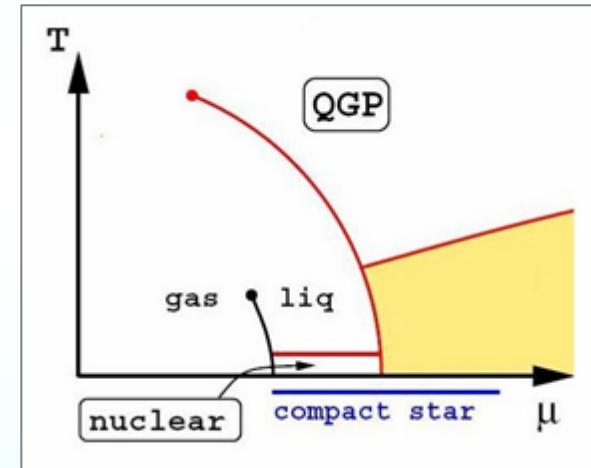
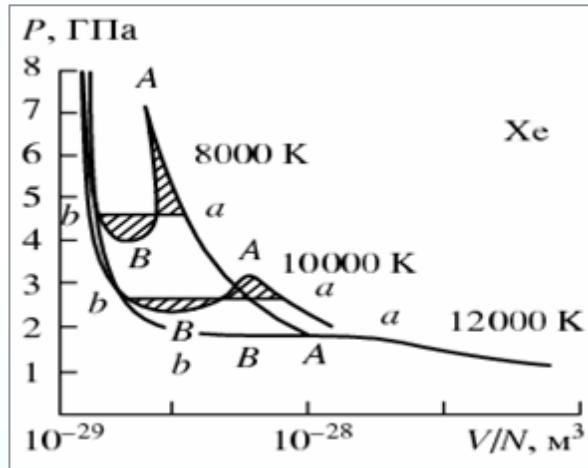




Entropic and Enthalpic Phase Transitions in high energy density matter

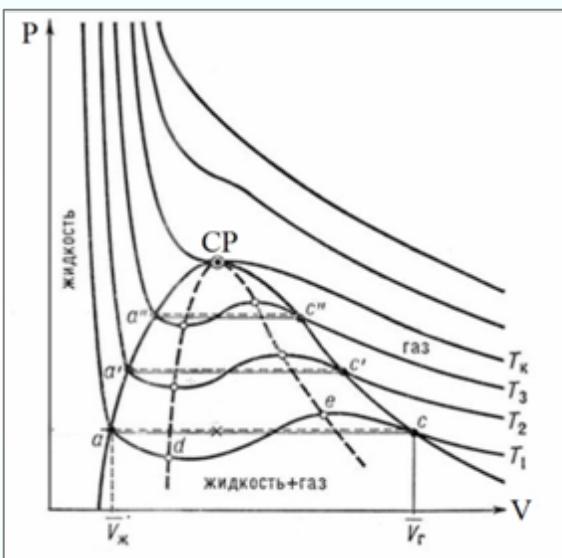


Igor Iosilevskiy

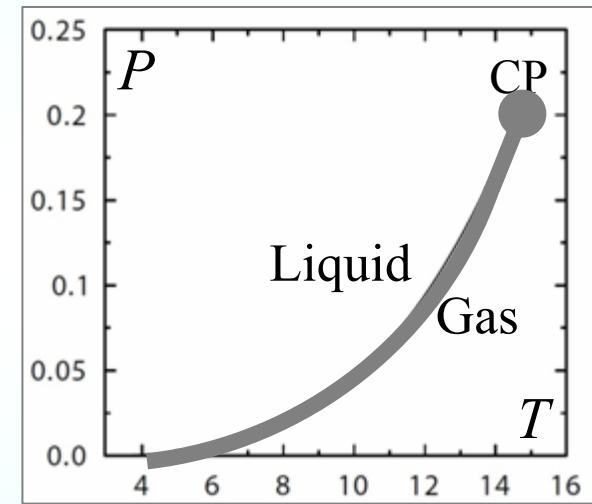
Joint Institute for High Temperature (Russian Academy of Science)
Moscow Institute of Physics and Technology (Federal Research University)

Van der Waals model *of* gas-liquid 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

142 years

Debye – Hückel non-ideality correction

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



Peter Debye



Erich Hückel

(1923)

92 years

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

NB!

$$\Gamma_D = 4$$

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

$$\Gamma_D > 6$$

$$\Leftrightarrow P < 0 !$$

Phase transitions *of 1st and 2nd order*

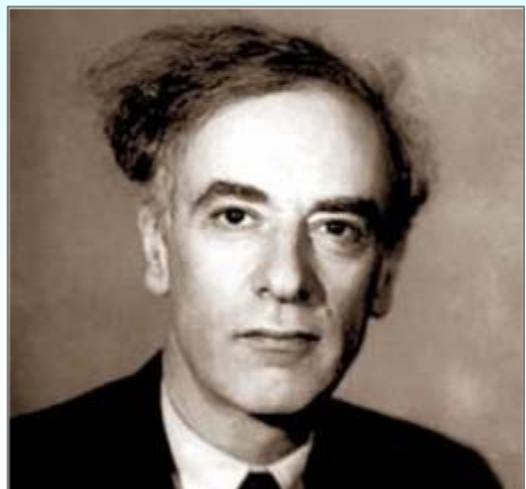


82 years

Пауль Эренфест
(1880 - 1933)

1st- and 2nd-order phase transitions
(1933)

Hypothesis *on* 1st order phase transition “dielectric-conductor” *in* metals



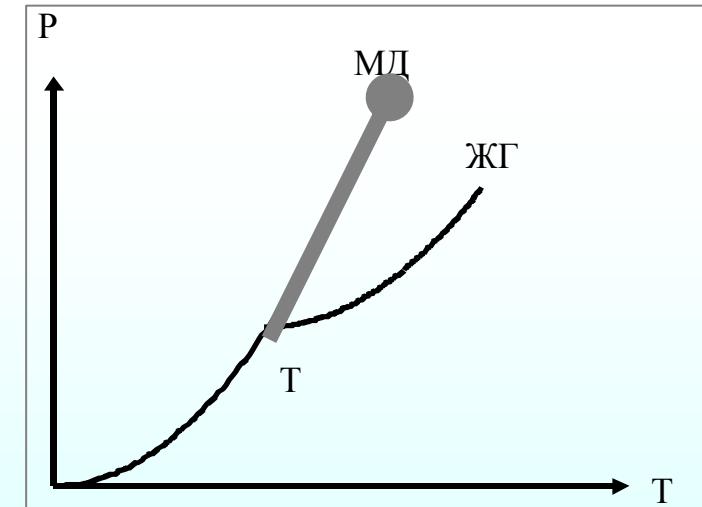
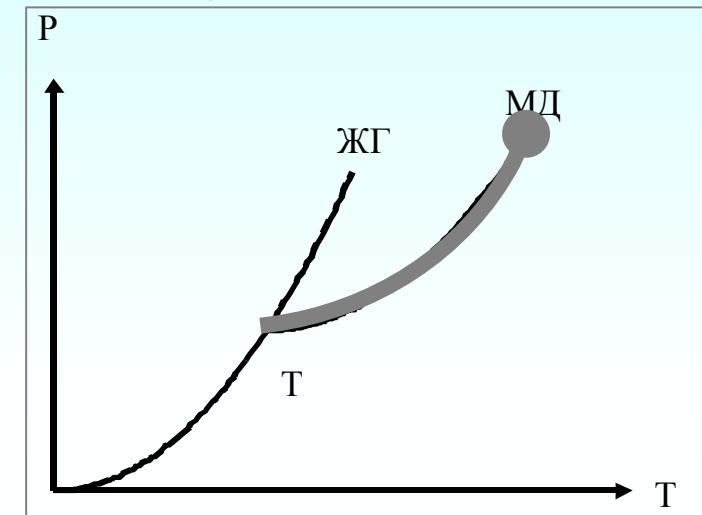
(1943)



Lev Landau

72 years

Yakob Zel'dovich
(1914 - 1987)



Landau L. and Zel'dovich Ya., *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)



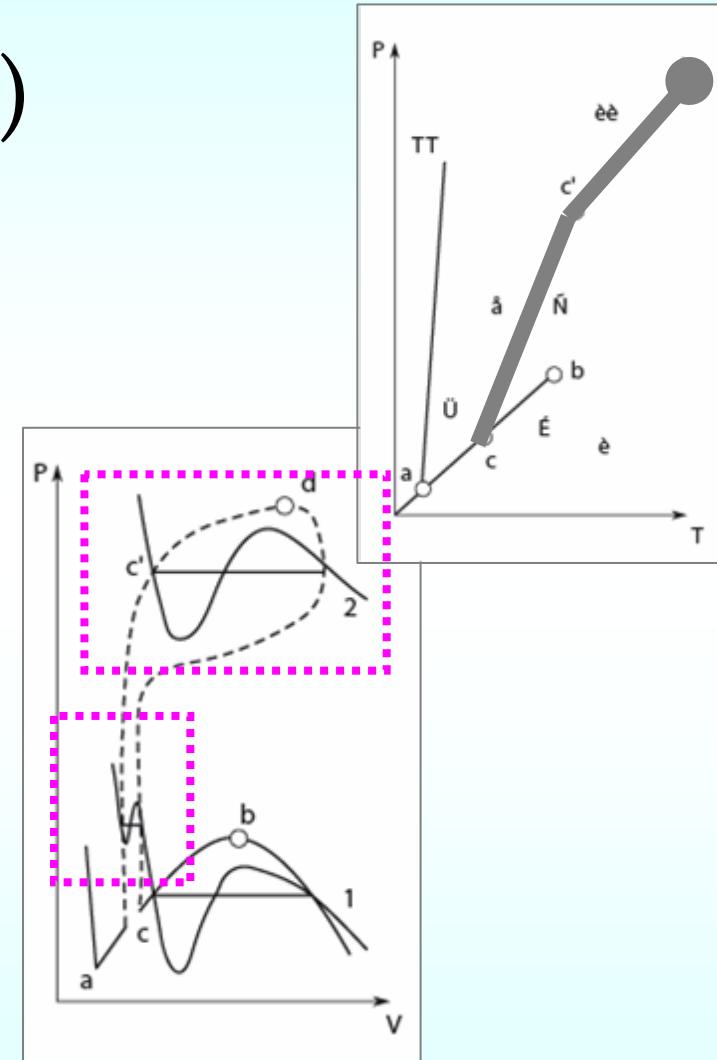
Andrew Starostin

45 years



Henry Norman

(1968-1970)



Norman H., Starostin A. *High Temperature*, 6, 410 (1968)
Plasma phase transitions

When one meets unexplored phase transition: - what should he classify ?

1st or 2nd order ?

Isostructural or non-isostuctural ?

Enthalpic or entropic ?

Congruent or non-congruent ?

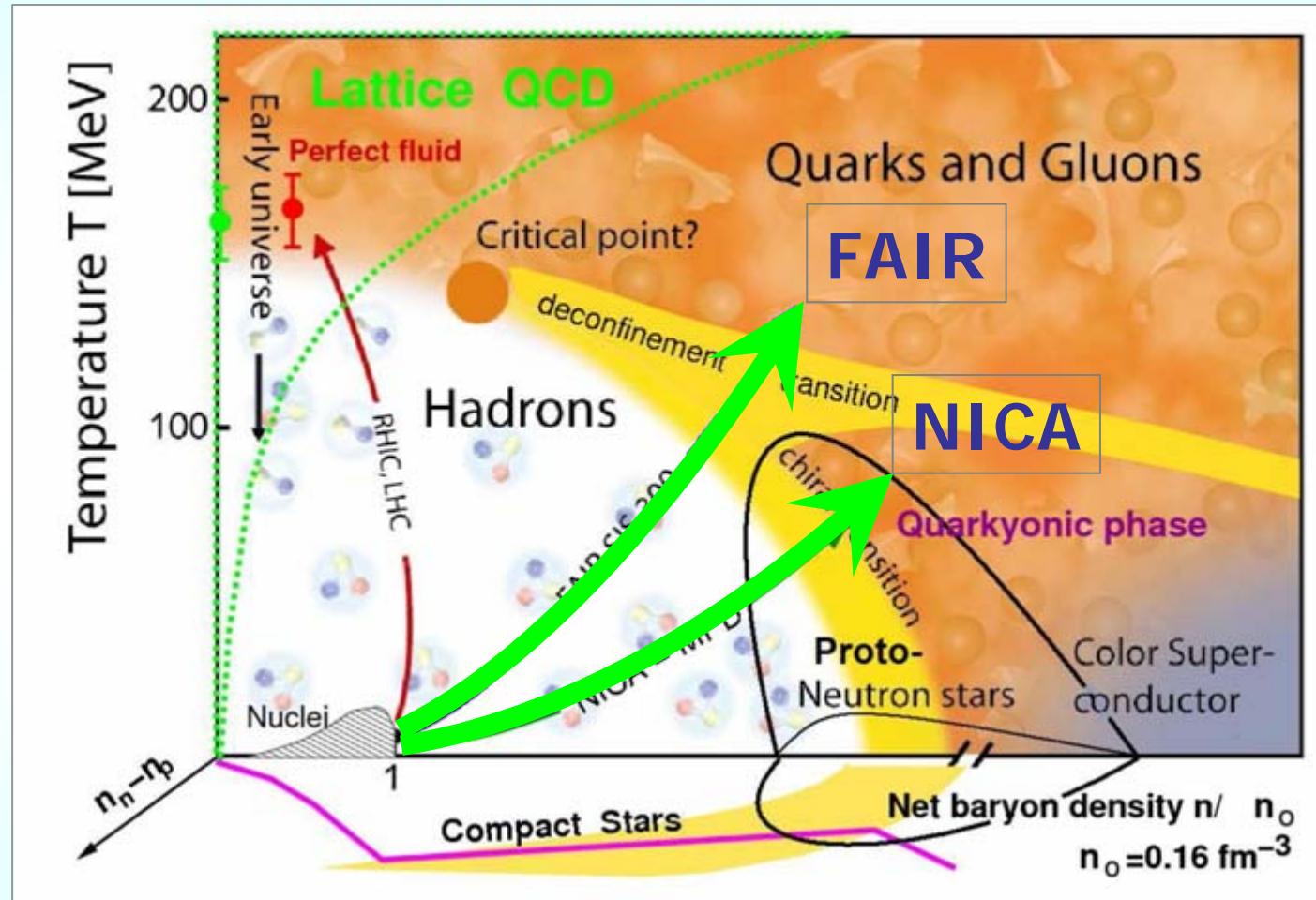
Do we use Coulomb-less approximation or we take into account all consequences of long-range nature of Coulomb interaction ?

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

Phase transitions *in* high energy density nuclear matter

Enthalpic *or* Entropic
?

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



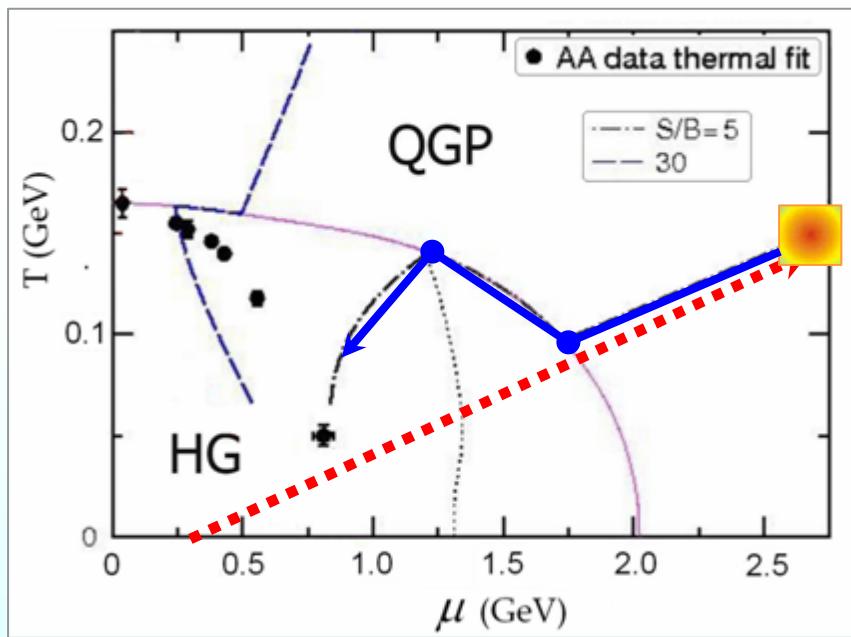
NICA White Book

After David Blaschke, NICA Workshop, Dubna, 2009

Impact and fireball hydrodynamics in RHIC

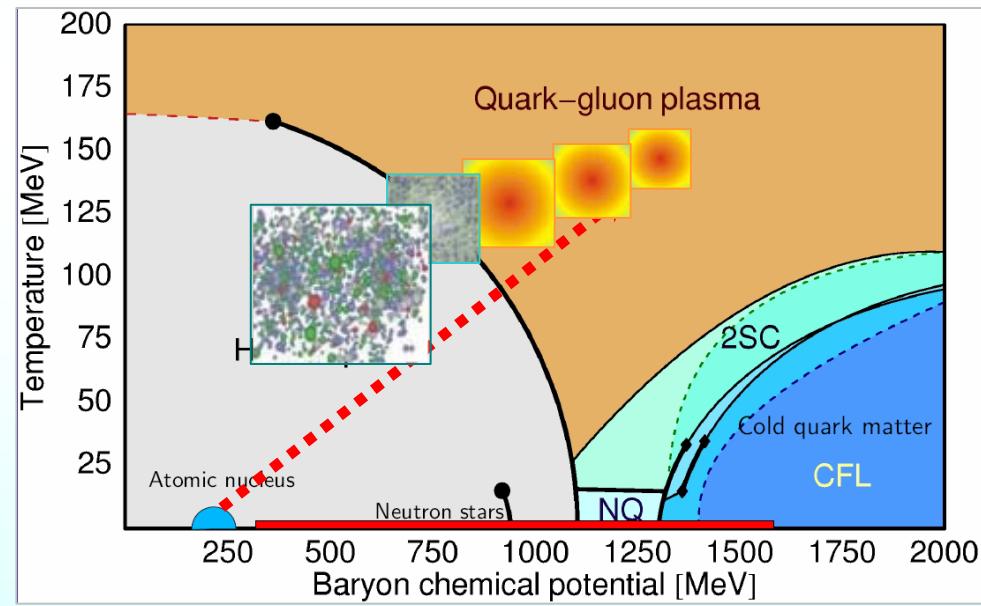


Hadronization



L. Satarov, M. Dmitriev, I. Mishustin //arXiv: 0901.1430

Shock adiabat of Renkine-Hugoniot-Taub

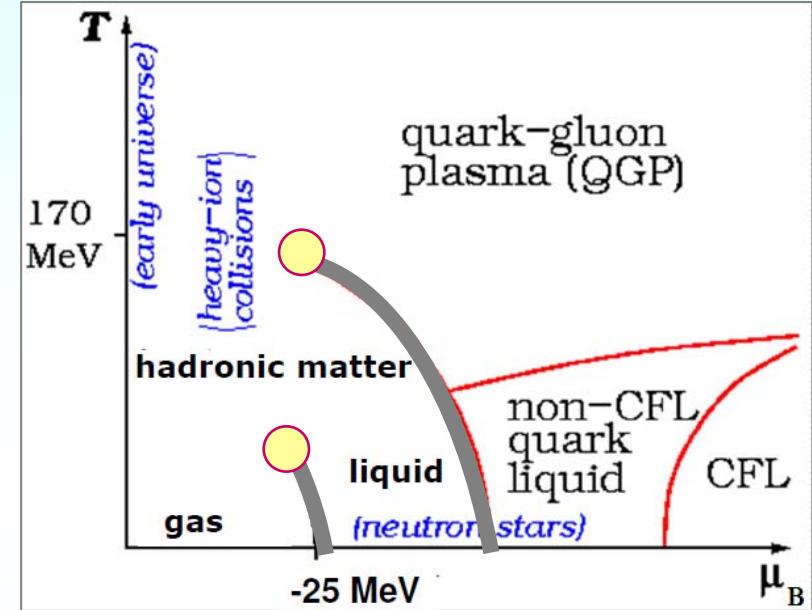
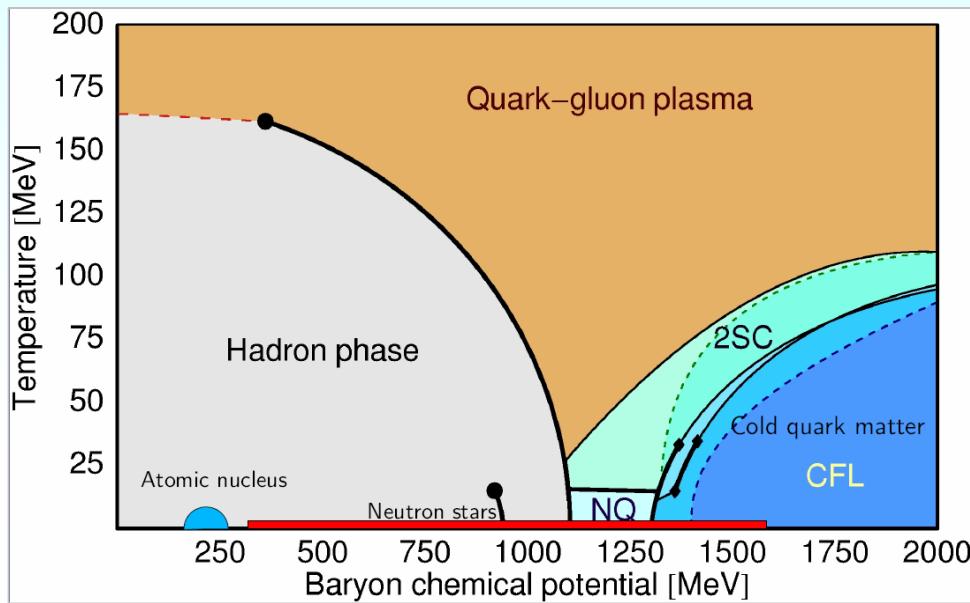


Widely accepted phase diagram of matter

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

Phase transitions in matter of ultra-high energy and density

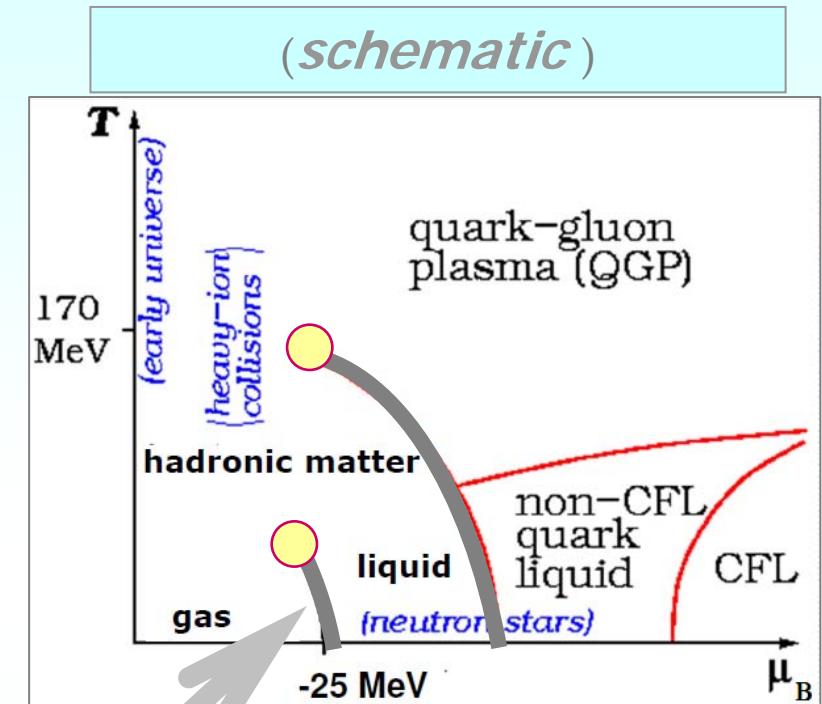
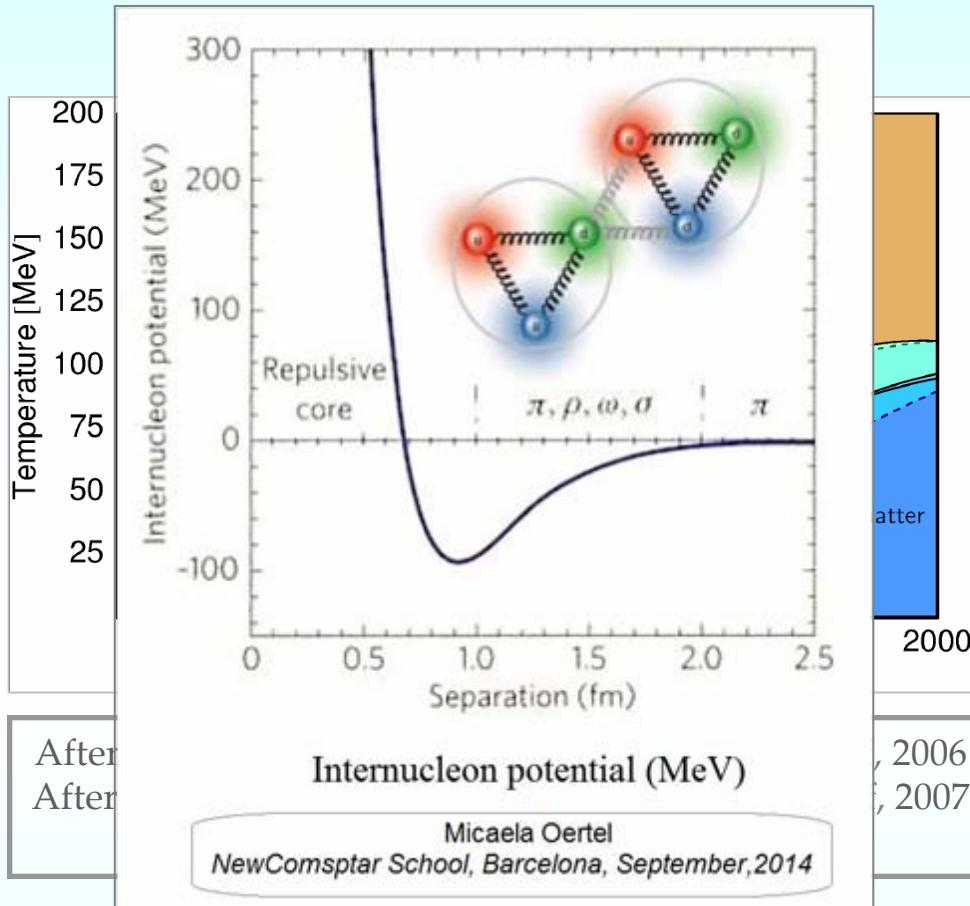
(schematic)



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

Source: WIKIPEDIA

Phase transitions in matter of ultra-high energy and density

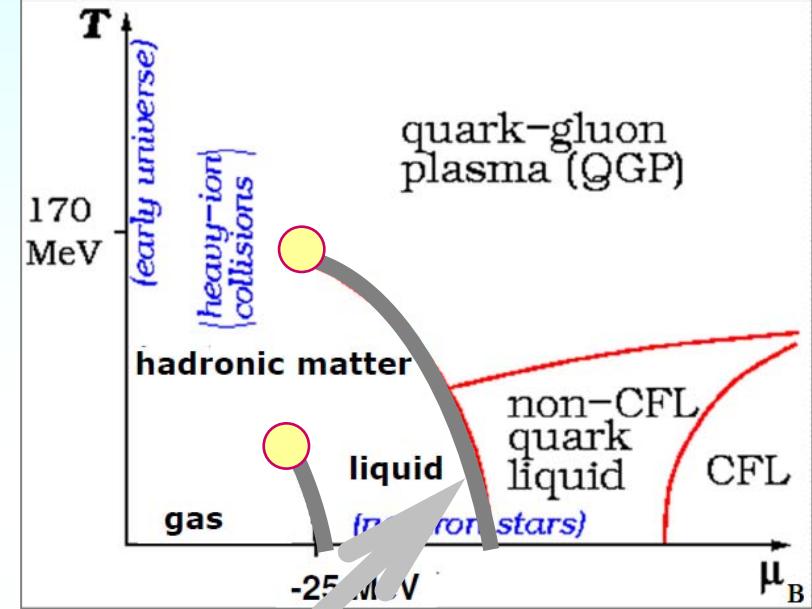
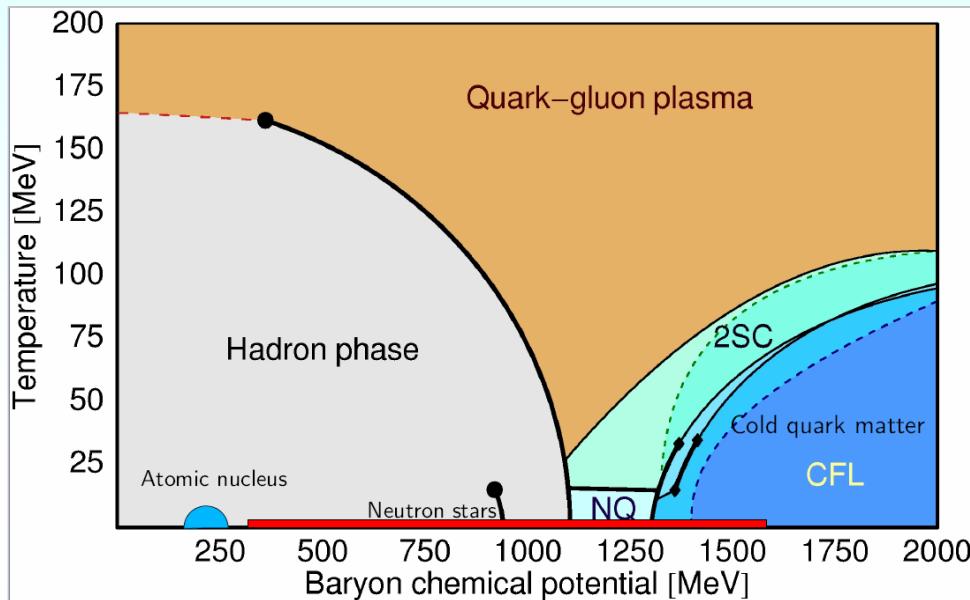


Source: WIKIPEDIA

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

Phase transitions in matter of ultra-high energy and density

(schematic)



After Fridolin Weber, WEHS Seminar, Bad Honnef, 2006

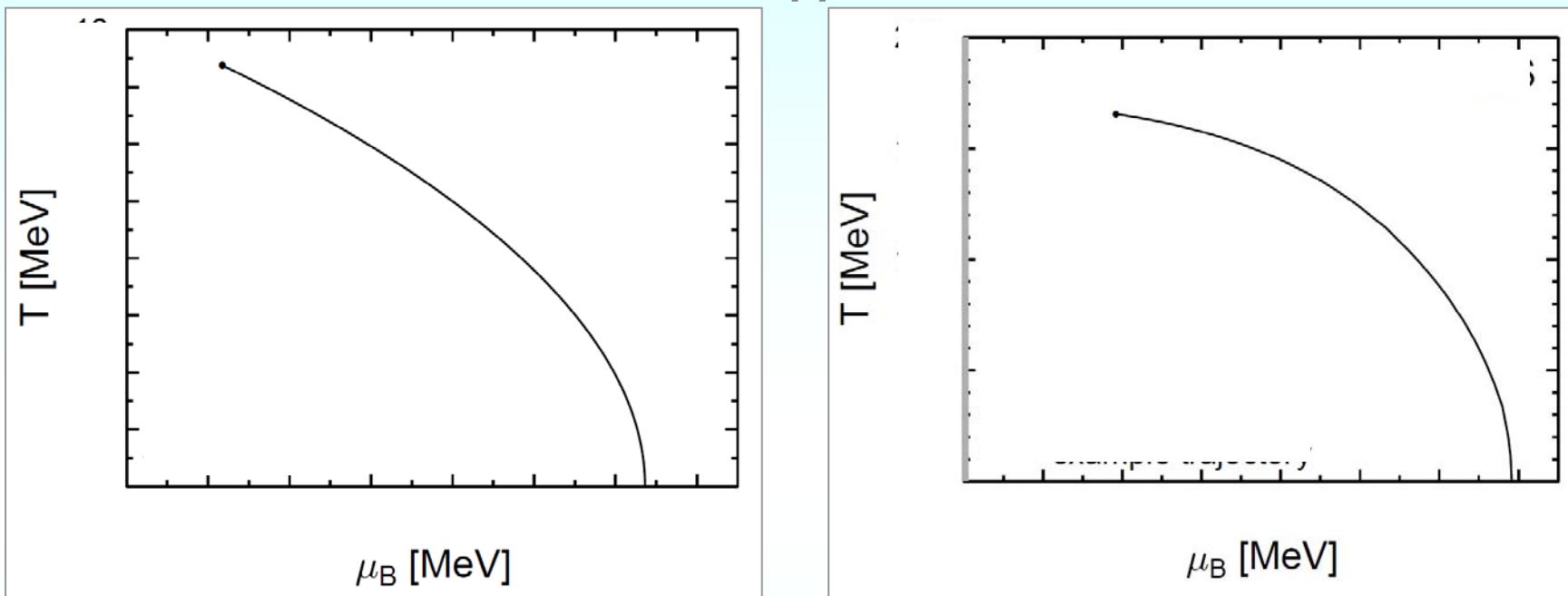
After David Blaschke, WEHS Seminar, Bad Honnef, 2007

Source: WIKIPEDIA

Quark-Hadron phase transition
/ QHPT /

T - μ phase diagram *of* 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:1302.2835

NB !

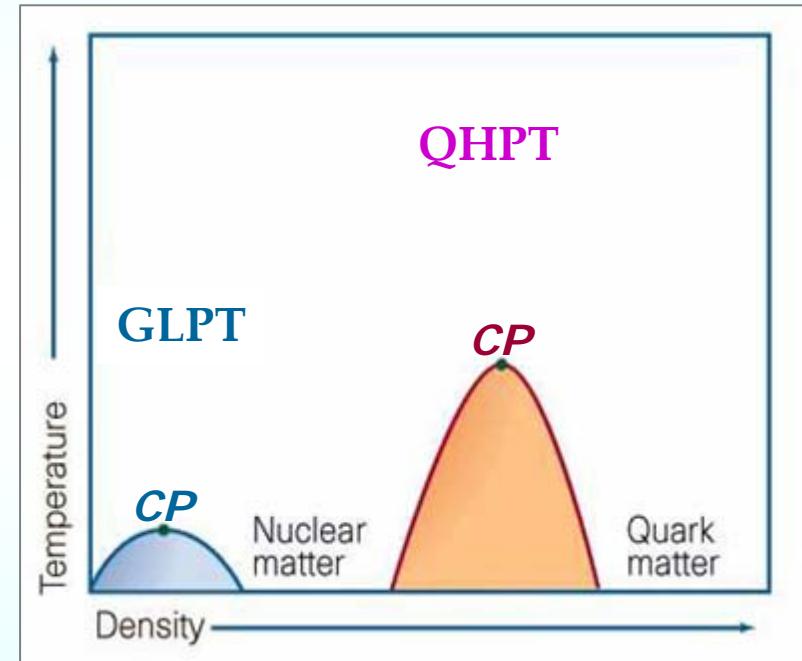
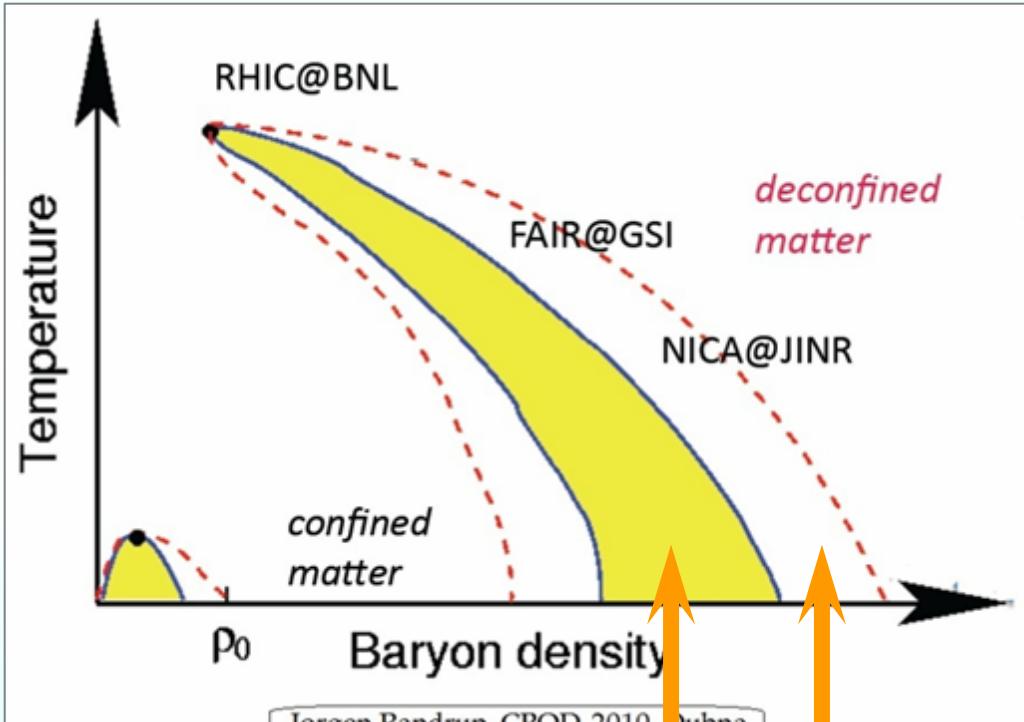
Gas-liquid and quark-hadron phase transitions are often considered as similar to each other within simple scaling / GLPT ~ ~ QHPT/

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

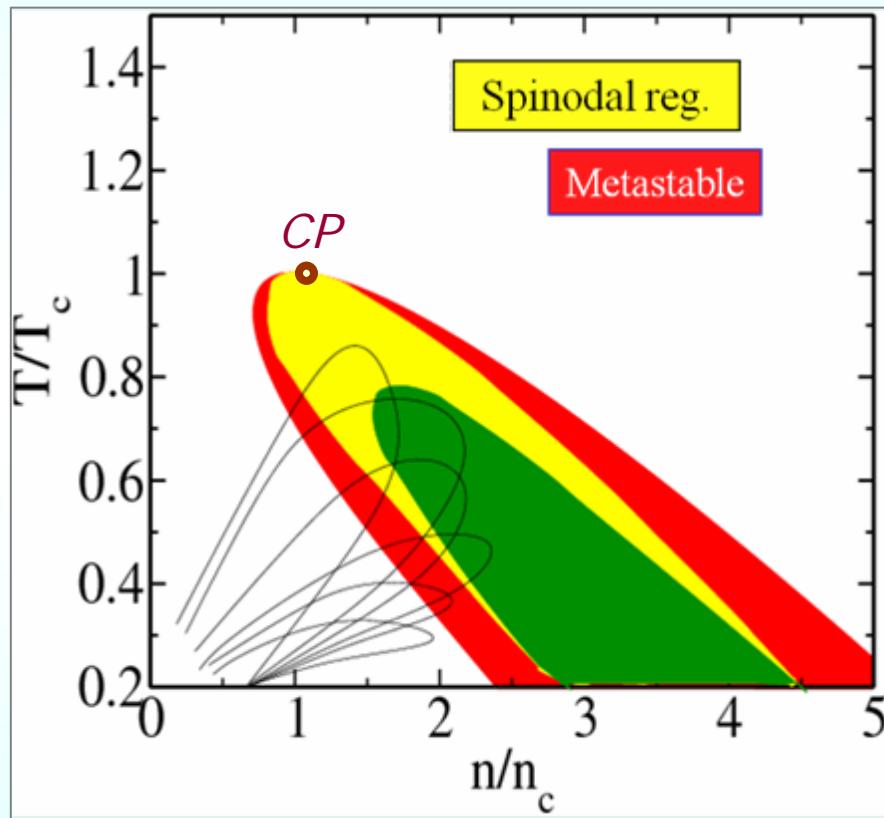


J. Steinheimer & J. Randrup, CPOD-2013

Spinodal reg.

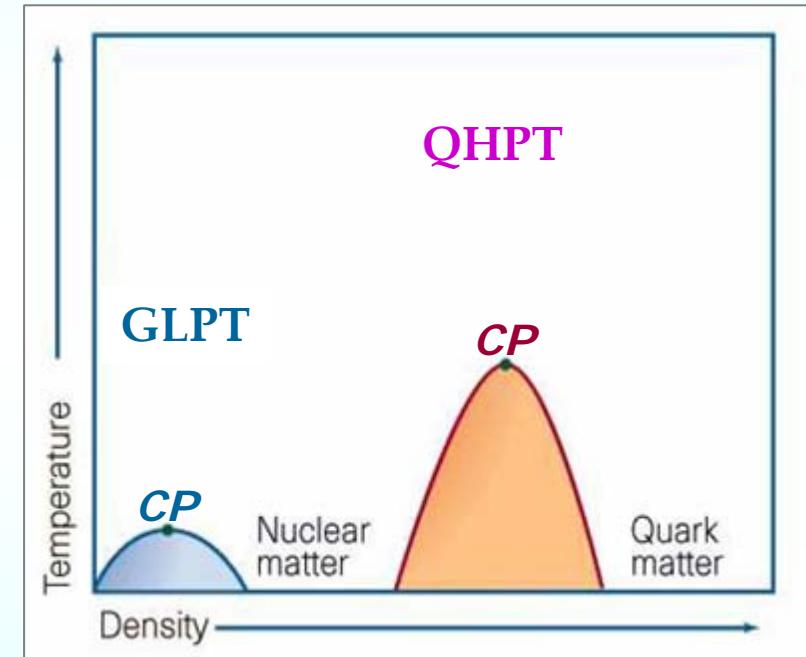
Metastable

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



Vladimir Skokov (GSI, Darmstadt)

"Critical Point and Onset of Deconfinement"
Int. Conference, Napa, USA, 2013

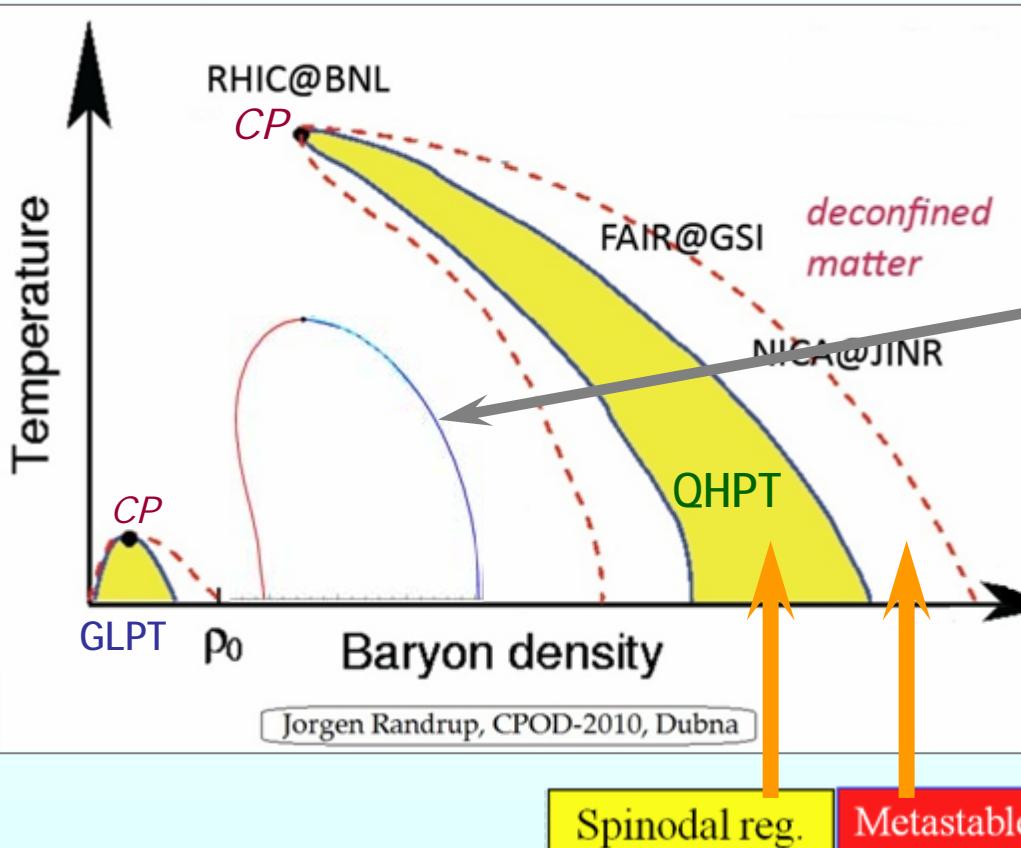


J. Steinheimer & J. Randrup, CPOD-2013

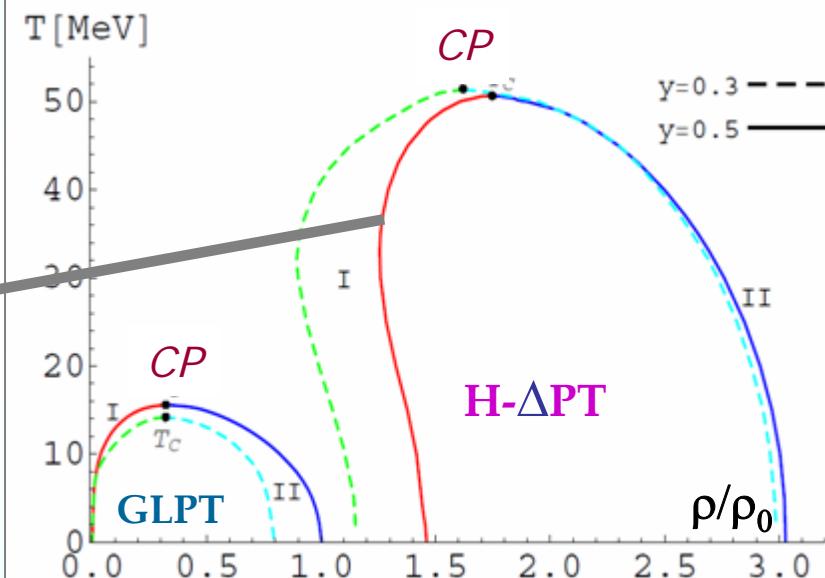
Gas–liquid, Quark–hadron *and* Hadron– Δ -meson phase transitions are considered as similar

Prerow 2009

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



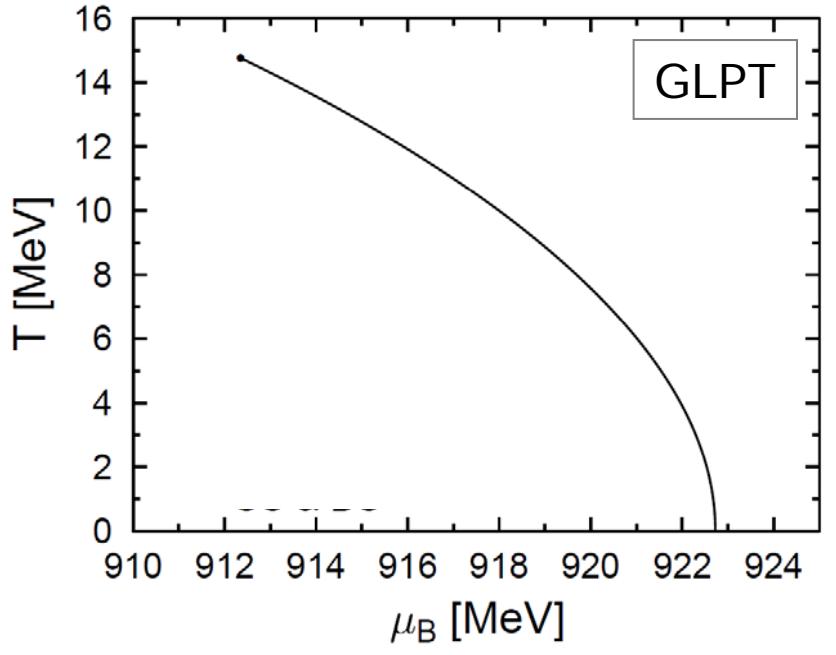
Phase diagram of the liquid-gas and the nucleon- Δ matter phase transition



Lavagno A., Pigato D.
Phys. Rev. C., **86**, (2012)
Thermodynamic instability in warm and dense nuclear matter

All three phase transitions: - are they isomorphic ?

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

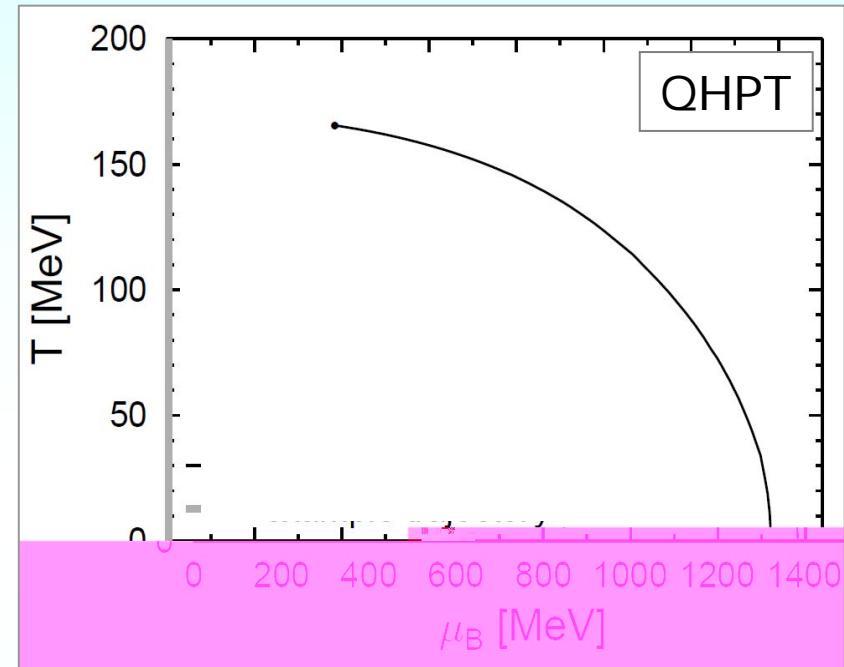


FSUGold (Matthias Hempel (*))

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

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

arXiv:1302.2835



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

Quark-hadron PT

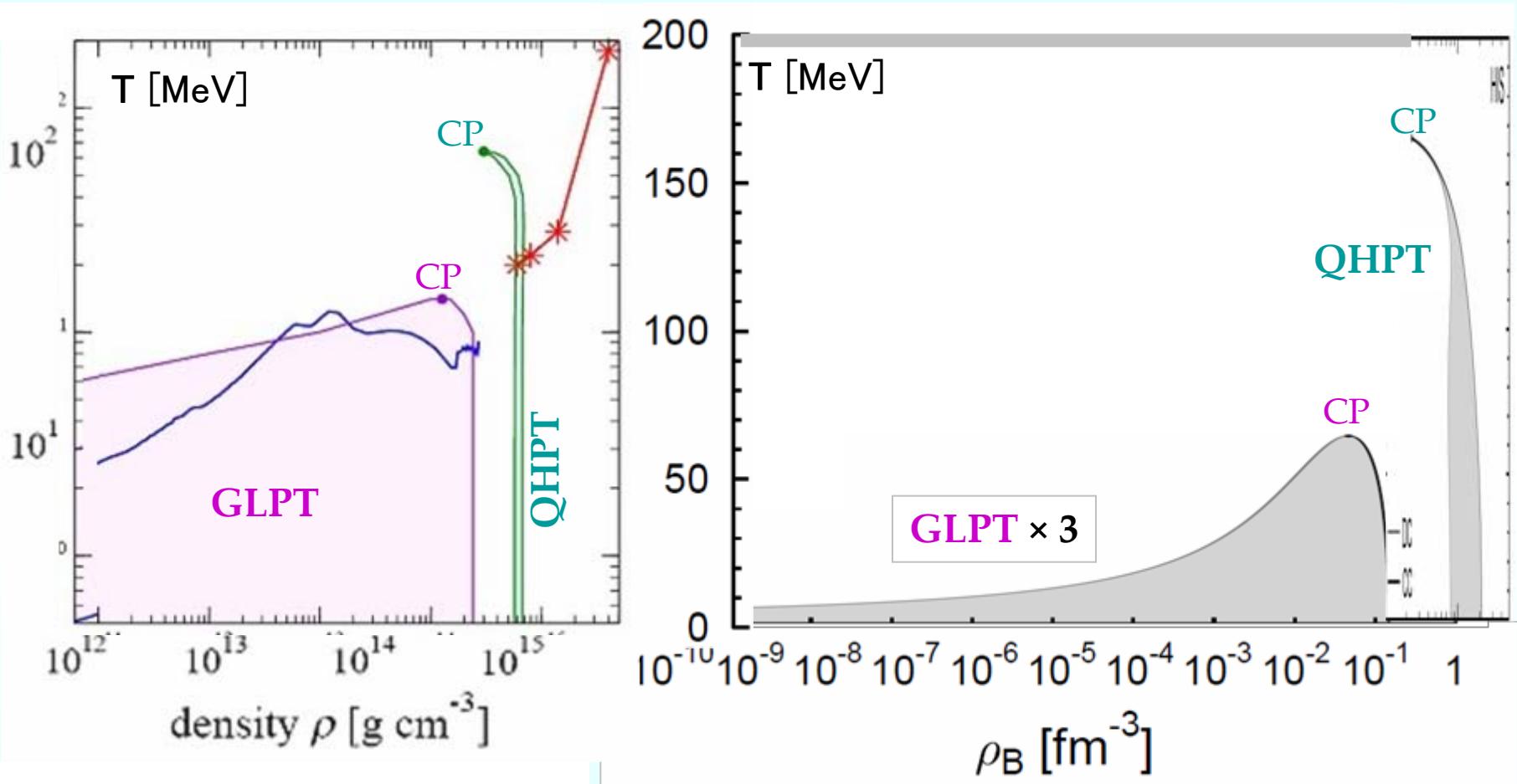
No!

Enthalpic PT



Entropic PT

T - ρ phase diagram of symmetric Coulomb-less GLPT and QHPT (the same structure in old and new calculations)



after David Blaschke,
"Extreme Matter", Elbrus-2010

FSUGold (Matthias Hempel)

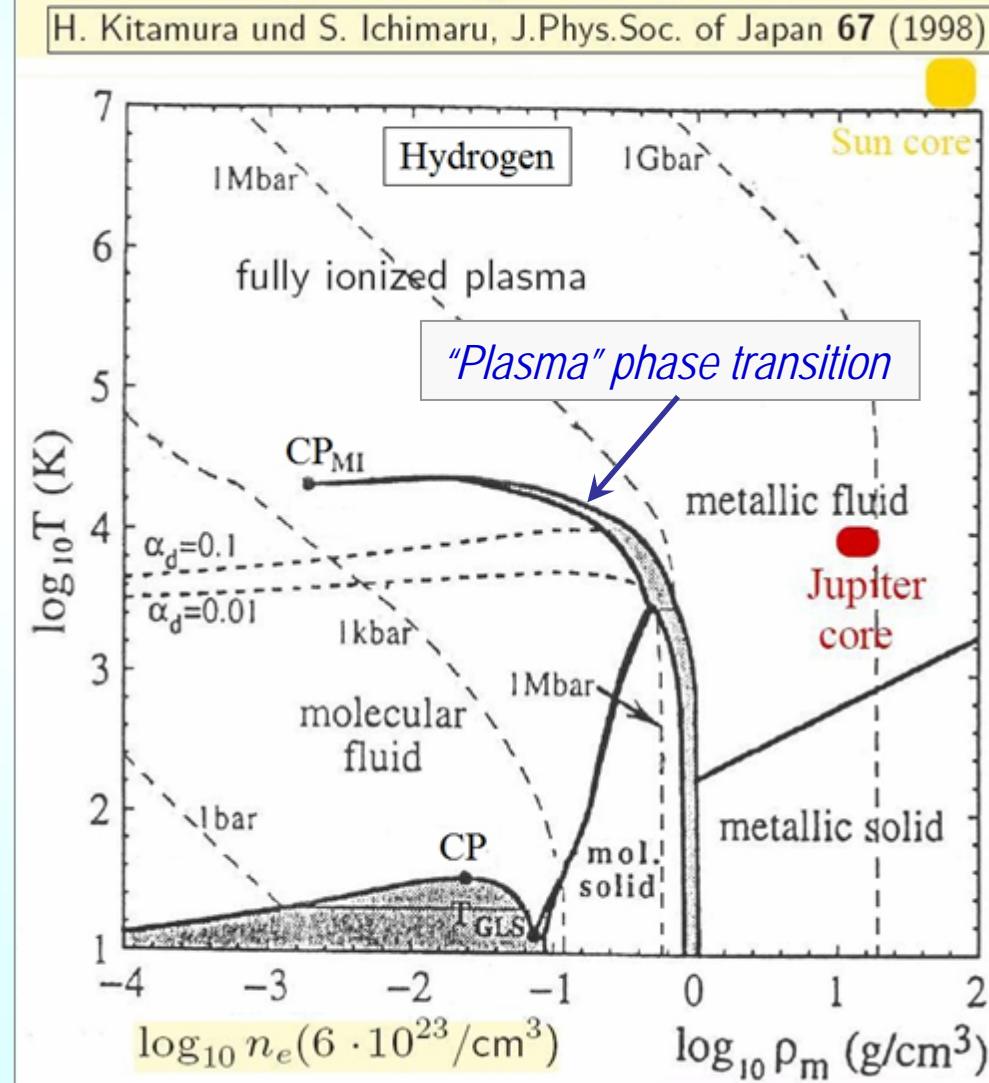
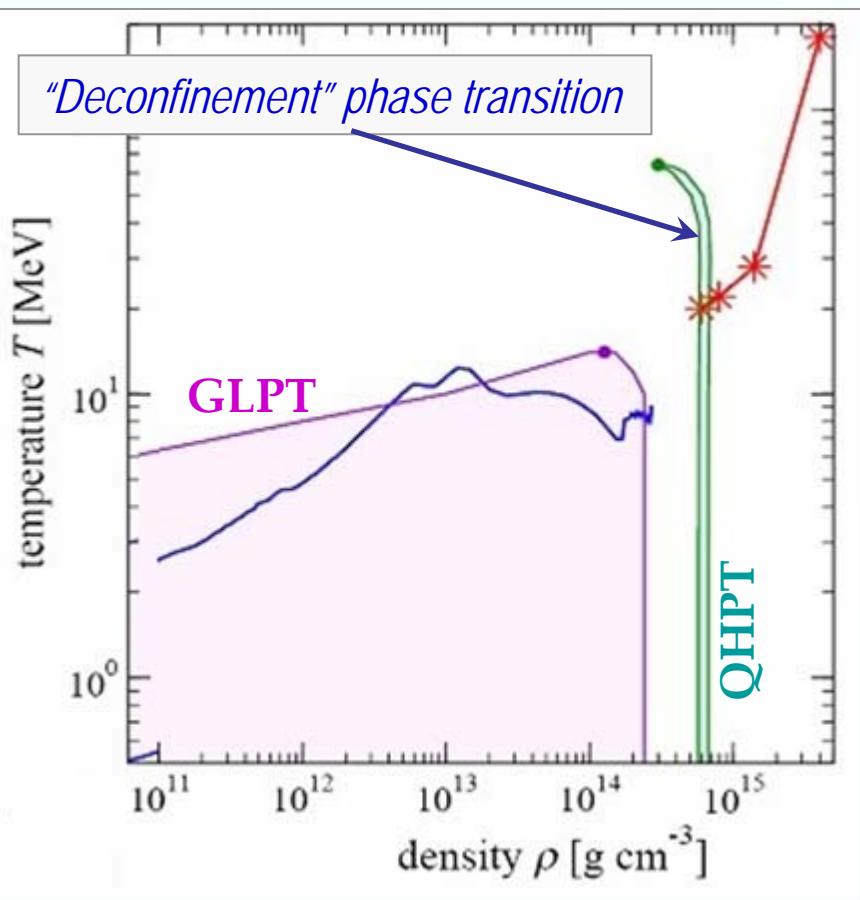
GLPT

SU(3) model (Veronica Dexheimer)

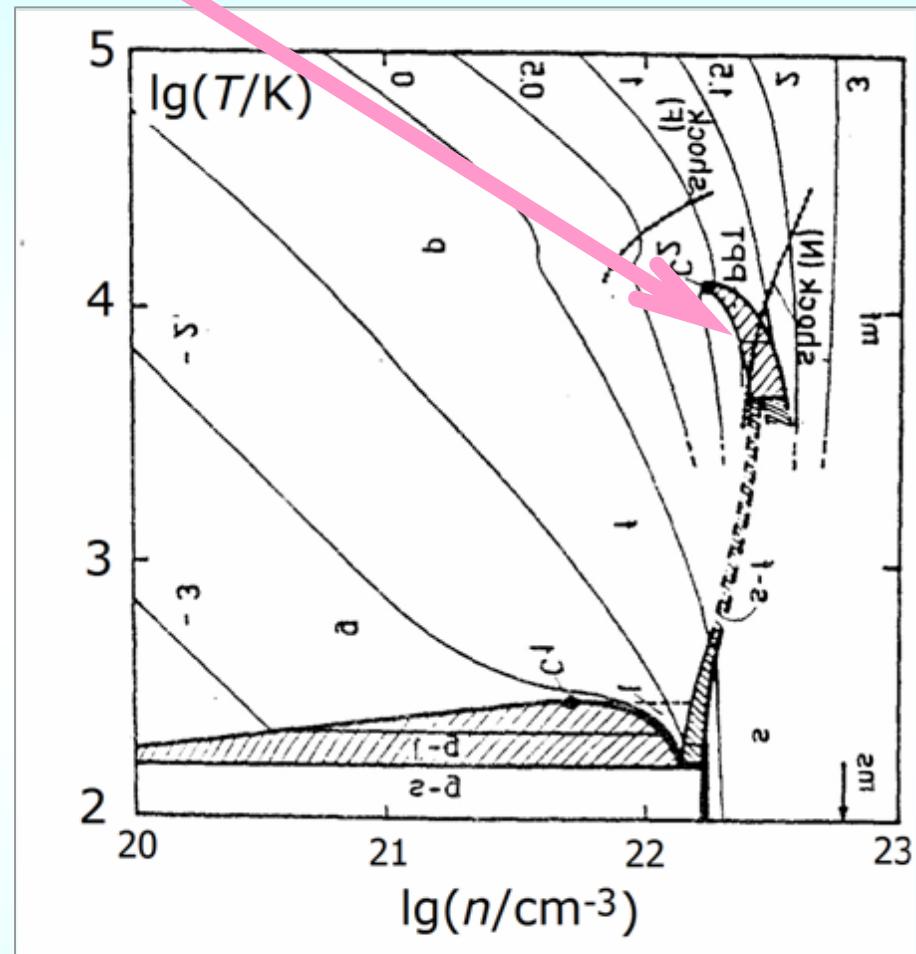
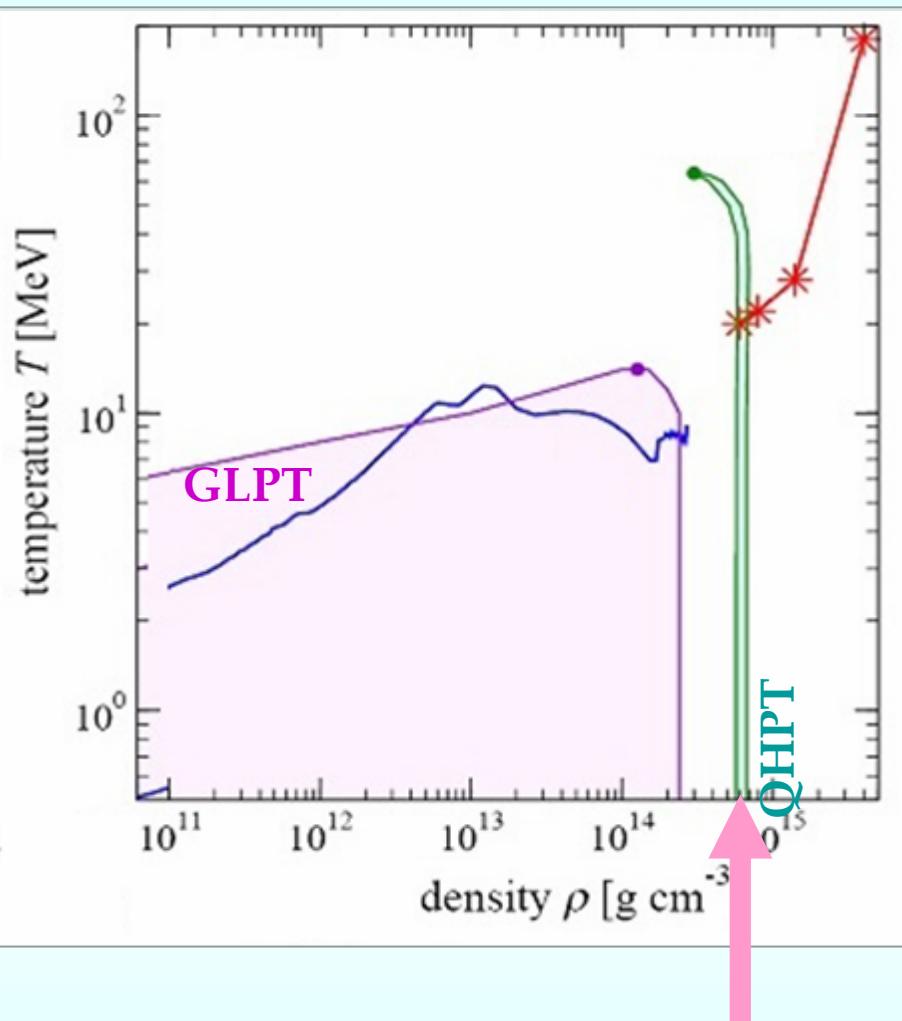
QHPT

Enthalpic *and* entropic phase transitions in electromagnetic plasma

Hydrogen phase diagram with hypothetical “plasma” phase transition



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

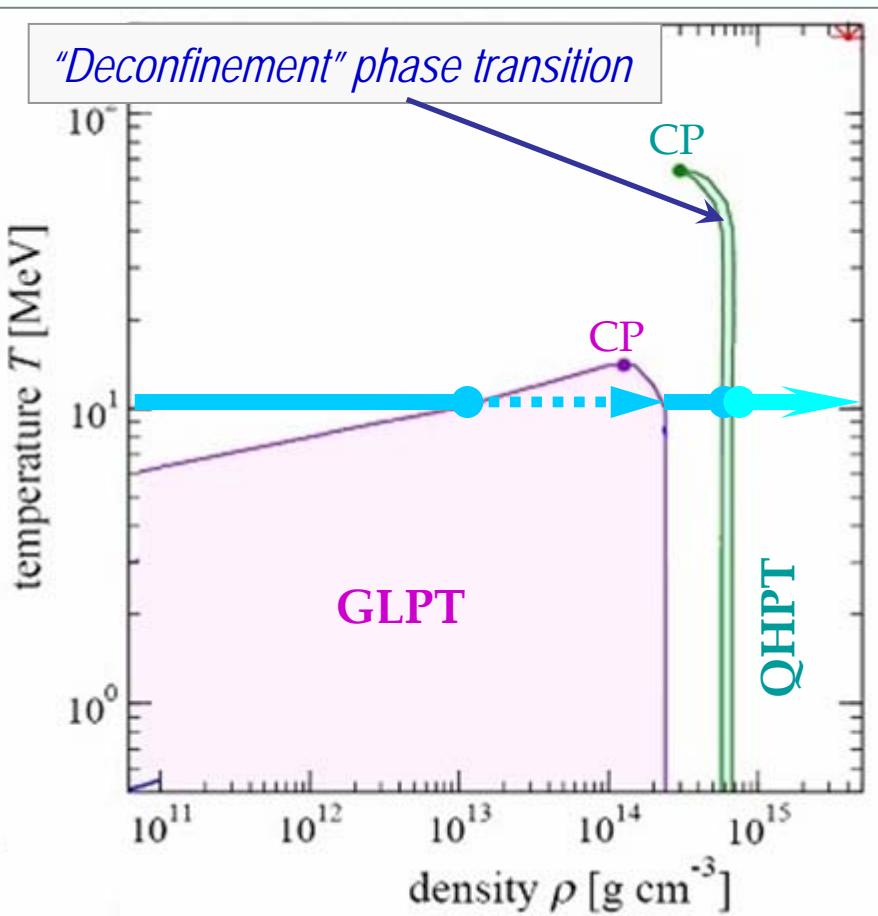
Enthalpic and entropic phase transitions in nuclear matter and electromagnetic plasma

PT under isothermal compression

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

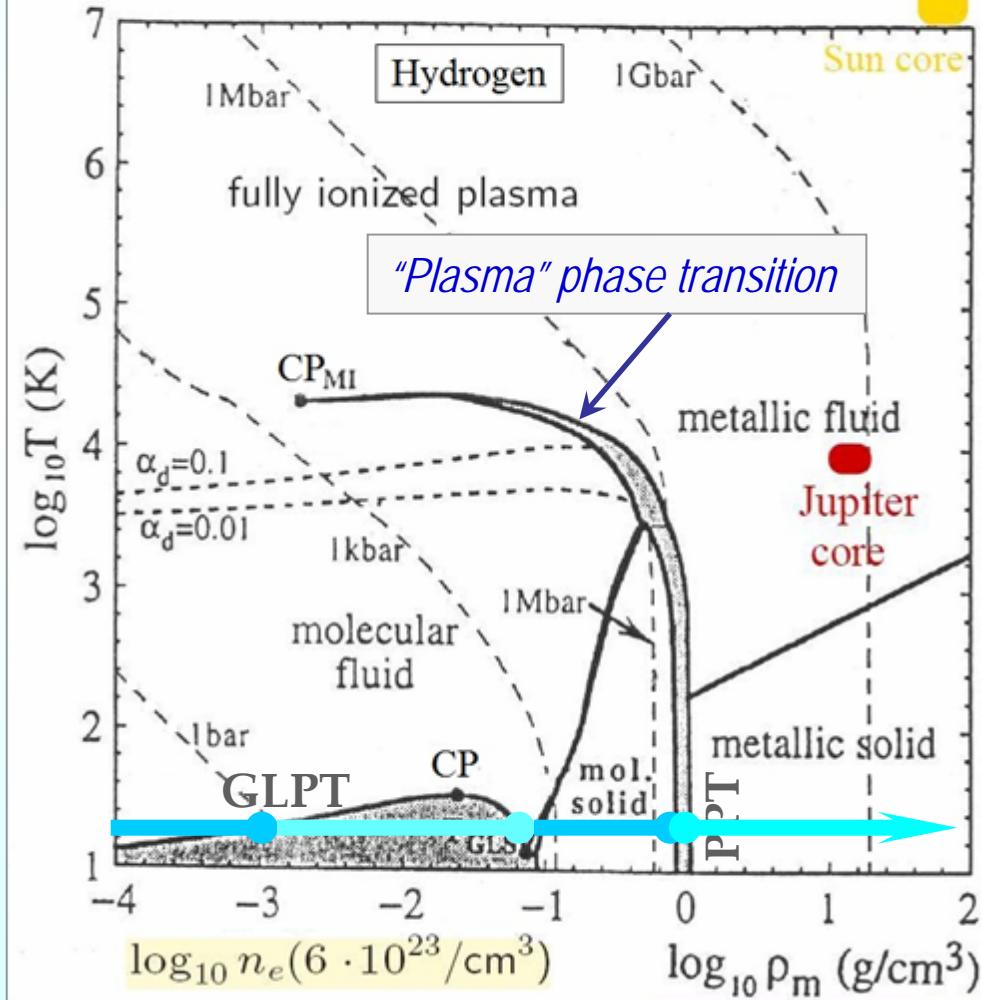
$$\text{QHPT} \Leftrightarrow -T\Delta S < 0 \Leftrightarrow \text{PPT}$$

"Deconfinement" phase transition



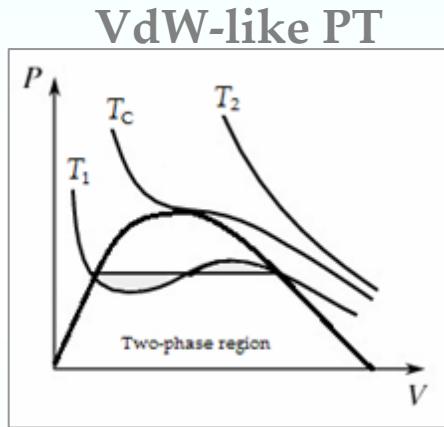
Hypothetical "Plasma" phase transition (PPT) in hydrogen

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

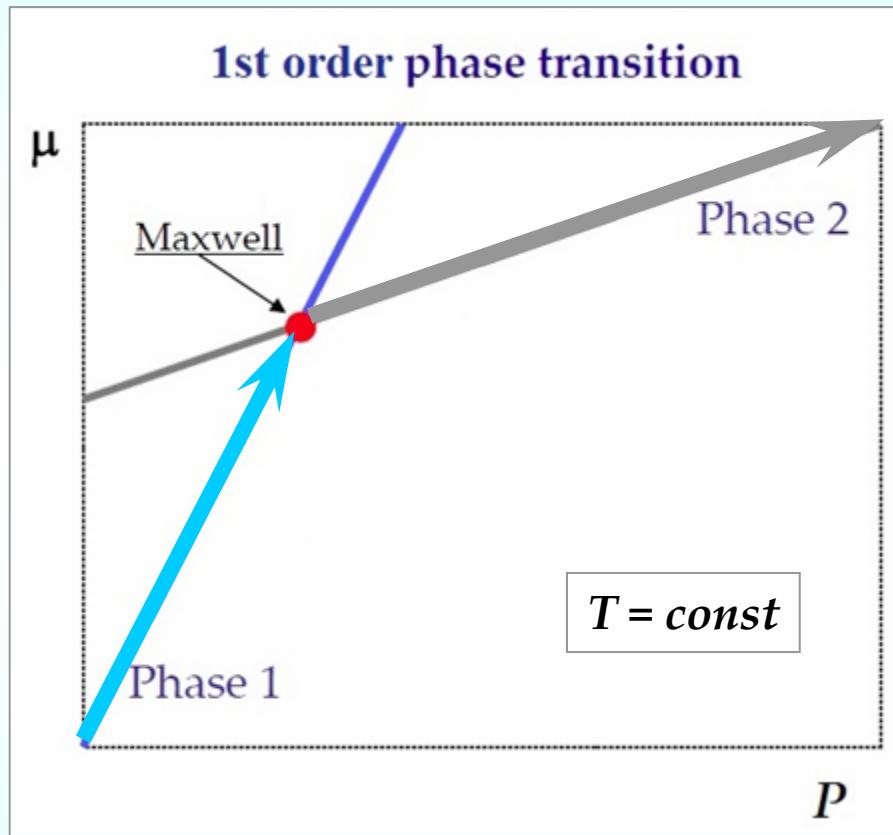


Phase transitions: Enthalpic vs. Entropic ?

$$G = H - TS$$



Maxwell “Equal squares”



Enthalpic PT

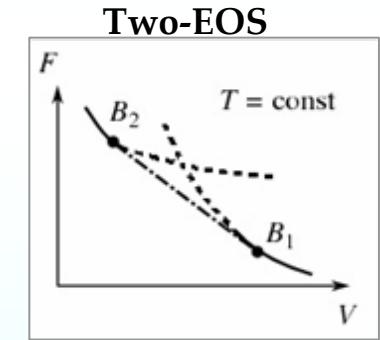
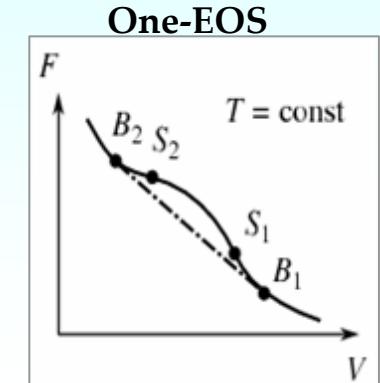
$$\Delta H = T\Delta S < 0$$



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

Iso-T compression

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



“Double tangent”

Entropic PT

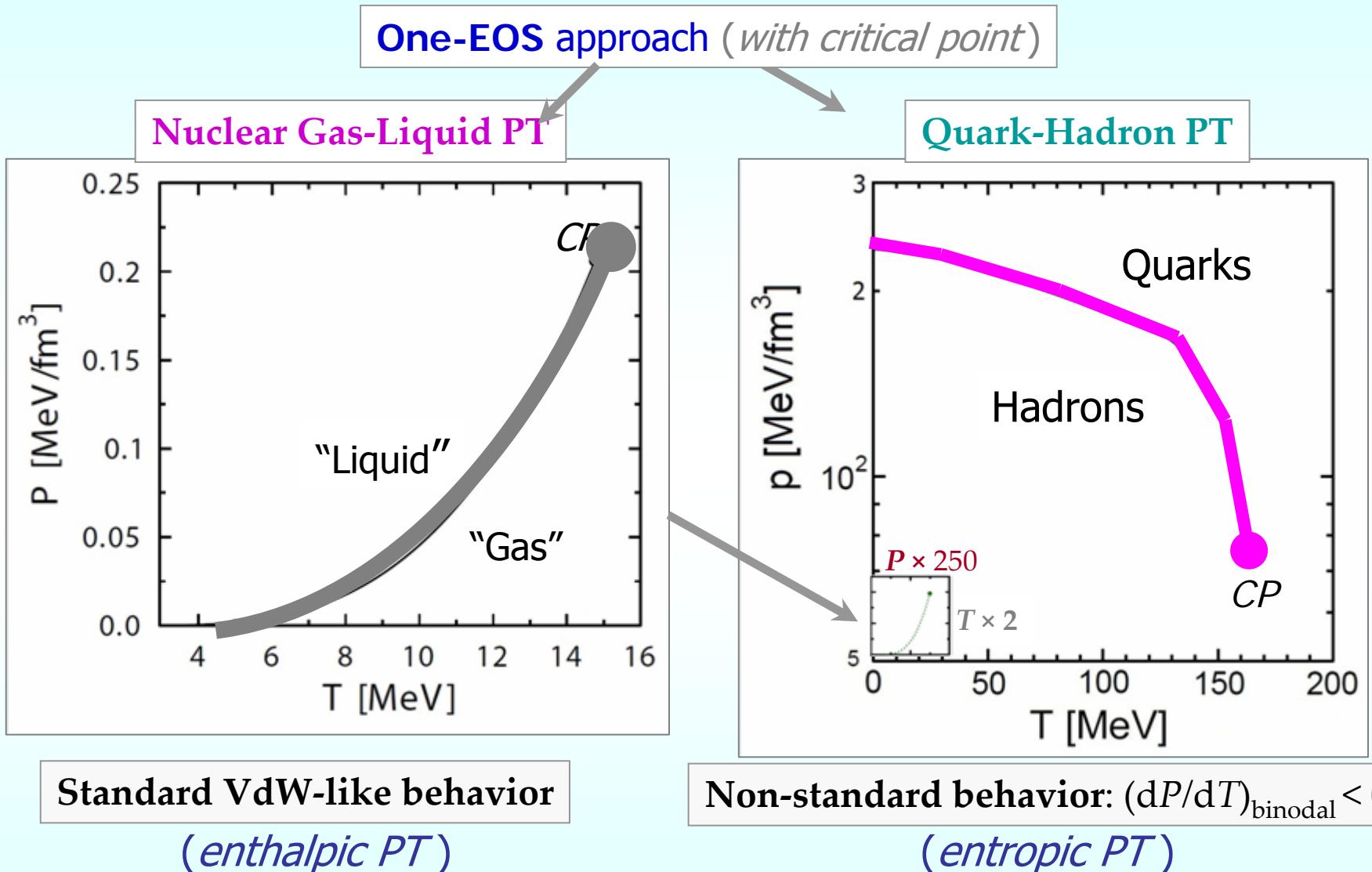
$$\Delta H = T\Delta S > 0$$



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

P-T phase diagram for GLPT and QHPT

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

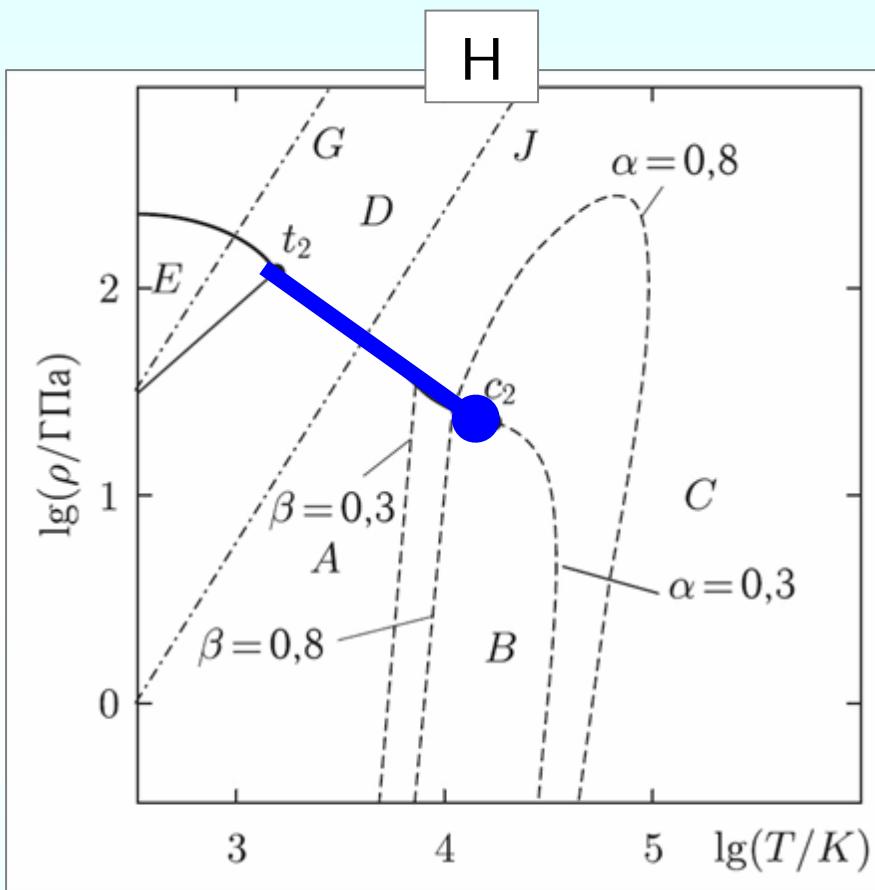


Non-congruence of the nuclear liquid-gas and the deconfinement phase transitions

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

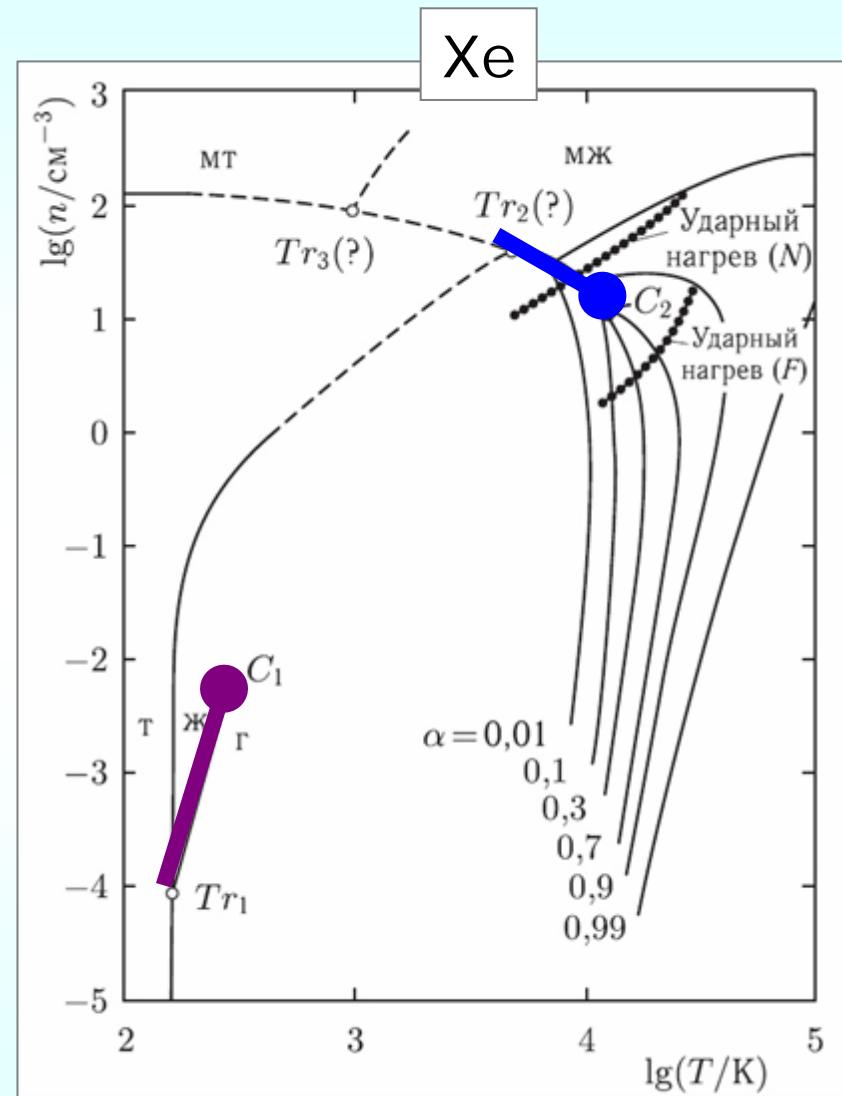
P-T diagram of plasma phase transitions

P-T diagram of plasma phase transition



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

- - enthalpic (*gas-liquid*) PT
- - entropic (*plasma*) PT



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

Ionization- and Dissociation-driven phase transitions in H₂

(mostly entropic)

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

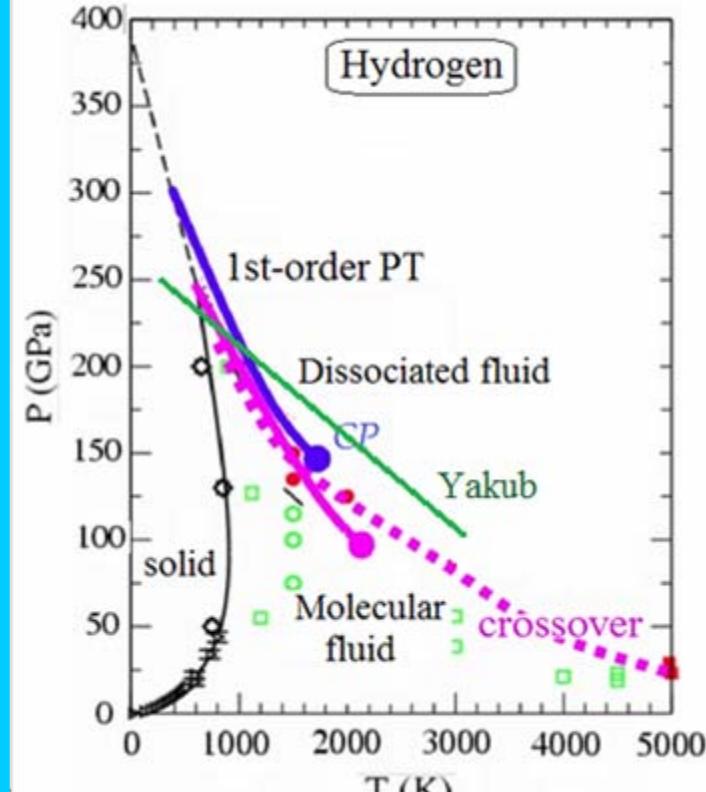
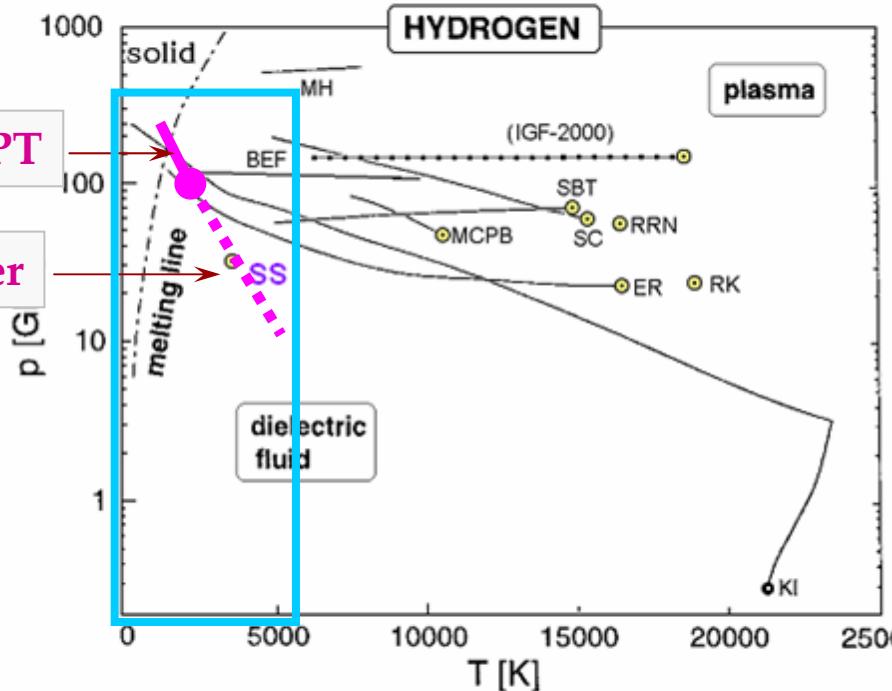
Dissociation-driven PT *ab initio* (DFT/MD)

1st-order PT

Crossover

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)



Dissociation-driven PT (*ab initio*)

SS - Stevenson D, Salpeter E. (1977) ApJ. Sp.35,2

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

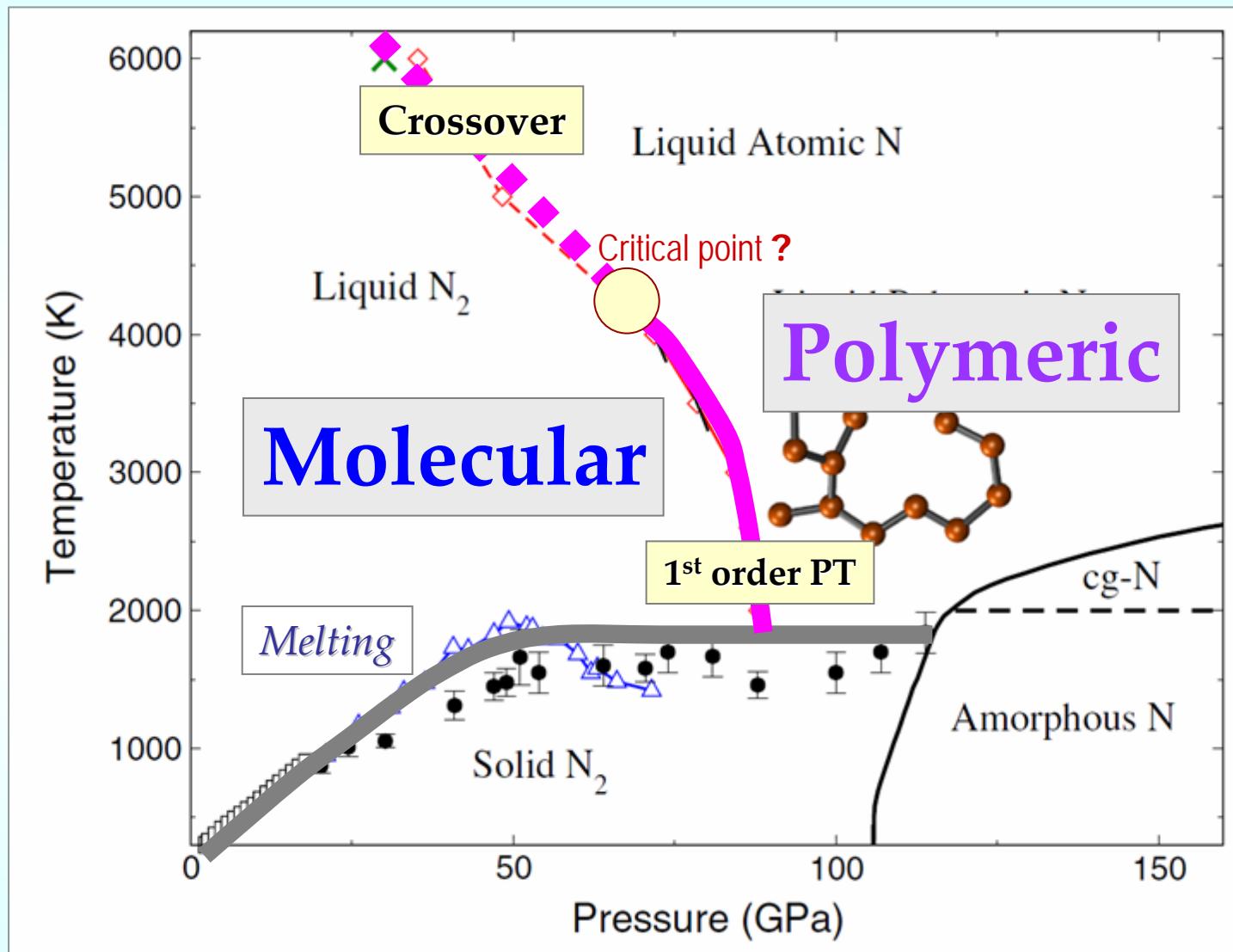
DFT/MD:

Bonev S., Militzer B. et al., PRB 69 (2004)

Morales M. et al. PNAS 107, (2010)

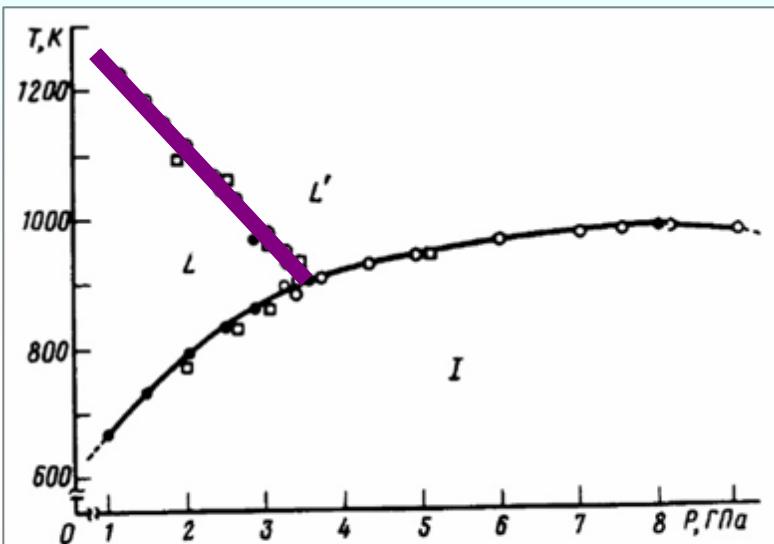
Lorenzen W., Holst B., Redmer R. PRB (2010)

Entropy-driven fluid-fluid phase transitions (N_2)



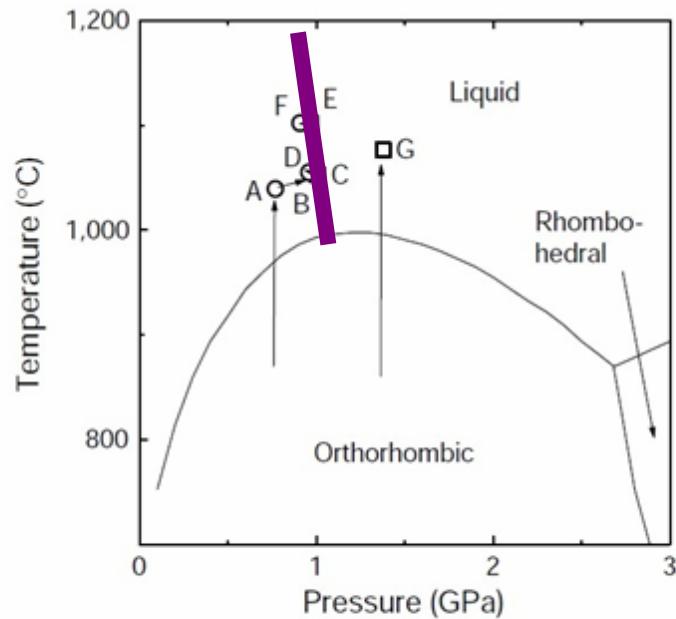
Entropy-driven fluid-fluid phase transitions

Selenium



V.V. Brazhkin, R.N. Voloshin, S.V. Popova,
Semiconductor- metall transition in liquid Se.
JETP Lett. **50** (1990)

Phosphor

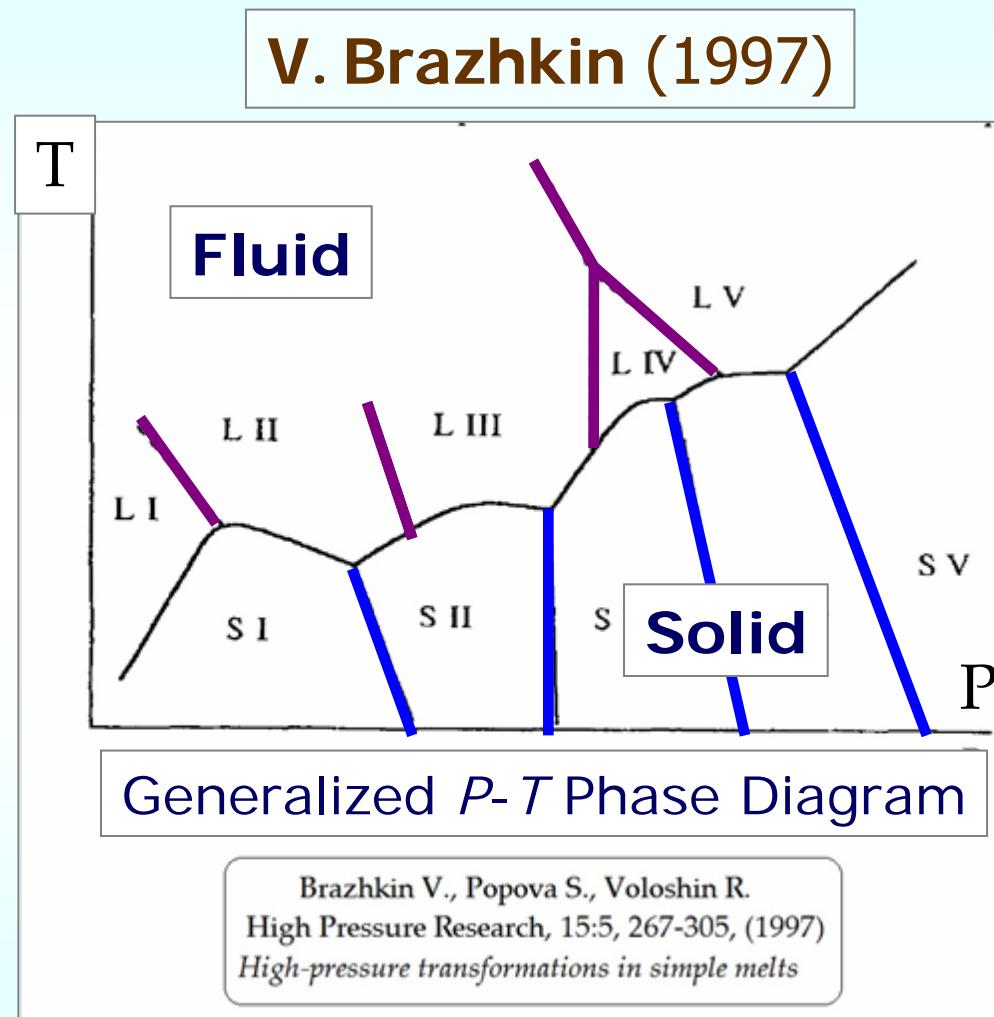


Katayama Y., Mizutani T. et al. (*Nature* **403**, 170 (2000))

Experiment

Experiment

Enthalpic vs Entropic Phase Transitions ?



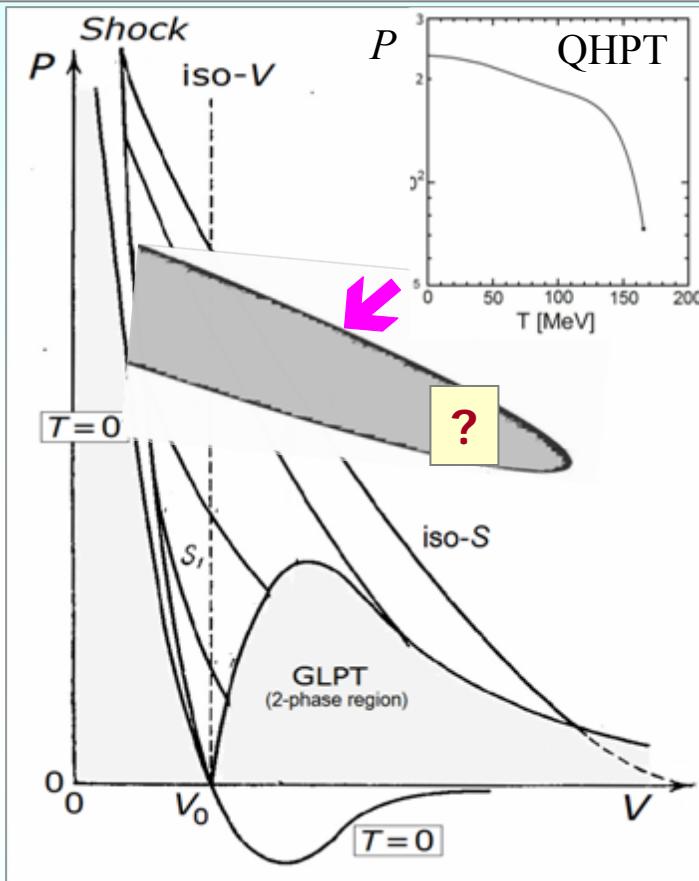
NB !

All polymorphic and all fluid-fluid PTs are Entropic !

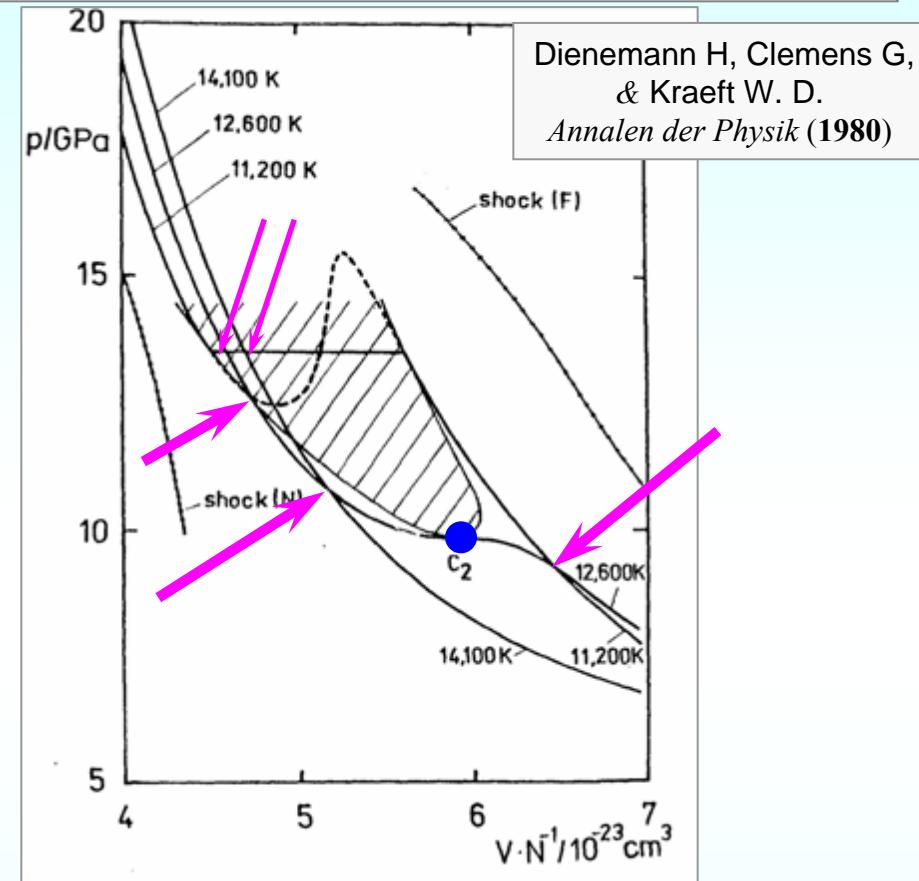
Enthalpic vs. Entropic phase transitions

P-V phase diagram

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** !

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

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 cross derivatives became *negative simultaneously* !

Normal

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

$$\Leftrightarrow (\partial P/\partial S)_V$$

$$\Leftrightarrow (\partial P/\partial U)_V$$

Abnormal

$$> 0$$

$$(\partial V/\partial T)_P$$

$$\Leftrightarrow (\partial V/\partial S)_P$$

$$\Leftrightarrow (\partial V/\partial H)_P$$

$$< 0$$

$$(\partial S/\partial V)_T \Leftrightarrow (-\partial S/\partial P)_T \Leftrightarrow (\partial T/\partial P)_S \Leftrightarrow (-\partial T/\partial V)_S$$

$$(\partial P/\partial U)_V$$

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

$$(\partial V/\partial T)_P$$

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

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 !

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



Isentropes go less steeper than isotherms !

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



Shock adiabats go less steeper than isentropes !

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



**Abnormal order + crossing of Hugoniots
(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) !**

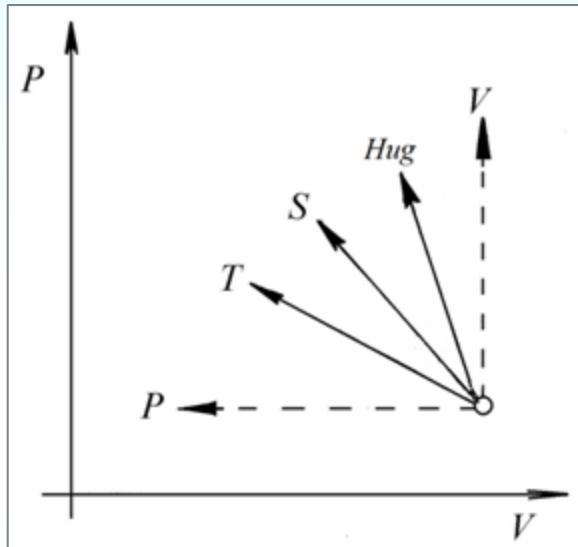
$$(\partial S / \partial V)_T < 0$$



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

ATR – abnormal thermodynamics region

ZB – Zero-boundary (ATR boundary)



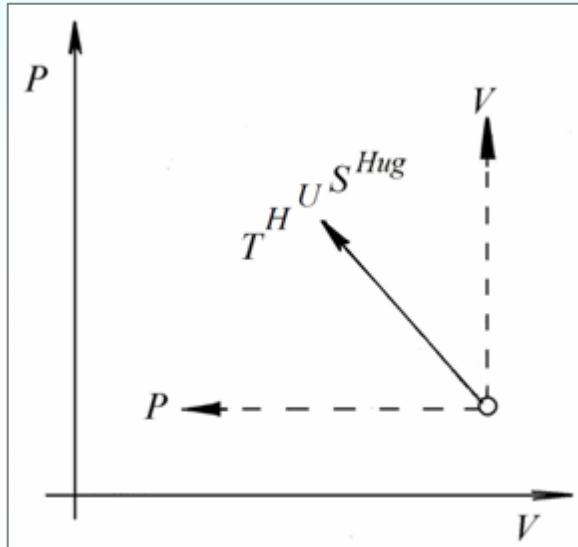
Normal

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

$$(\partial P / \partial U)_V > 0$$

$$(\partial V / \partial T)_P > 0$$

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



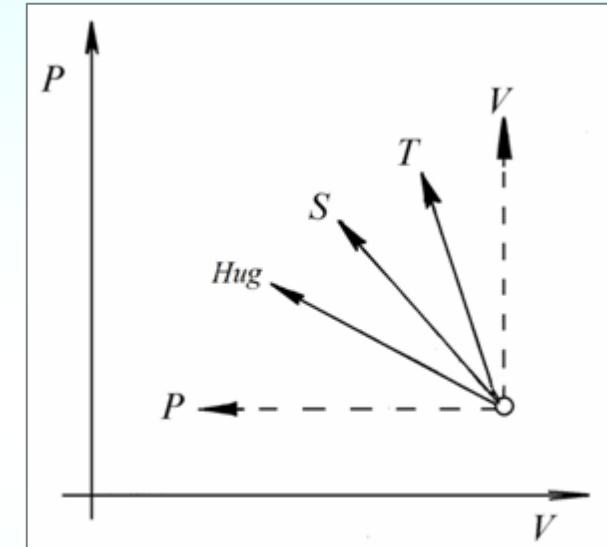
Zero-line

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

$$(\partial P / \partial U)_V = 0$$

$$(\partial V / \partial T)_P = 0$$

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



Ubnormal

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

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

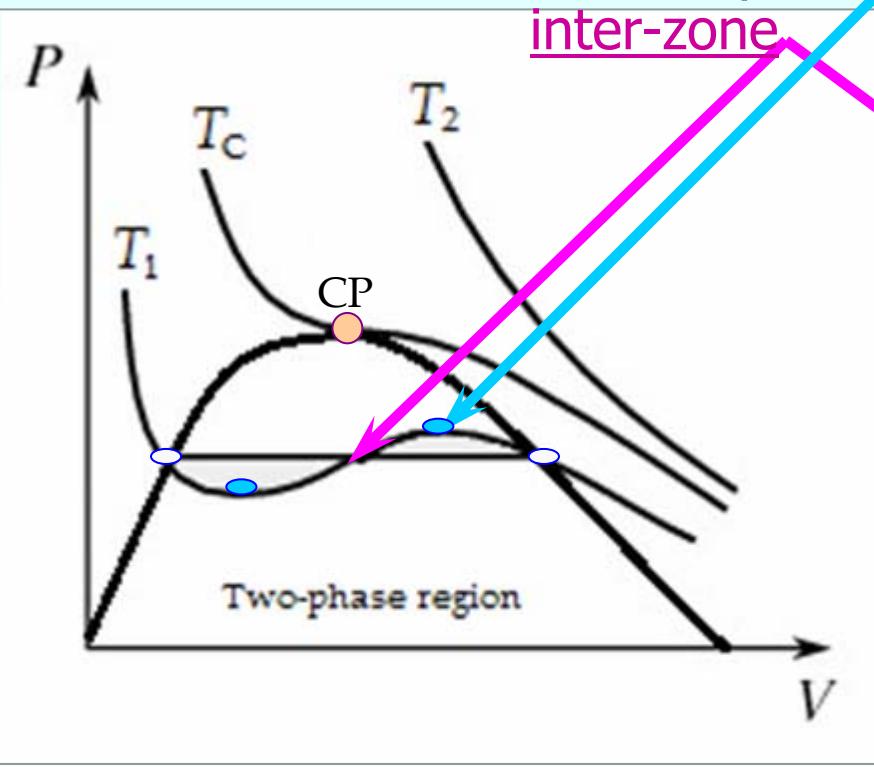
$$(\partial V / \partial T)_P < 0$$

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

Enthalpic (GLPT) vs Entropic (PPT)

(continued)

spinodal points



VdW-like phase transition

NB ! (*enthalpic PT*)

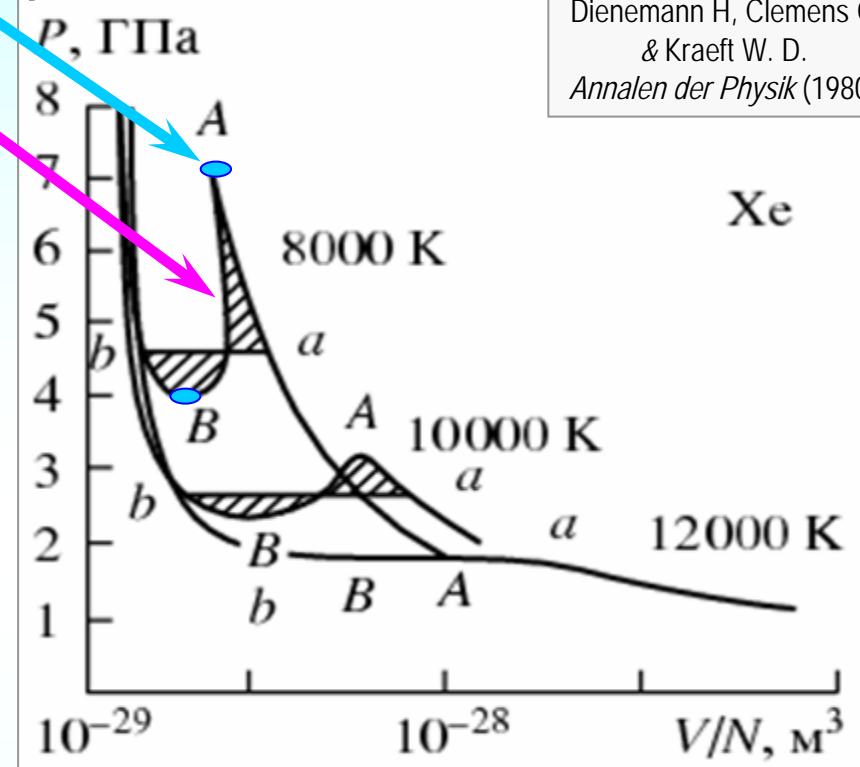
$T \ll T_c$

(*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 !

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



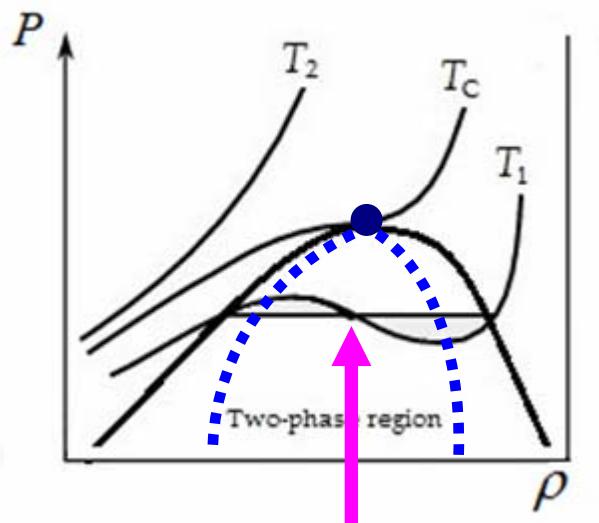
Ionization-driven phase transition in xenon

Hypothetical dissociation-driven PT

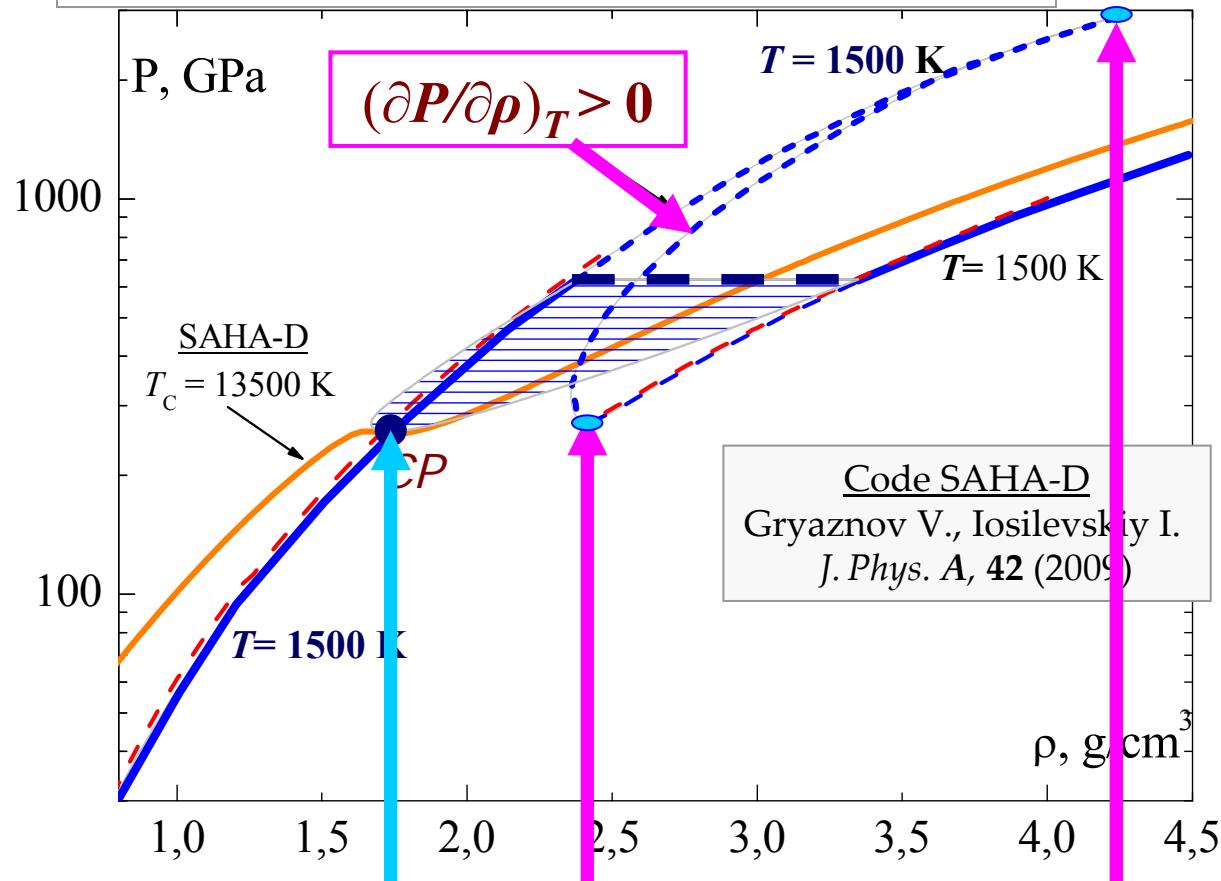
(entropic PT)

(enthalpic PT)

VdW-like phase transition



Dissociation-driven phase transition (deuterium)



NB !

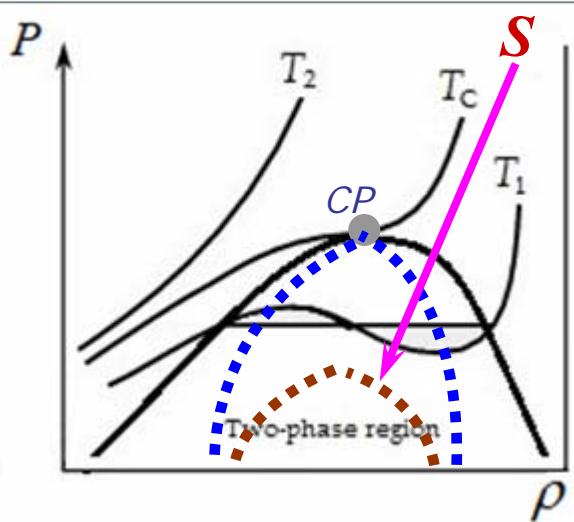
Not one, but **three isotherms intersect critical point** in P - V plane!

Spinodal point of **rare phase** may be of **higher density** than **spinodal** point of **dense phase** !

Hypothetical dissociation-driven (*entropic*) PT

Zeldovich Ya., *Zh. Eksp. Teor. Fiz.* **32**, (1957)

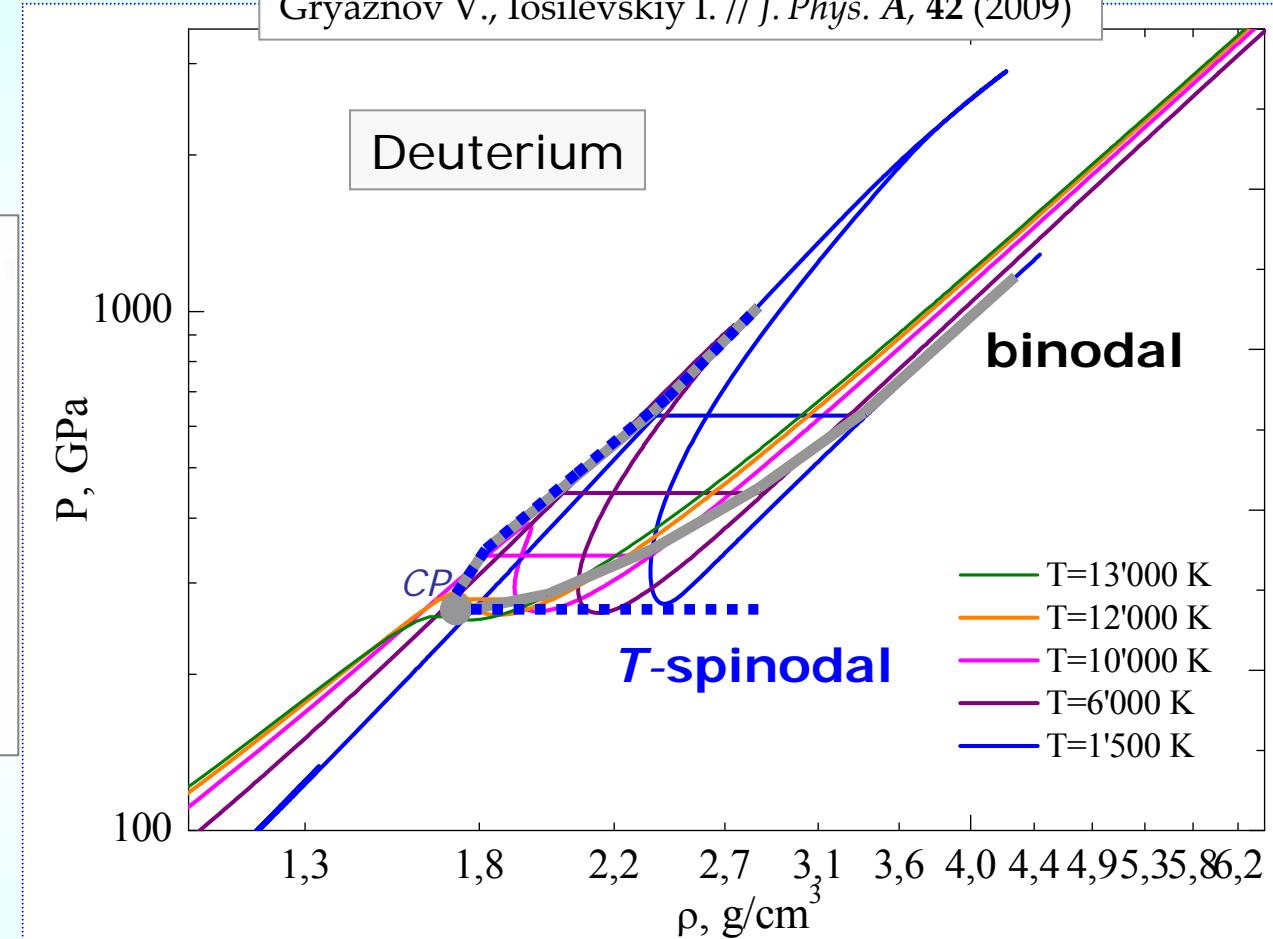
CP
Binodal
T-spinodal
S-spinodal



VdW-like (*enthalpic*)
phase transition

Code SAHA-D

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



NB !

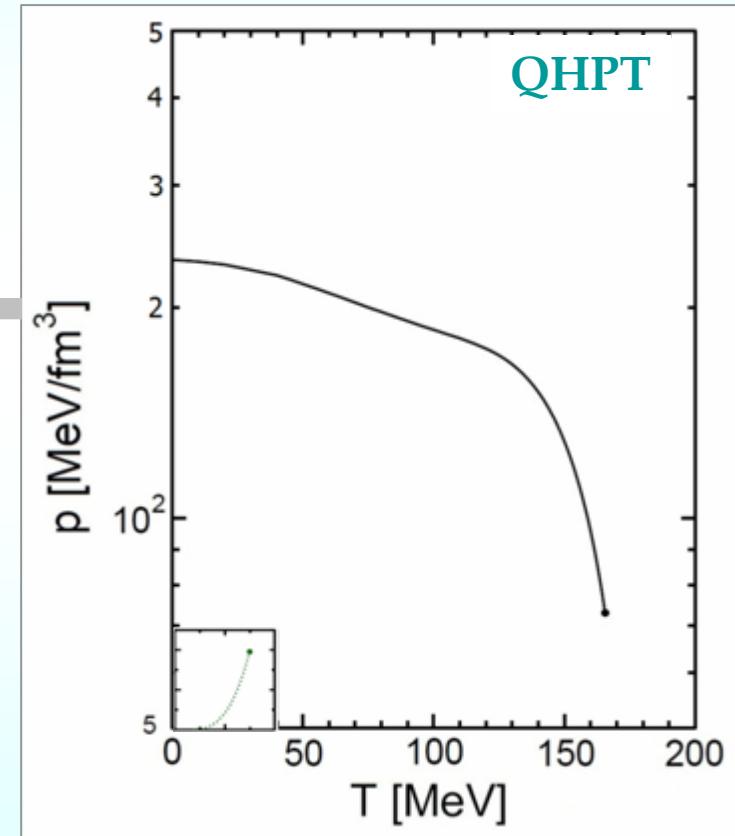
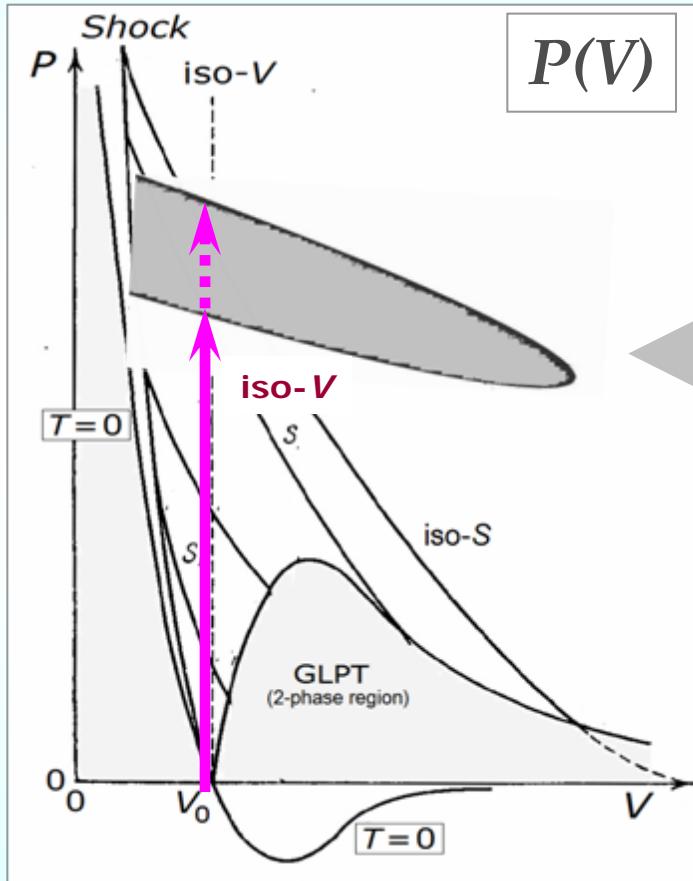
Iso-*T* spinodal $\{(\partial P / \partial V)_T = 0\}$ is located **outside** of **binodal**

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

Multy-layered structure of thermodynamic surfaces for entropic phase transition over p - V plane

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

Path under two-phase region via lower layer



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

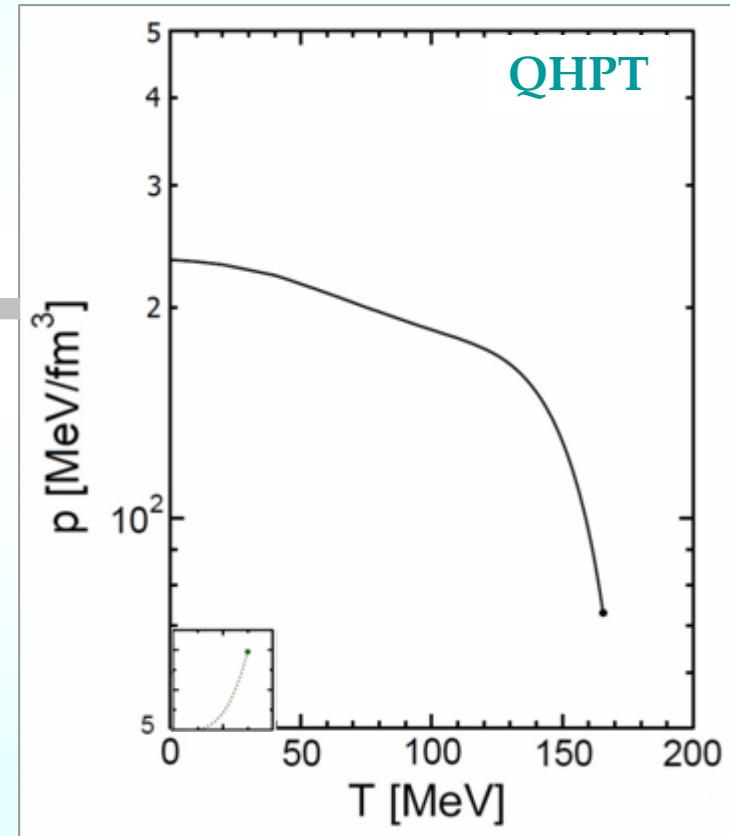
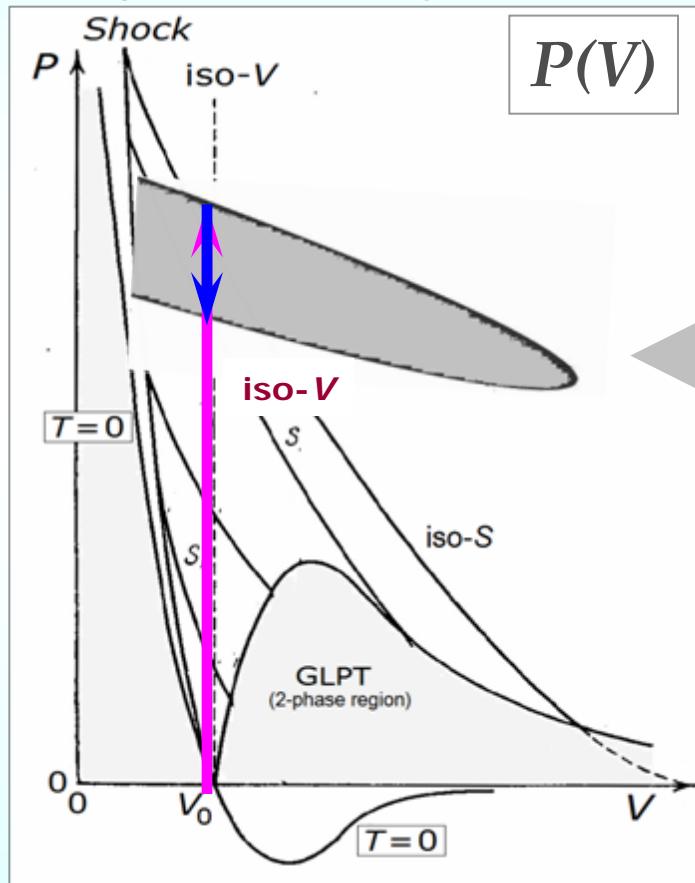
Entropic (deconfinement-driven) phase transition
SU(3) model (Veronica Dexheimer & Stefen Schramm)

Crossing of two-phase region via isochoric heating

Multy-layered structure of thermodynamic surfaces for entropic phase transition over p - V plane

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

Path through two-phase region via middle layer



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

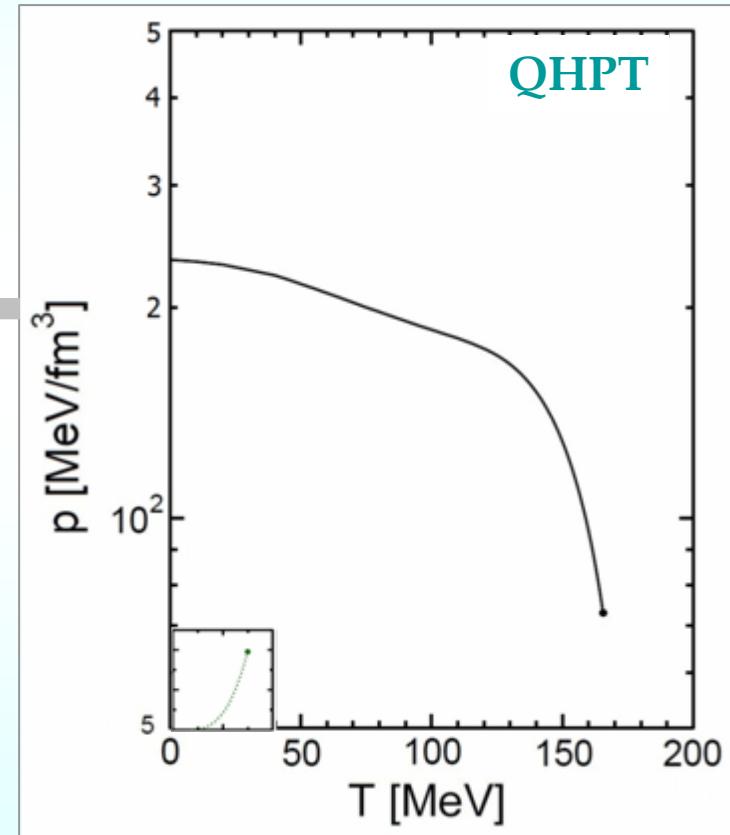
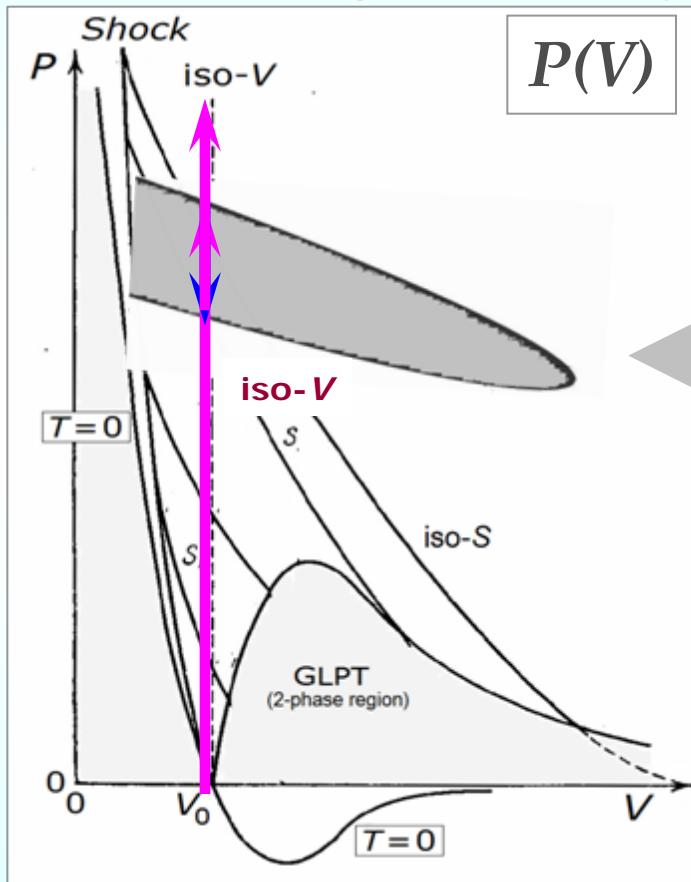
Entropic (deconfinement-driven) phase transition
SU(3) model (Veronica Dexheimer & Stefen Schramm)

Crossing of two-phase region via isochoric heating

Multy-layered structure of thermodynamic surfaces for entropic phase transition over p - V plane

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

Path over two-phase region via upper layer



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

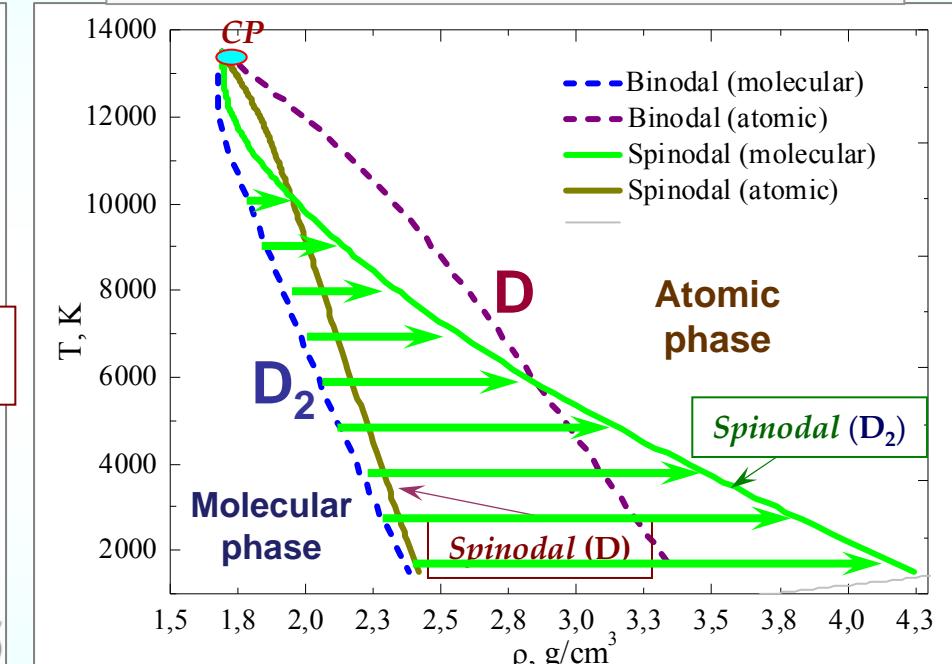
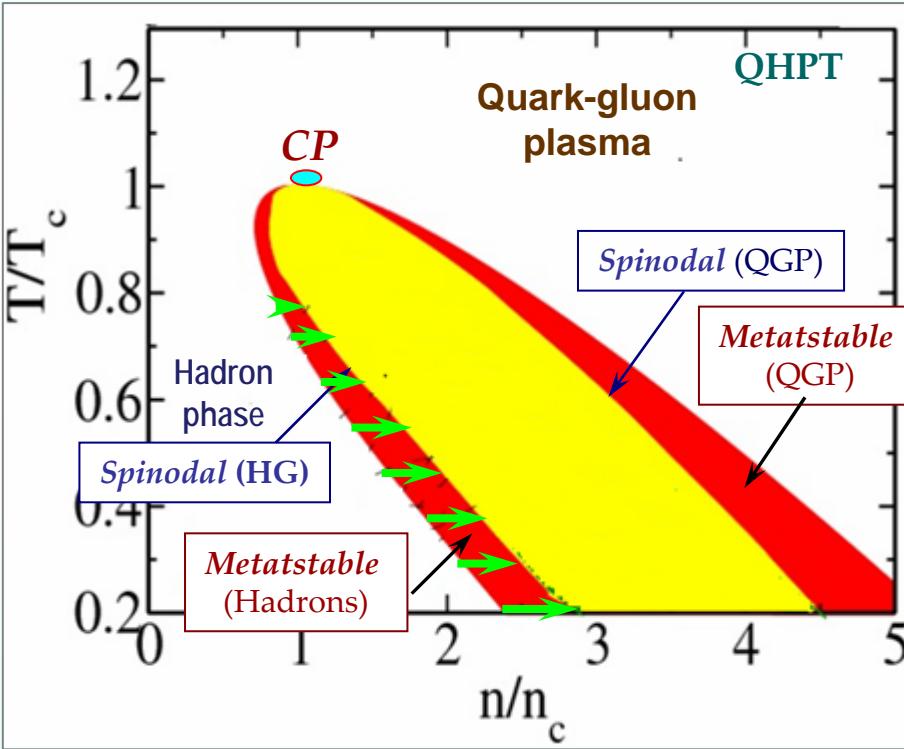
Entropic (deconfinement-driven) phase transition
SU(3) model (Veronica Dexheimer & Stefen Schramm)

Crossing of two-phase region via isochoric heating

Abnormal 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"

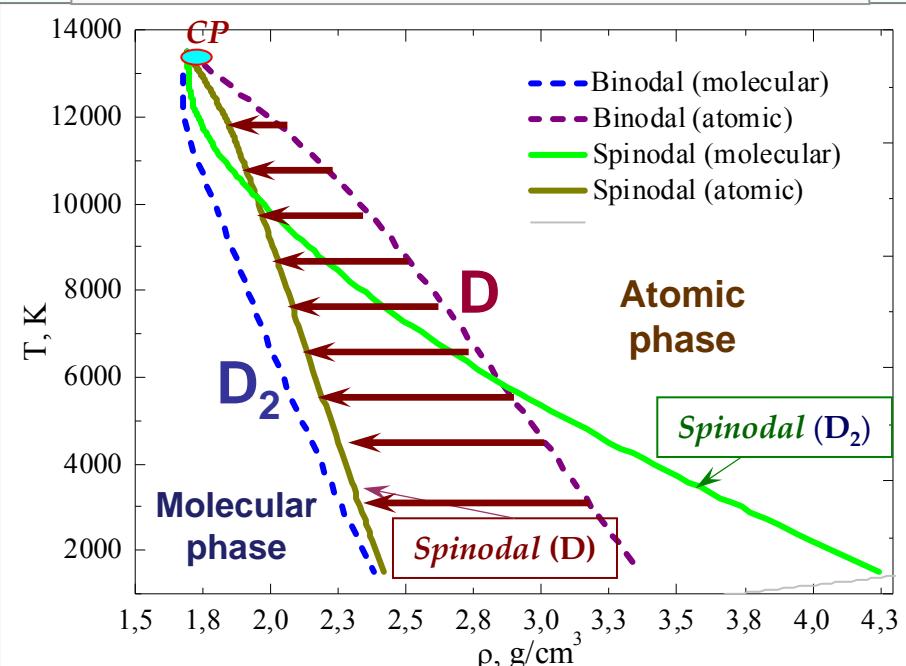
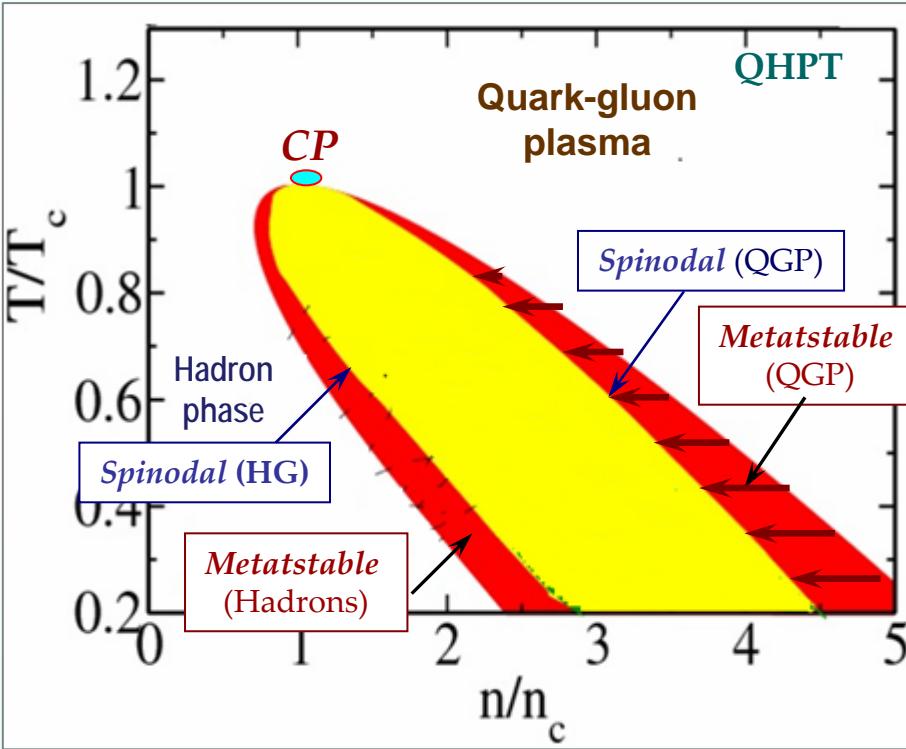
NB !

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

Abnormal 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 !

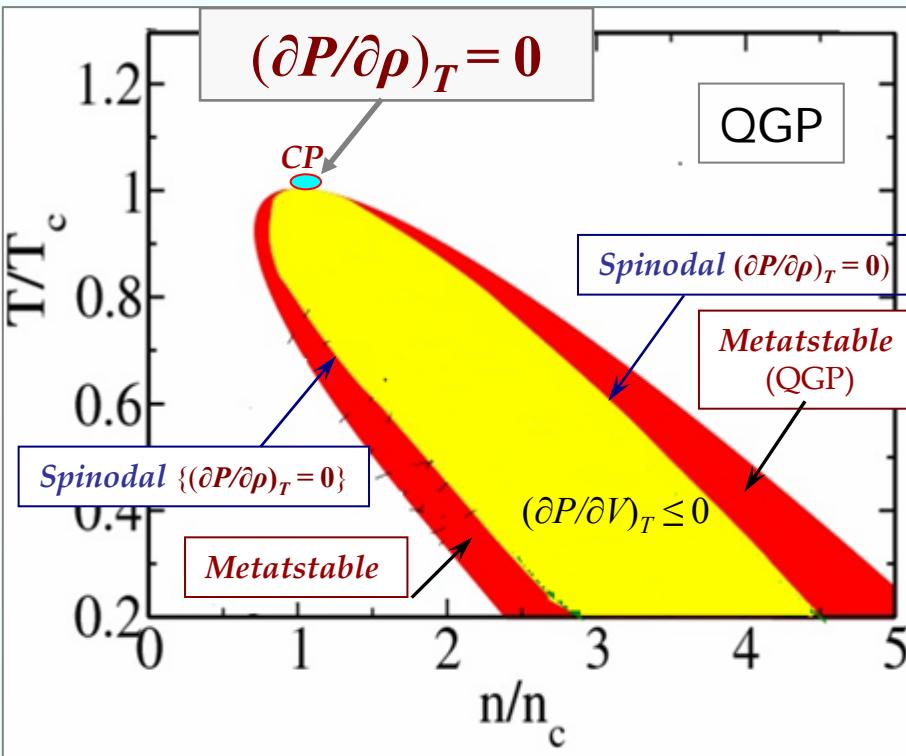
Abnormal features of entropic phase transition are due to multi-layered structure of thermodynamic surfaces !

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

(T - ρ diagram)

QHPT

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

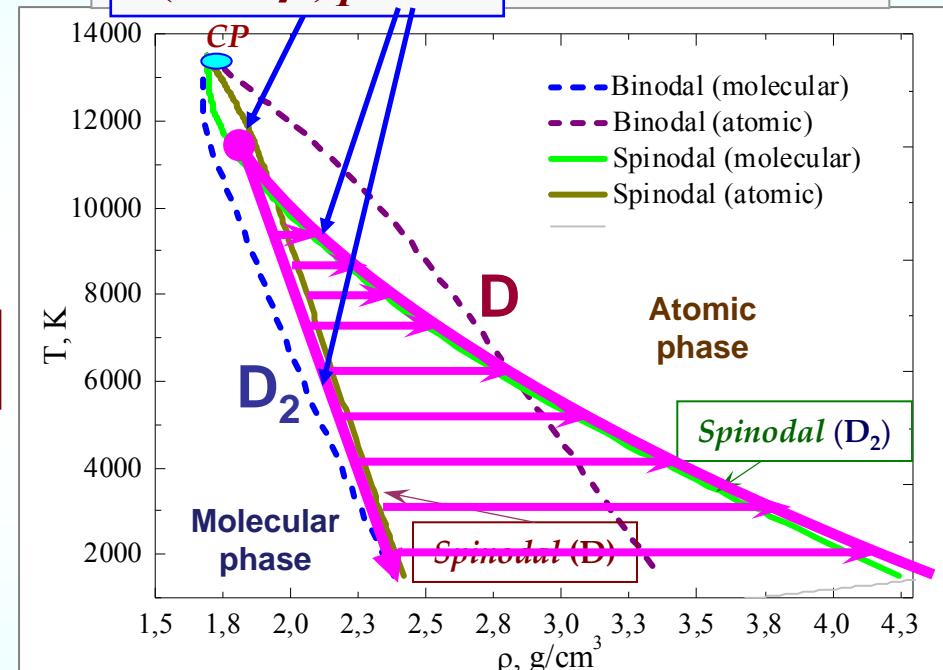


QHPT

$(\partial P/\partial \rho)_T = \infty$

HA-D

[J. Phys. A, 42 (2009)]



NB !

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

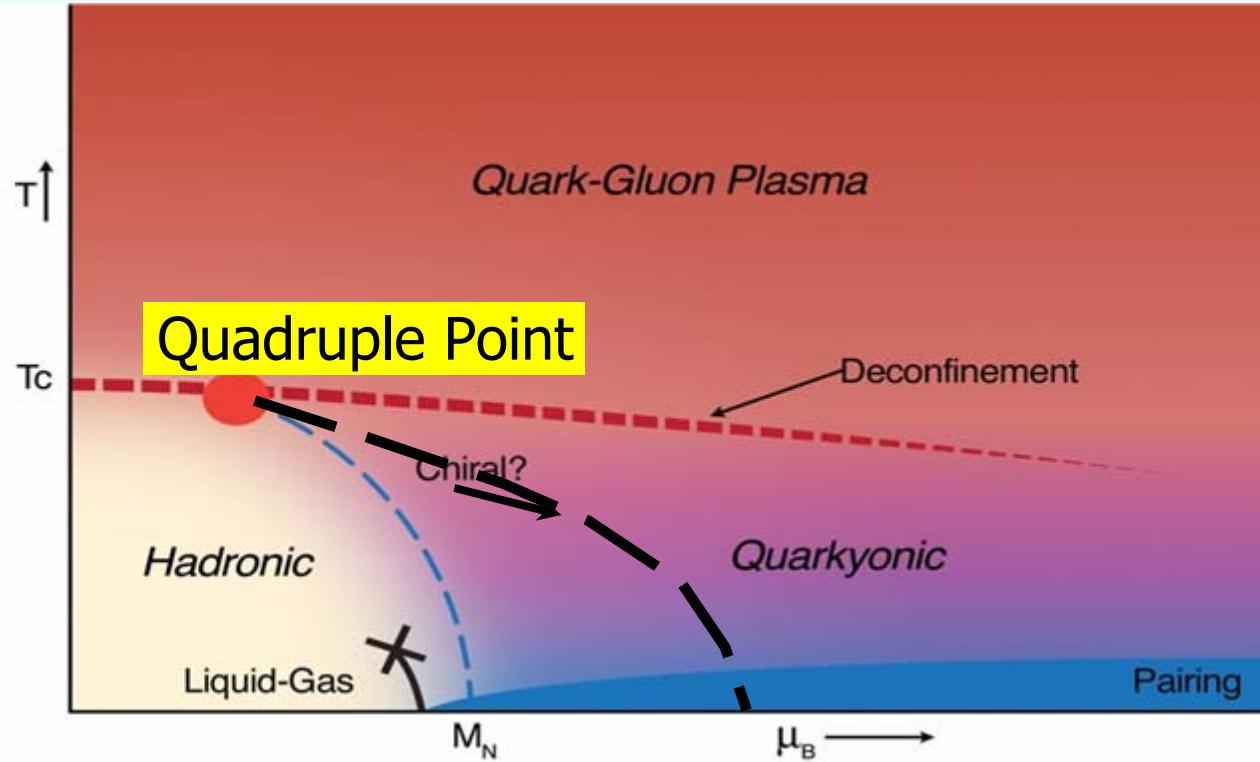
Features of entropic phase transitions (ionization- and dissociation-driven)

Entropic PT obeys to anomalous thermodynamics !

- negative Gruneisen parameter $(\partial P/\partial U)_V < 0$
- 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.
- abnormal order of isotherms (!)
- abnormal order of isentropes (!)
- abnormal order of iso-H and iso-U (!)
- abnormal order of shock adiabats (Hugoniots !)
- etc. etc.
- abnormal form of isotherms in two-phase region
- abnormal interconnection of spinodals and binodals
- etc. etc.

Outlook

Inventory of new hypothetical phase transitions



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

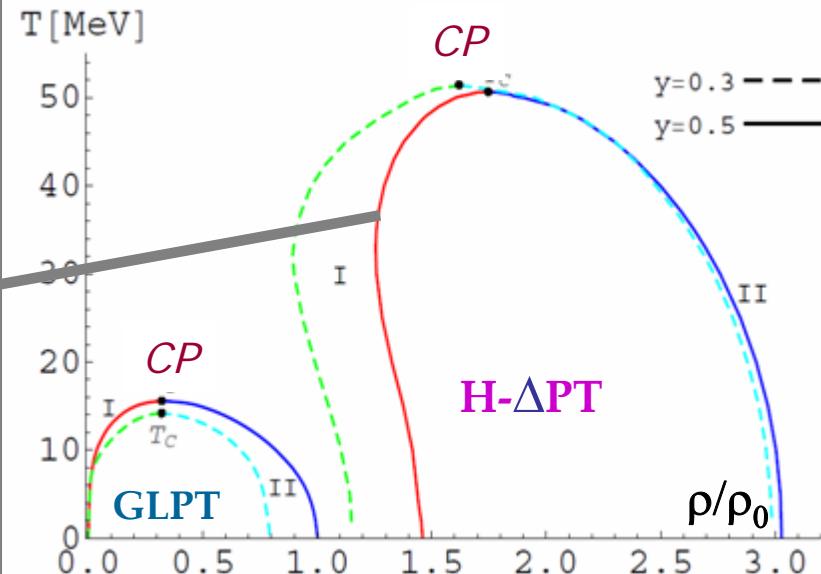
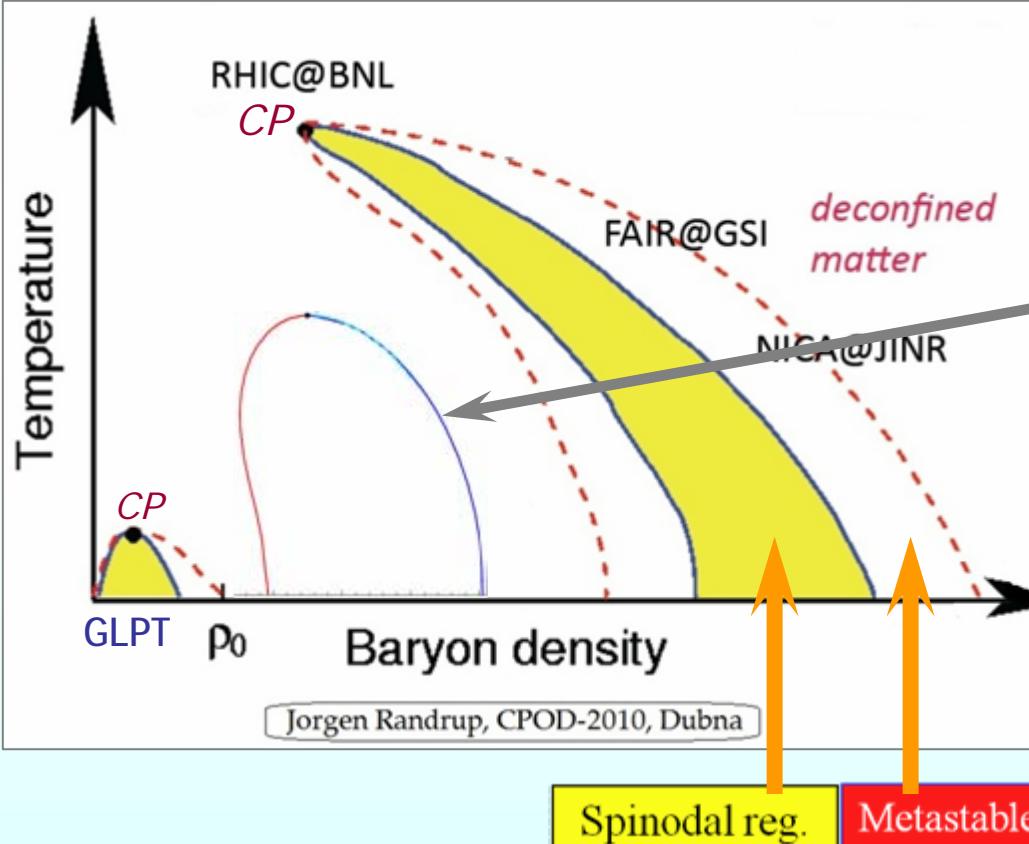
What type of all these hypothetical phase transitions:
- are they enthalpic or entropic PTs ?

Gas–liquid, **Hadron** – Δ -meson and quark–hadron phase transitions are 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. and Pigato D.
Phys. Rev. C., **86**, (2012)
Thermodynamic instability in warm and dense nuclear matter

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

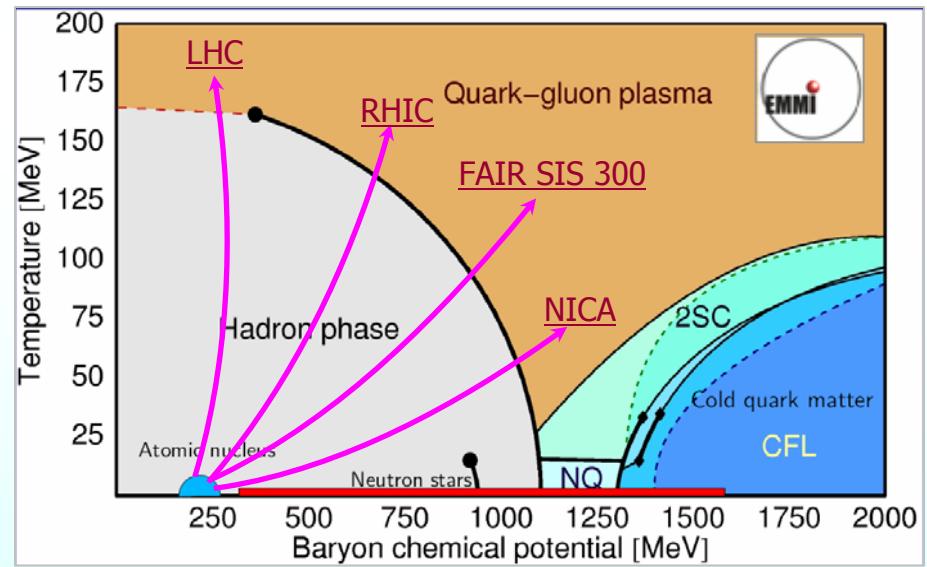
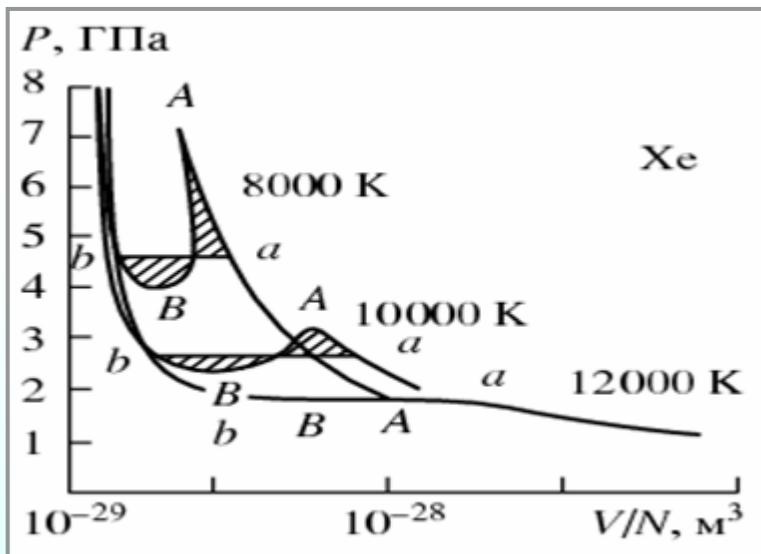
Conclusions *and* perspectives

- **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* { $U(p, V)$, $T(p, V)$, $S(p, V)$... }



Features of phase transitions in cosmic matter and in the laboratory

Thank you!



Support: INTAS 93-66 // ISTC 3755 // RAS Scientific Program "Physics of Extreme States of Matter"

Russian Scientific Fund (Grant No: 14-50-00124)

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