Quantum van der Waals equation

and its applications

Volodymyr Vovchenko

Institute for Theoretical Physics, Goethe University Frankfurt, Germany
Frankfurt Institute for Advanced Studies, Frankfurt, Germany

$$p(T,n) = p_q^{\mathrm{id}}\left(T, \frac{n}{1-bn}\right) - an^2$$

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UNIVERSITÉ DU LUXEMBOURG

FIAS Frankfurt Institute for Advanced Studies

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Outline

1. Physics of strongly interacting matter
    - Motivation for new applications of the van der Waals equation

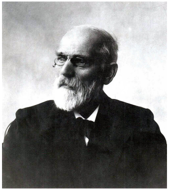
2. van der Waals equation in the grand canonical ensemble
    - Particle number fluctuations and their relation to phase transitions

3. Quantum van der Waals equation
    - Nuclear matter as a QvdW system of nucleons
    - Multi-component van der Waals
    - Thermal Model with van der Waals equation

4. Phase diagram of atomic He-4
    - Importance of Bose statistics

5. Summary

van der Waals equation



Formulated in 1873.

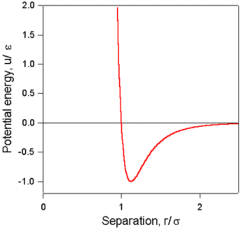
$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = N k_B T$$

Nobel Prize in 1910.

A semi-quantitative theory modeling systems with short-range repulsive (excluded-volume) and intermediate range attractive (vdW force) intermolecular/atomic interactions

Equation is classical, but the underlying forces are of quantum mechanical origin

see, e.g., J. Hermann, R. DiStasio Jr., A. Tkatchenko, Chem. Rev. (2017) for review



Our motivation to use the van der Waals equation comes from high-energy nuclear physics. . .

Physics of strongly interacting matter

Strongly interacting matter

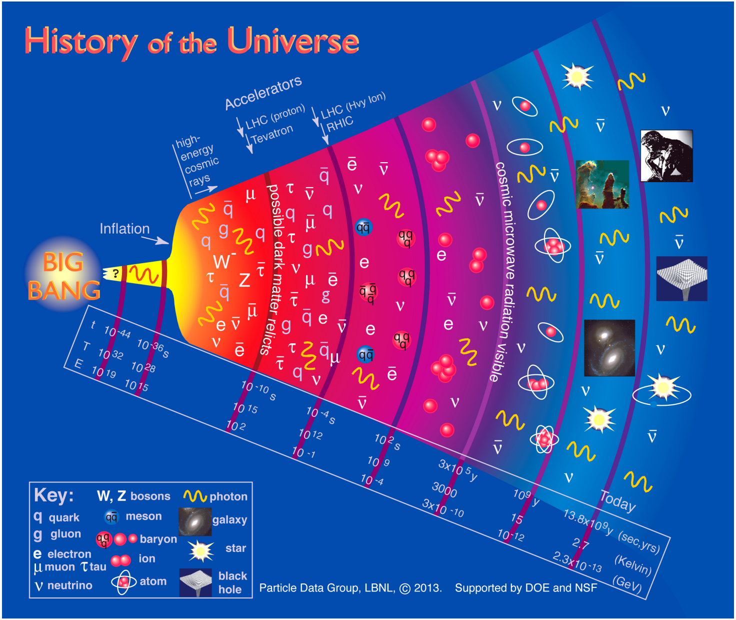
Quantum Chromodynamics (QCD)

$$\mathcal{L} = \sum_{\mathrm{q=u,d,s,c,b,t}} \bar{q}[i\gamma^\mu(\partial_\mu - igA^a_\mu\lambda_a) - m_q]q - \frac{1}{4}G^a_{\mu\nu}G^{\mu\nu}_a$$

- Fundamental theory of strong nuclear force, part of the Standard Model
- A gauge theory with non-abelian SU(3) group gauge symmetry
- Basic degrees of freedom: quarks and gluons which carry color charge

Features

- **Confinement:** free quarks never observed, confined into hadrons baryons (qqq), such as protons (uud) and neutrons (udd), and mesons ($q\bar{q}$)
- **Asymptotic freedom:** QCD is asymptotically free at high energies/densities $\rightarrow$ new state of matter called **quark-gluon plasma (QGP)** expected
  Gross, Wilczek, Politzer (1973), 2004 Nobel Prize in Physics
- QCD dynamics is the origin of about 95% of the mass of ordinary matter, only the rest 5% comes from Higgs



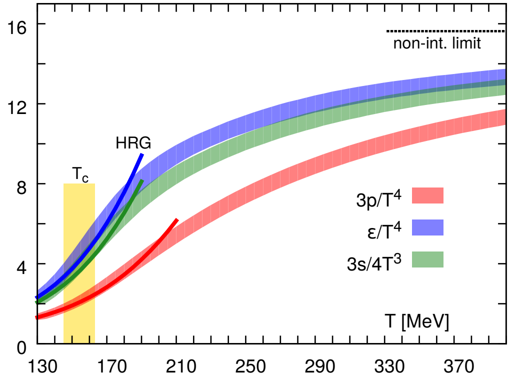
QGP $\rightarrow$ ordinary matter transition 100's μs after Big Bang

QCD transition

Equilibrium properties of QCD characterized by the equation of state

Partition function: $Z = \mathrm{Tr}(e^{-(\hat{H}-\mu\hat{N})/T})$

Numerical solution of QCD with Lattice QCD at zero net baryon number ($\mu = 0$):



Consistent with ordinary (hadronic) matter at low temperatures, and quark-gluon plasma at high temperatures, the transition is **smooth crossover**

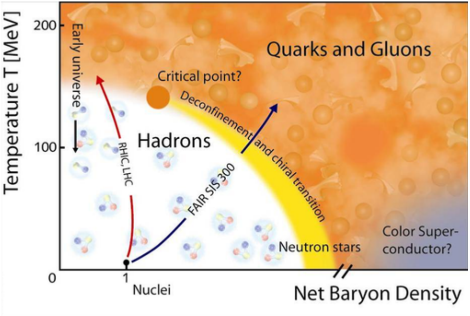
Aoki, Endrodi, Fodor, Katz, Szabo, Nature 443, 675 (2006)
Precision LQCD data from 1407.6387 (HotQCD, plotted), 1309.5258 (Wuppertal-Budapest)

QCD Phase Diagram

More relevant QCD applications are at non-zero baryon density

Lattice QCD breaks down due to sign problem $\Rightarrow$ **no first-principle tool**

Sketch of the QCD Phase Diagram



Where is it relevant?

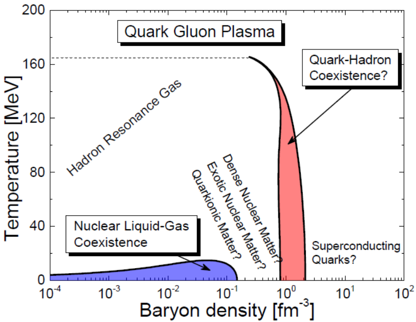
- Early universe
- Neutron stars
- Heavy-ion collisions (laboratory!)

Present knowledge of QCD phase diagram is mostly qualitative and is a field of active research, dominated by phenomenology

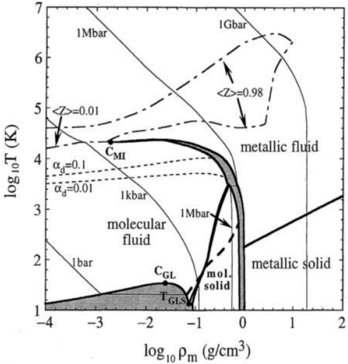
QCD phase diagram

Credit: Jan Steinheimer

Curious similarity to some ordinary fluids, albeit at different scales



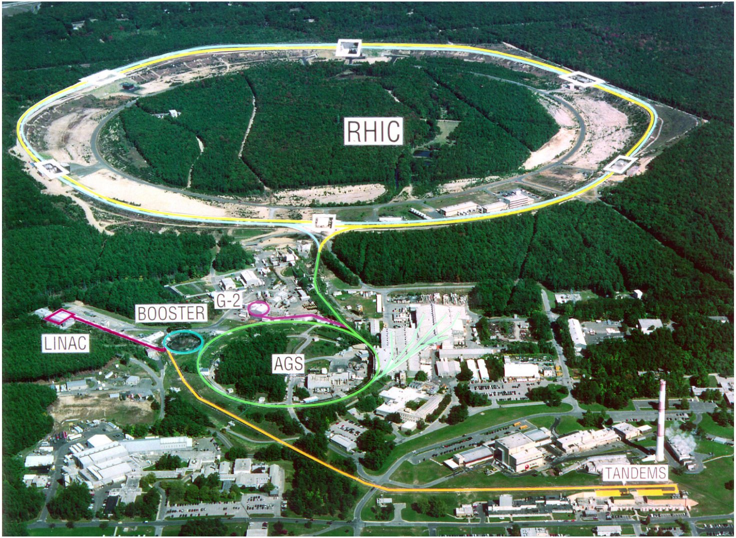
M. Hempel, V. Dexheimer, S. Schramm and I. Iosilevskiy, Phys. Rev. C 88, no. 1, 014906 (2013)



Kitamura H., Ichimaru S., J. Phys. Soc. Japan 67, 950 (1998).

Our laboratory: ultrarelativistic heavy-ion collisions

QCD laboratories



Relativistic heavy-ion collider (RHIC) at
Brookhaven National Laboratory (BNL)

QCD laboratories

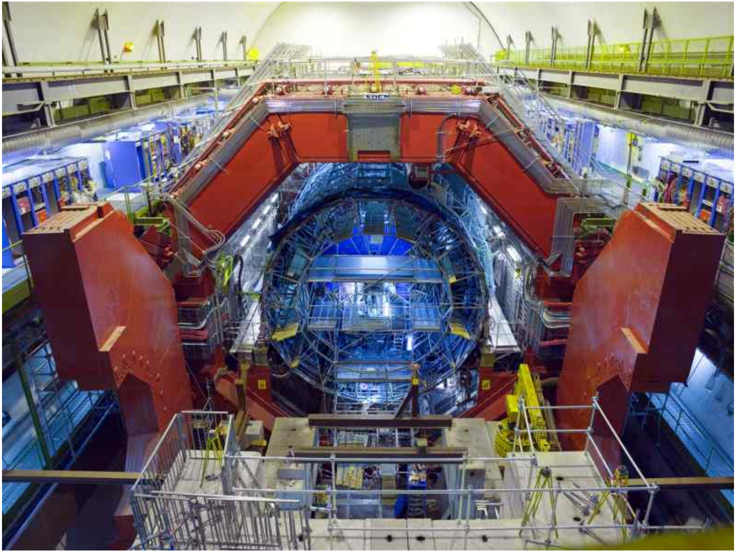
Large Hadron Collider (LHC) at CERN

QCD laboratories: future

GSI-FAIR, Darmstadt, Germany

A number of future heavy-ion accelerators being constructed: GSI-FAIR in Darmstadt, NICA in Dubna, J-PARC in Japan

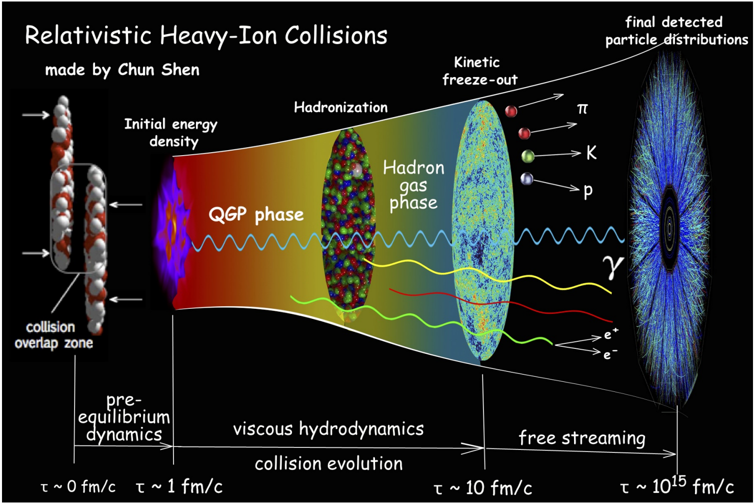
QCD laboratories: detector



(c) CERN

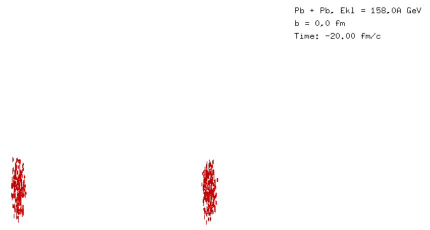
Detector of the ALICE experiment at CERN

Physics of heavy-ion collisions

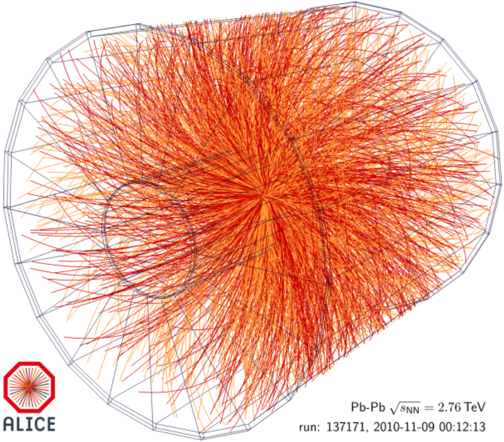


- Collision energy: from several GeV to several TeV in c.m. frame
- Length scale: $L \sim 10$ fm $= 10^{-14}$ m $= 10^{-4}$ Å
- Time scale: $t \sim 10^{-23}s$

Physics of heavy-ion collisions



What do experiments measure?



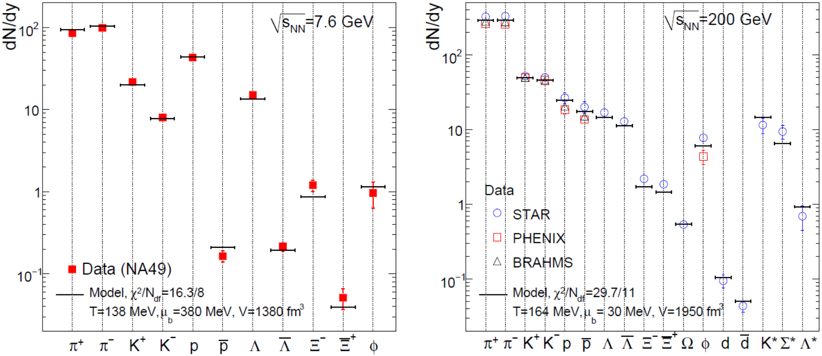
Event display of a Pb+Pb collision in ALICE at LHC (Source)

- Abundances of different species of produced hadrons
- Their momentum distributions
- More recently, event-by-event particle number fluctuations

Is equilibrium reached in heavy-ion collisions?

Thermal Model – ideal gas of all known hadrons ($\sim$ 400 species)

$$N_i \propto \exp\left(-\frac{m_i}{T}\right)\,\exp\left(-\frac{b_i\,\mu_B}{T}\right)$$



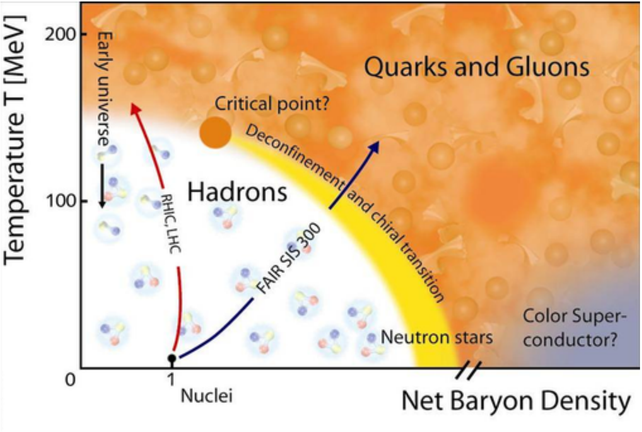
A. Andronic, P. Braun-Munzinger, J. Stachel, Phys. Lett. B 673, 142 (2009)

- Good (10% level) description across several orders of magnitude
- Maps heavy-ion collisions on T-μ_B QCD phase diagram
- $T \sim 150$ MeV $\sim 10^{12}$ K – hottest fluid ever created in a lab!

Limitations of Thermal Model

Standard Thermal Model has no interactions between hadrons and no phase transitions

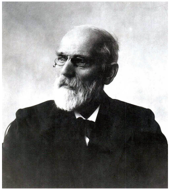
Therefore it cannot shed light on QCD phase structure



We need a model with phase transition(s) and interactions to define and analyze sensitive observables van der Waals equation

van der Waals equation

$$P(T,V,N) = \frac{NT}{V-bN} - a\frac{N^2}{V^2}$$



Formulated in 1873.

Simplest model which contains attractive and repulsive interactions

Contains 1st order phase transition and critical point

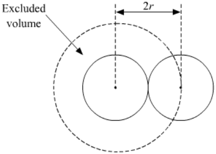
Nobel Prize in 1910.

1. Short-range repulsion: excluded volume (EV) procedure

   $V \to V - bN, \qquad b = 4\frac{4\pi r_c^3}{3}$

2. Intermediate range attraction in mean-field approx.

   $P \to P - a\, n^2, \qquad a = \pi \int_{2r_c}^{\infty} |U_{12}(r)| r^2 dr$

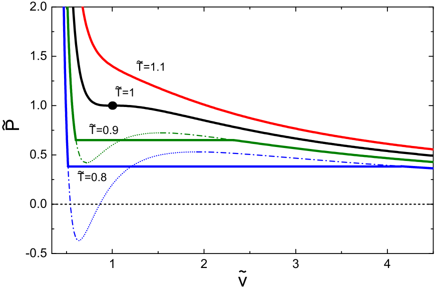


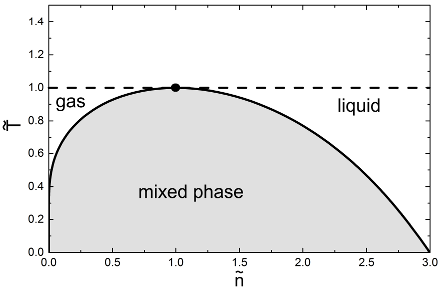
Motivation:

- Toy model to study fluctuations near critical point
- Include essential features of nuclear matter physics

van der Waals equation

- vdW isotherms show irregular behavior below certain temperature T_C
- Below T_C isotherms are corrected by Maxwell's rule of equal areas
- Results in appearance of mixed phase





Critical point

$$\frac{\partial p}{\partial v} = 0, \quad \frac{\partial^2 p}{\partial v^2} = 0, \quad v = V/N$$

$$p_C = \frac{a}{27b^2}, \; n_C = \frac{1}{3b}, \; T_C = \frac{8a}{27b}$$

Reduced variables

$$\tilde{p} = \frac{p}{p_C}, \; \tilde{n} = \frac{n}{n_C}, \; \tilde{T} = \frac{T}{T_C}$$

Statistical ensembles

vdW equation originally formulated in the canonical ensemble

Canonical ensemble (CE)

- System of N particles in fixed volume V exchanges energy with large reservoir (heat bath)
- State variables: T, V, N
- Thermodynamic potential – free energy $F(T,V,N) = -T \log Z(T,V,N)$

Grand canonical ensemble (GCE)

- System of particles in fixed volume V exchanges both energy and particles with large reservoir (heat bath)

$$\Xi(T,V,\mu) = \sum_N e^{\mu N/T} Z(T,V,N)$$

- State variables: T, V, μ. Chemical potential μ regulates *average* $\langle N \rangle$
- Thermodynamic potential – pressure $p(T,\mu) = \frac{T}{V} \log \Xi(T,V,\mu)$

GCE is more natural for systems with variable numbers of particles that cannot be externally regulated, such as those created in heavy-ion collisions

From the CE to the GCE

How to transform the CE pressure $P(T,V,N)$ into the GCE pressure $P(T,\mu)$?

- Calculate $\mu(T,V,N)$ from standard TD relations
- Invert the relation to get $N(T,V,\mu)$ and put it back into $P(T,V,N)$

Result: transcendental equation for $n(T,\mu)$

$$\frac{N}{V} \equiv n(T,\mu) = \frac{n_{\rm id}(T,\mu^*)}{1 + b\, n_{\rm id}(T,\mu^*)}\,, \qquad \mu^* = \mu - b\,\frac{n\,T}{1-b\,n} + 2a\,n$$

$n_{\rm id}(T,\mu^*) = (g/\lambda_{dB}^3)\, e^{\mu^*/T}$

- Implicit equation in the GCE, now depends on mass and degeneracy
- May have multiple solutions below T_C
- Choose one with largest pressure – equivalent to the Maxwell rule in CE

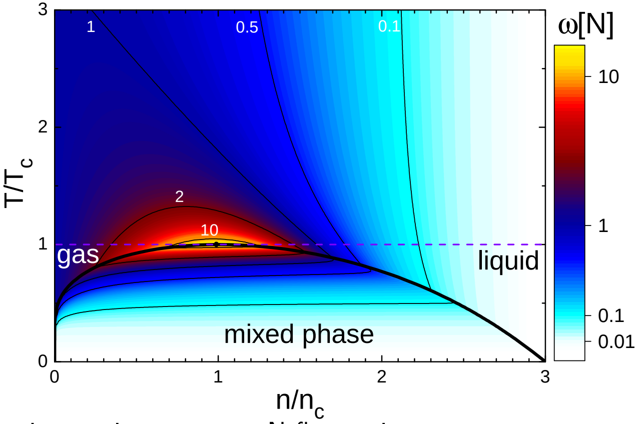
Advantages of the GCE formulation

1. High-energy physics applications: number of hadrons usually not conserved.
2. CE cannot describe particle number fluctuations. N-fluctuations in a small ($V \ll V_0$) subsystem follow GCE results.

Scaled variance for classical vdW equation

New application: Particle number fluctuations within the GCE

$$\omega[N] = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \left[\frac{1}{(1-bn)^2} - \frac{2an}{T}\right]^{-1}$$

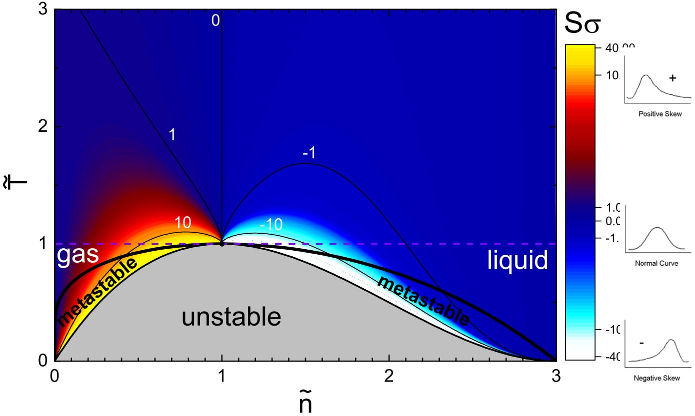


- Repulsive interactions suppress N-fluctuations
- Attractive interactions enhance N-fluctuations

V.V., Anchishkin, Gorenstein, J. Phys. A 48, 305001 (2015)

Classical vdW equation: Skewness

Skewness: $$S\sigma = \frac{\langle (\Delta N)^3 \rangle}{\sigma^2} = \omega[N] + \frac{T}{\omega[N]} \left(\frac{\partial \omega[N]}{\partial \mu} \right)_T$$ asymmetry



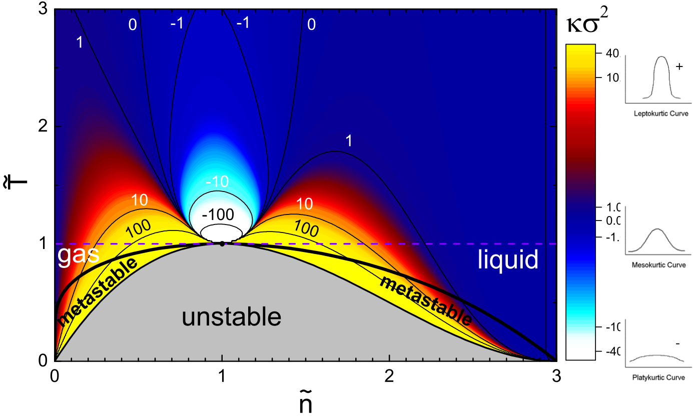
Skewness is

- Positive (right-tailed) in gaseous phase
- Negative (left-tailed) in liquid phase

V.V., R. Poberezhnyuk, D. Anchishkin, M. Gorenstein, J. Phys. A 49, 015003 (2016)

Classical vdW equation: Kurtosis

Kurtosis: $\kappa\sigma^2 = \dfrac{\langle(\Delta N)^4\rangle - 3\langle(\Delta N)^2\rangle^2}{\sigma^2}$ peakedness



Kurtosis is negative (flat) above critical point (crossover), positive (peaked) elsewhere and very sensitive to the proximity of the critical point

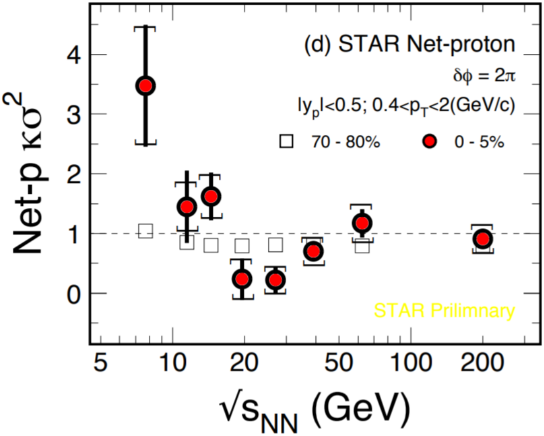
V.V., R. Poberezhnyuk, D. Anchishkin, M. Gorenstein, J. Phys. A 49, 015003 (2016)

Search for CP in heavy-ion collision experiments

Experimental search for QCD CP using non-Gaussian fluctuations is underway

Measurements at BNL-STAR and CERN-NA61/SHINE experiments

X. Luo (STAR collaboration), Quark Matter 2015 conference



Interpretation challenging, many “background” things contribute

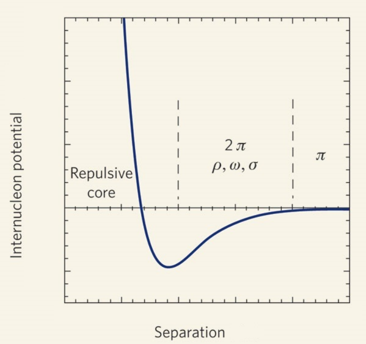
No definitive conclusions regarding the location or existence of QCD CP yet

Quantum van der Waals equation

Nucleon-nucleon interaction

Nucleon-nucleon potential:

- Repulsive core at small distances
  Vector ω meson exchange
- Attraction at intermediate distances
  Scalar σ meson exchange
- Suggestive similarity to vdW interactions
- Could nuclear matter be described by the vdW equation?



Standard vdW equation is for Boltzmann statistics

Nucleons are fermions, obey Pauli exclusion principle

Nuclear matter corresponds to small temperatures and high densities

Unlike for most classical fluids, quantum statistics is important here

Quantum statistical van der Waals fluid

Free energy of classical vdW fluid:

$$F(T,V,N) = F^{\mathrm{id}}(T, V - bN, N) - a\,\frac{N^2}{V}$$

Ansatz: $F^{\mathrm{id}} \Rightarrow F_q^{\mathrm{id}}(T, V - bN, N)$ is free energy of ideal *quantum* gas

Quantum van der Waals equation:

$$p(T,n) = p_q^{\mathrm{id}}\left(T, \frac{n}{1-bn}\right) - an^2$$

$p_q^{\mathrm{id}}(T,n)$ corresponds to Fermi-Dirac or Bose-Einstein distribution

Model properties:

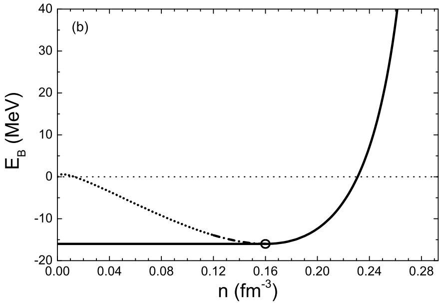
- Reduces to the classical vdW equation when quantum statistics are negligible
- Reduces to ideal quantum gas for $a = 0$ and $b = 0$
- Entropy density non-negative and $s \to 0$ with $T \to 0$

V.V., Anchishkin, Gorenstein, Phys. Rev. C 91, 064314 (2015)
K. Redlich, K. Zalewski, Acta Phys. Polon. B 47, 1943 (2016)
a=0 $\Rightarrow$ (quantum) excluded-volume model, D. Rischke et al., Z. Phys. C 51, 485 (1991)

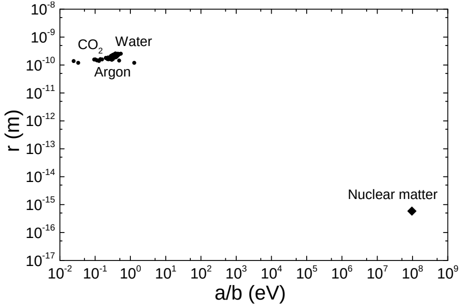
Nuclear matter as a fermionic vdW nucleon fluid

How to fix a and b for nucleons? For classical fluid usually tied to CP location.
Different approach: Reproduce saturation density and binding energy at $T = 0$

$$n_0 = 0.16 \text{ fm}^{-3},\ E/A = -16 \text{ MeV} \Rightarrow a \cong 329 \text{ MeV fm}^3 \text{ and } b \cong 3.42 \text{ fm}^3$$



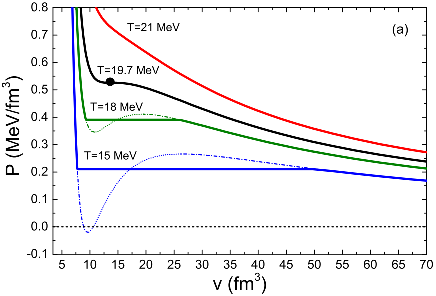
Mixed phase at $T = 0$ is special:
A mix of vacuum ($n = 0$) and liquid at $n = n_0$

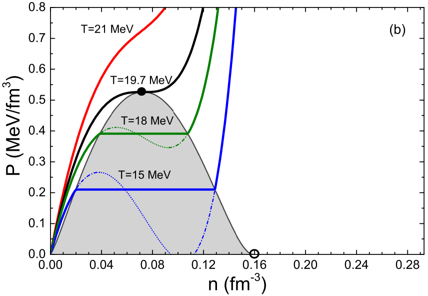


vdW eq. now at very different scales!

Nuclear matter as a quantum vdW nucleon fluid

Predictions for finite temperature behavior





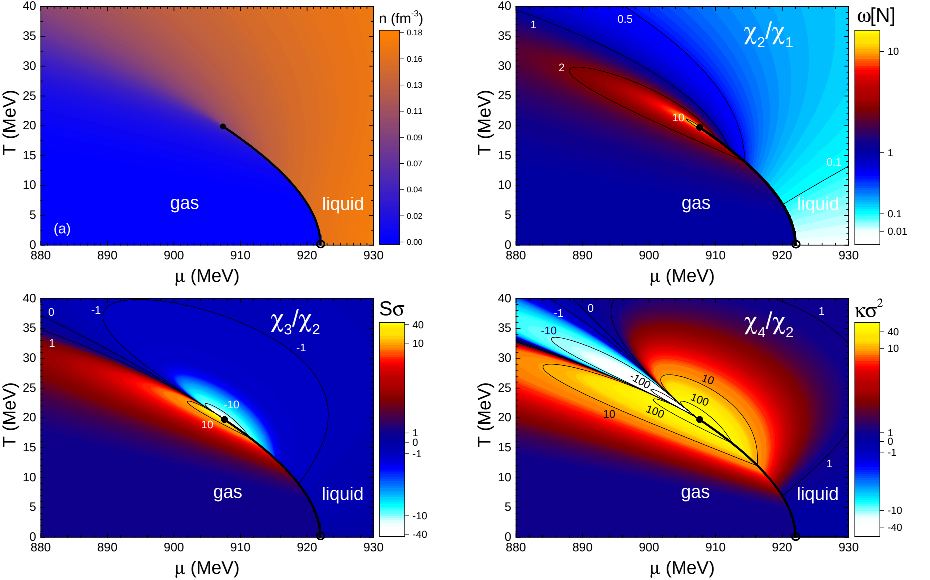
Critical point at $T_c \cong 19.7$ MeV and $n_c \cong 0.07$ fm^{-3}

Experimental estimate[1]: $T_c = 17.9 \pm 0.4$ MeV, $n_c = 0.06 \pm 0.01$ fm^{-3}

[1] J.B. Elliot, P.T. Lake, L.G. Moretto, L. Phair, Phys. Rev. C 87, 054622 (2013)

QvdW fluid of nucleons: (T,μ) plane

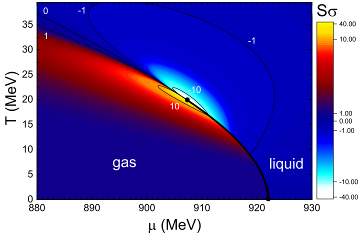
(T,μ) plane: structure of critical fluctuations $\chi_i = \partial^i (p/T^4)/\partial(\mu/T)^i$



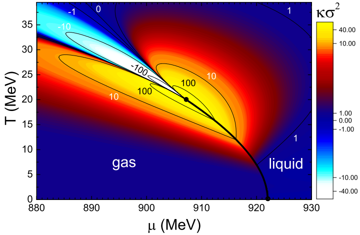
V.V., D. Anchishkin, M. Gorenstein, R. Poberezhnyuk, PRC 91, 064314 (2015)

QvdW gas of nucleons: skewness and kurtosis

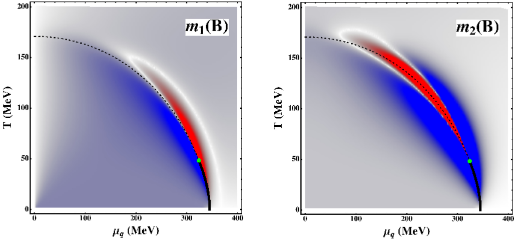
QvdW Skewness



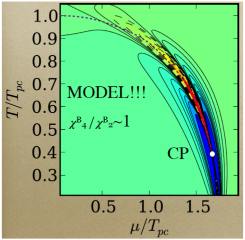
QvdW Kurtosis



NJL, J.W. Chen et al., PRD 93, 034037 (2016)



PQM, V. Skokov, QM2012



Fluctuation patterns in vdW very similar to effective QCD models with CP

This illustrates universality of the critical behavior

Quantum real gas models

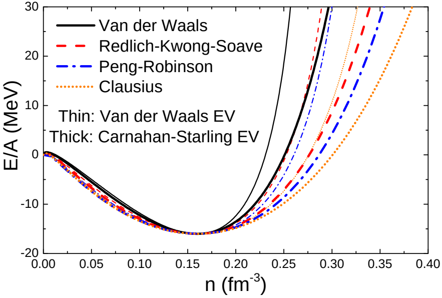
Modifications of the classical vdW equation

$$p(T,n) = \frac{nT}{1-bn} - an^2 \quad \Rightarrow \quad p(T,n) = nT\,g(bn) - \frac{an^2}{u(T,n)}$$

yield a class of real gas models that give more quantitative description.

Examples: Redlich-Kwong-Soave, Peng-Robinson, Carnahan-Starling models

Quantum real gas: $\quad F(T,V,N) = F_q^{\mathrm{id}}[T, V\,f(bn), N] - N\,u(T,n;a,b,\ldots)$



Quantum real gas models extend the applicability to higher densities

V.V., Phys. Rev. C 96, 015206 (2017)

Multi-component quantum van der Waals equation

Classical multi-component vdW equation (most "general" form)

$$p(T, n_1, \dots, n_f) = \sum_i \frac{T\, n_i}{1 - \sum_j b_{ji}\, n_j} - \sum_{i,j} a_{ij}\, n_i\, n_j \ .$$

Quantum statistical version, following the same procedure

$$p(T, n_1, \dots, n_f) = \sum_i p^{\rm id}_{q,i} \left(T, \frac{n_i}{1 - \sum_j b_{ji}\, n_j} \right) - \sum_{i,j} a_{ij}\, n_i\, n_j \ .$$

Grand canonical ensemble formulation,

$$p(T, \mu) = \sum_i p_i^{\rm id}(T, \mu_i^*) - \sum_{i,j} a_{ij}\, n_i\, n_j,$$

$$\sum_j [\delta_{ij} + b_{ji}\, n_i^{\rm id}(T, \mu_i^*)]\, n_j = n_i^{\rm id}(T, \mu_i^*), \qquad i = 1 \dots f,$$

$$\mu_i^* + \sum_j b_{ij}\, p_j^* - \sum_j (a_{ij} + a_{ji})\, n_j = \mu_i \ , \quad i = 1, \dots, f \ ,$$

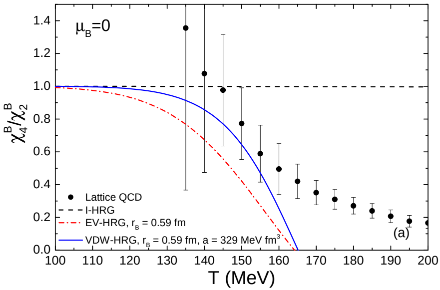
describes chemical equilibrium in multi-component interacting system where number of independent chemical potentials is smaller than number of species.

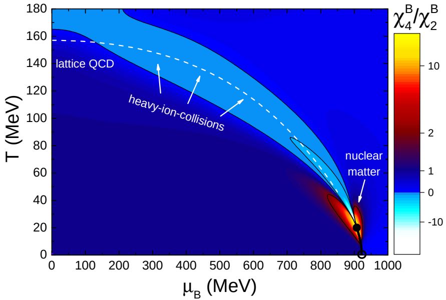
V.V., A. Motornenko, P. Alba, et al., Phys. Rev. C 96, 045202 (2017)

Thermal Model with van der Waals interactions

Let us include vdW interactions into the Thermal Model:

Thermal Model with attractive and repulsive vdW interactions between baryons





vdW interactions capture the drop of net baryon kurtotsis seen in lattice QCD simulations at $\mu_B = 0$

A shockingly strong effect of vdW interactions on fluctuation observables in heavy-ion collisions!

V.V., M. Gorenstein, H. Stoecker, Phys. Rev. Lett. 118, 182301 (2017)

Quantum van der Waals equation and atomic He-4

What about atomic systems? Let's take atomic He-4!

Spin 0 $\Rightarrow g = 1$, Bose-Einstein statistics, is known to undergo a liquid-gas transition

Van der Waals constants (data page)

From Wikipedia, the free encyclopedia

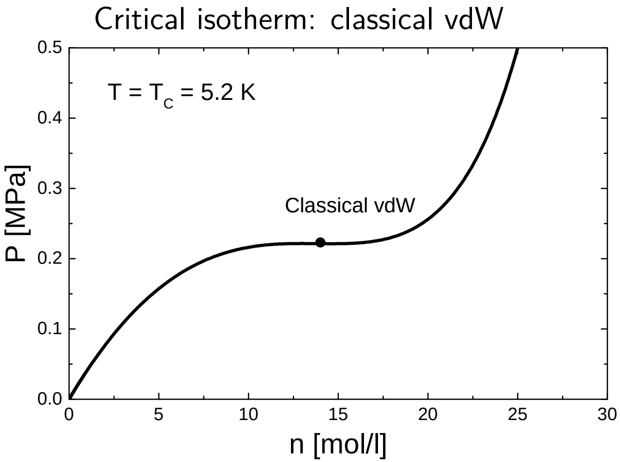
	a (L^{2}bar/mol^2)	b (L/mol)
Helium	0.0346	0.0238
Neon	0.2135	0.01709
Hydrogen	0.2476	0.02661
Argon	1.355	0.03201

First, take classical vdW equation

Critical point: $T_c = \frac{8a}{27b} \approx 5.2$ K, $P_c = \frac{a}{27b^2} \approx 0.229$ MPa

Experiment: $T_c \approx 5.2$ K, $P_c \approx 0.227$ MPa

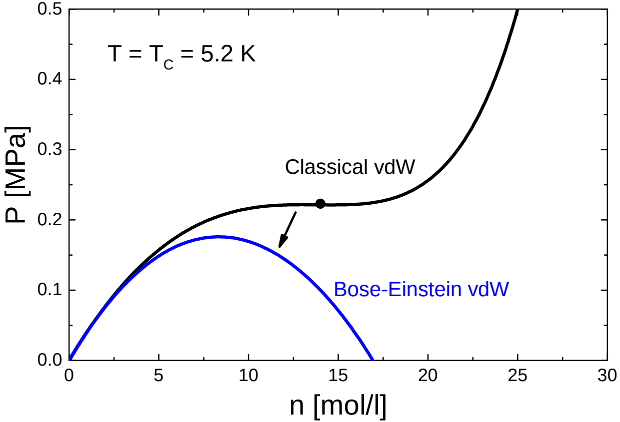
Quantum van der Waals equation and atomic He-4



So far, so good...

Quantum van der Waals equation and atomic He-4

Critical isotherm: classical vdW vs quantum vdW



So far, so good... not anymore!

A reasonable description of liquid-gas transition in atomic He-4 requires explicit treatment of Bose-Einstein effects

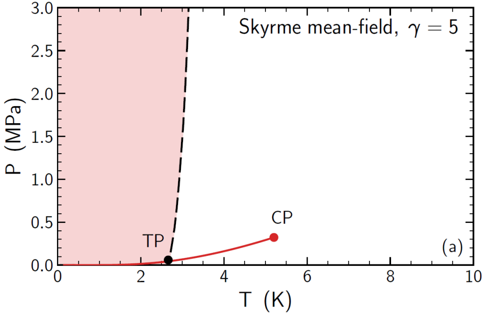
Phase diagram of atomic He-4 within Skyrme model

by Anton Motornenko

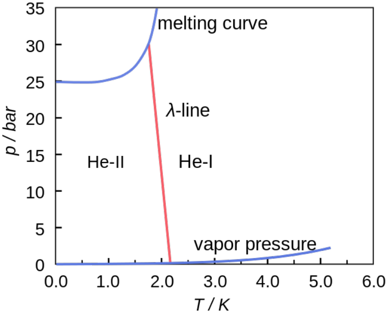
Applying model from nuclear physics to an atomic system

Skyrme model: $p(T,n) = \underbrace{p_q^{\mathrm{id}}(T,n)}_{\text{ideal gas}} + \underbrace{\alpha\, n^2}_{\text{attraction}} - \underbrace{\beta\, n^{2+\gamma}}_{\text{repulsion}},\quad \alpha,\, \beta,\, \gamma > 0$

Skyrme model



Empirical



A (semi) reasonable description of the phase diagram

Tools from nuclear physics are useful for atomic systems

Summary

- Thermodynamically consistent formulation of the quantum statistical van der Waals equation in the grand canonical ensemble opens new applications in the field of high energy nuclear physics
- Enhanced particle number fluctuations, as well as a non-monotonic response of their skewness and kurtosis to the control parameters of an experiment, signal the presence of a phase transition and critical point
- van der Waals like interactions between nucleons/baryons are surprisingly important for observables in high-temperature QCD
- Reasonable description of liquid-gas transition in atomic He-4 must take into account the Bose-Einstein statistics and condensation

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Thanks for your attention!

Backup slides