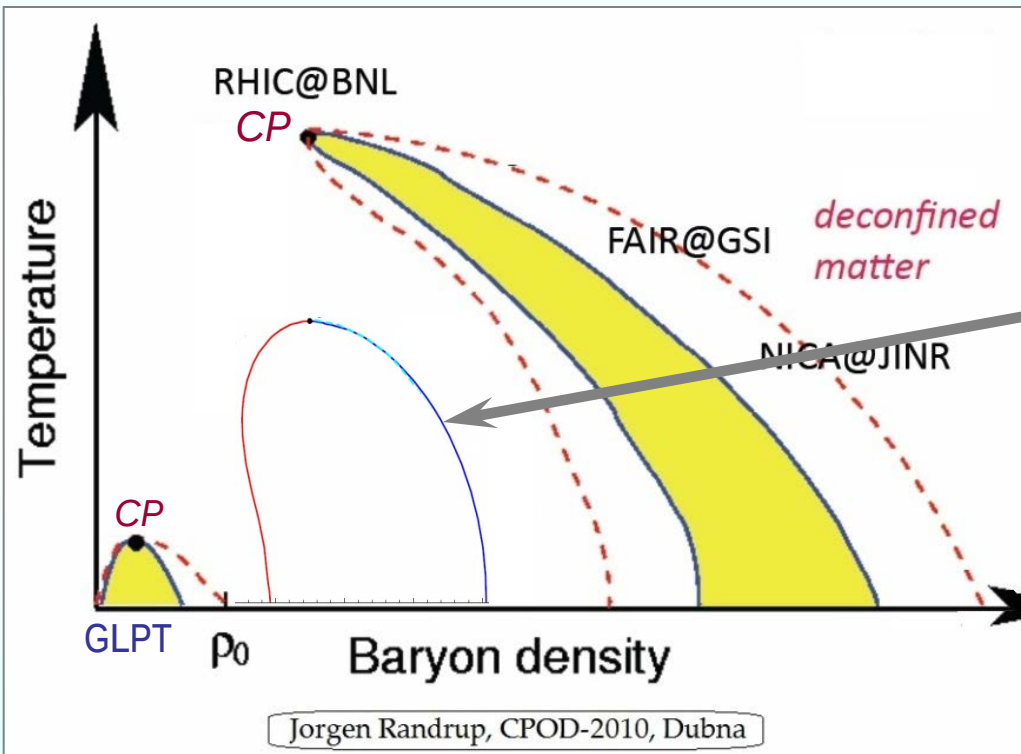
Driver K.P. & Militzer B., *Phys. Rev. B*, 93 (2016)
Principles Equation of State of Warm Dense Nitrogen

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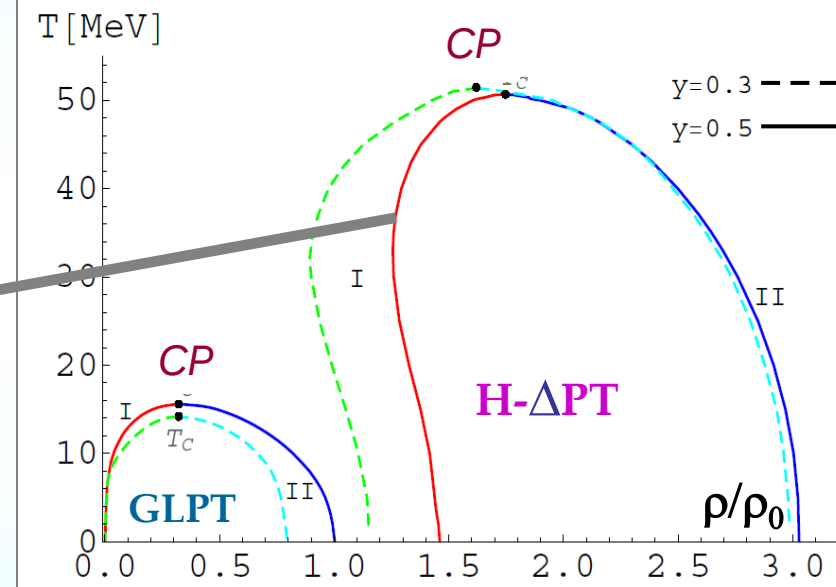
Gas-liquid, **Hadron- Δ -meson** and Quark-hadron phase transitions are often considered as similar

Prerow 2009

"Critical Point and Onset of Deconfinement"
Dubna, Russia, 2009



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

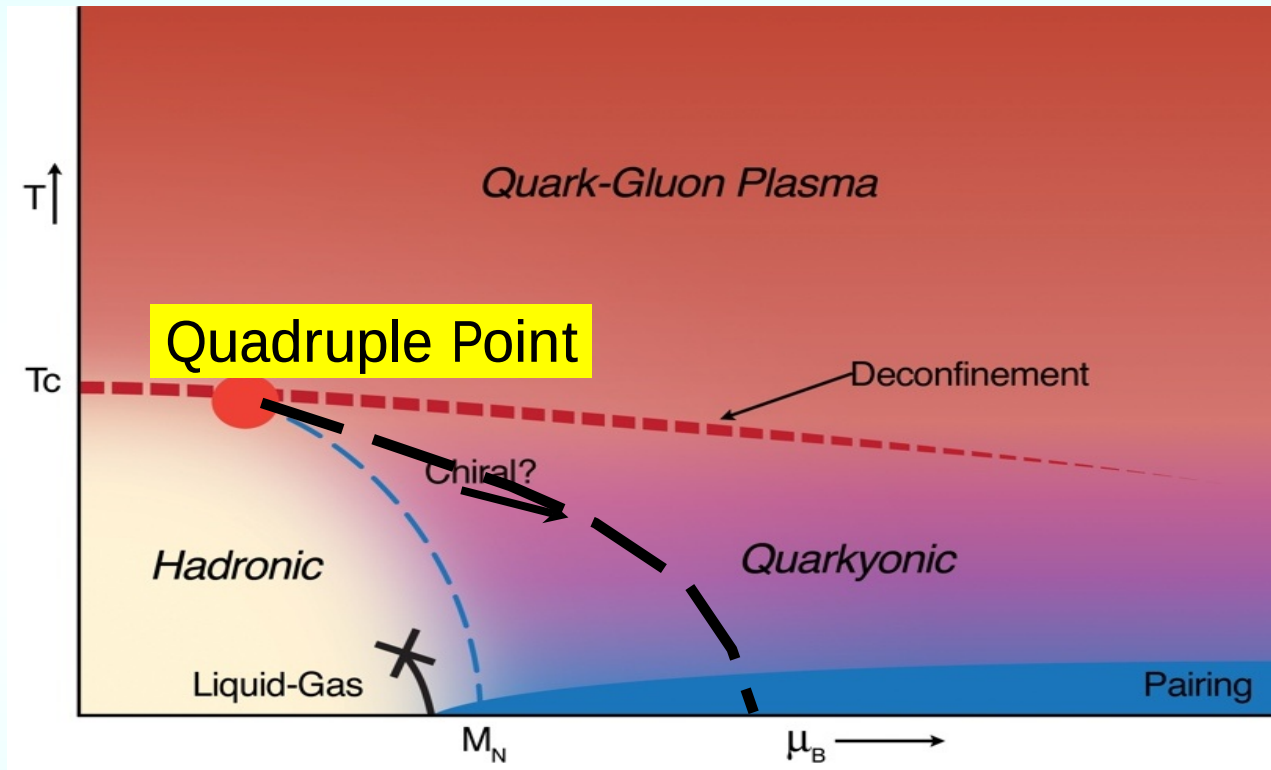


Lavagno A., Drago A., Pagliara G., Pigato D.
J. of Phys. 527 (2014)
**Thermodynamic instability in nuclear matter
and in compact stars**

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

Outlook

Inventory of new hypothetical phase transitions



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

What type of all these hypothetical phase transitions:
- 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...) the both have many **common features** because both are **entropic PTs**.
- **Properties** of **entropic PTs** **differ significantly** from those of **enthalpic PTs**.
- **Anomalous** features of **entropic phase transition** are due to **multi-layered structure of thermodynamic surfaces** $\{U(p,V), T(p,V), S(p,V) \dots \}$

Thank you!



(Lawrence Alma-Tadema)

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Welcome to Elbrus-2017
(01-06 March 2017)
“Equation of State for Matter”

<http://www.ihed.ras.ru/Elbrus17>