How Many is Different ?

- *Answer from ideal Bose gas*

朴廷爀 Jeong-Hyuck Park 박정혁

Sogang University, Seoul

IPMU Tokyo, Queen Mary London, DAMTP-2013, Prague, York, Cavendish, Southhampton, NTU-Taiwan, Hsinchu-Taiwan, Tours, Durham, Imperial London, DAMTP-2011, MPI-Munchen, KIAS-Seoul, Ehwa-Seoul, SNU-Seoul, SKKU-Suwon, UOS-Seoul, Sogang-Seoul.

Talk is based on

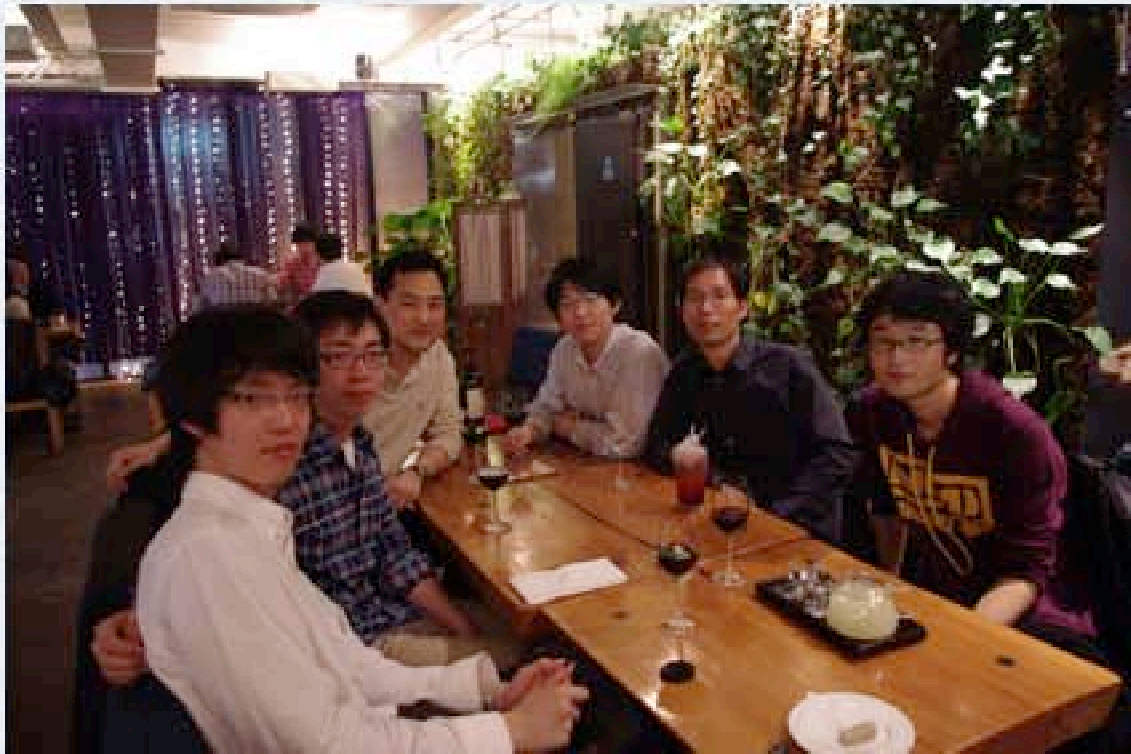
1. *Thermodynamic instability and first-order phase transition in an ideal Bose gas*
   Phys. Rev. A 81, 063636 (2010) with Sang-Woo Kim

2. *Existence of a critical point in the phase diagram of ideal relativistic neutral Bose Gas*
   New J. Phys. 13, 033003 (2011) with Sang-Woo Kim

3. *Isobar of an ideal Bose gas within the grand canonical ensemble*
   Phys. Rev. A 84, 023636 (2011) with Imtak Jeon and Sang-Woo Kim

4. *How many is different? Answer from ideal Bose gas*
   Conference Proceeding, arXiv:1310.5580

5. *Work in progress* with Wonyoung Cho



Organization of the talk

I. General Analysis

II. Ideal Bose Gas

- Canonical ensemble $Z_N(T,V)$
- Grand Canonical Ensemble $Z(T,V,z)$

III. Discussion

Emergence :

* Quantitative increase leads to Qualitative change.

* The whole is greater than the sum of its part.

* Key idea in condensed matter / statistical physics.

``More Is Different" Anderson (Science, 1972)

Question is .....

How Many is Different ?

In statistical physics

- Key quantity is partition function,

$$Z = \mathrm{Tr}\left(e^{-\beta H}\right) \qquad \beta = (k_{\mathrm{B}} T)^{-1}$$

- Physical quantities are typically given by the fractions

$$\frac{\partial Z}{Z} \qquad \frac{\partial^2 Z}{Z}$$

- They are finite/analytic for a finite system.

  No singularity arises ! $e.g.$ $C_V << \infty$

- Thermodynamic limit:

$$N \longrightarrow \infty \qquad V \longrightarrow \infty \qquad N/V \equiv \text{fixed}$$

In this limit, singularity may appear and a first-order or discrete phase transition can be realized.

* *It seems that ...*

only infinity system can feature singularity ! ?

``More is the Same: infinitely more is Different"

Kadanoff 2009

However, our daily experiences seem to suggest

Finite systems feature first-order phase transitions

: Boiling water

* In fact, at the Van der Waals memorial meeting in 1937, the audience could not agree on the question, whether partition function for a finite system could or could not explain a sharp phase transition. So the chairman of the session, Kramers, put it to a vote !

- Despite the above old controversies, these days statistical physics has become a branch of mathematics, and phase transitions are `defined' only for infinite systems.

How many is Different ?

- Infinity (conventional answer):

There is No critical finite size for 1st-order phase transition. Needs to take the Thermodynamic Limit.

- The present talk aims to deliver an alternative definite answer, like $N = 7616$

Canonical Ensemble

- Our primary interest lies on a system with definite number of particles, N, in a finite volume, V, in contact with heat reservoir.

- We wish to study the precise dependence on N.

- The key quantity is **canonical partition function,**

$$Z_N(T, V)$$

- All the physical quantities are functions of T, V

  For example, **pressure**:

$$P(T, V) = k_{\rm B} T \partial_V \ln Z_N(T, V)$$

- Spinodal curve is defined by

$$\partial_V P(T,V) = 0$$

- It is the boundary between stable and unstable regions [Huang] :

$$\partial_V P(T,V) < 0 \quad \text{and} \quad \partial_V P(T,V) > 0$$

- Moreover, if it exists, the spinodal curve amounts to a discrete phase transition under constant pressure, as we see shortly.

- This will reveal a novel mechanism how a finite system can manifest genuine mathematical singularities without taking the thermodynamic limit.

For $P(T, V)$, chain rule gives

$$\mathrm{d}P = (\partial_T P)\mathrm{d}T + (\partial_V P)\mathrm{d}V \,.$$

Hence, on isobar:

$$\mathrm{d}P = 0 \,,$$

the volume changes as

$$\left.\frac{\mathrm{d}V}{\mathrm{d}T}\right|_P = -\frac{\partial_T P(T, V)}{\partial_V P(T, V)} \,.$$

This expression can be substituted into

$$\left.\frac{\partial}{\partial T}\right|_P = \left.\frac{\partial}{\partial T}\right|_V + \left.\frac{\mathrm{d}V}{\mathrm{d}T}\right|_P \left.\frac{\partial}{\partial V}\right|_T \,.$$

- The temperature derivative at fixed pressure acting on an arbitrary function of T & V :

$$\left.\frac{\partial}{\partial T}\right|_P = \left.\frac{\partial}{\partial T}\right|_V - \left[\frac{\partial_T P(T,V)}{\partial_V P(T,V)}\right] \left.\frac{\partial}{\partial V}\right|_T$$

- On the spinodal curve it diverges !

- The previous `no-go' argument against the singularity from a finite system assumes the volume to be fixed.

- Instead, if we fix the pressure, a singularity may occur.

- Physically, if we fill a rigid box with water to full capacity and heat the box, the temperature will increase but hardly the water evaporates.

- However, opening the lid will set the pressure as constant (1 atm), and the water will surely start to boil at 100 degree Celsius.

It is hard to boil water if we keep the volume (or density) fixed, whereas it becomes easy under constant pressure!

No need to take the thermodynamic limit!

That is to say, for a finite system, C_V is finite never diverges, but C_P may become singular,

$$C_V << \infty \qquad \text{vs.} \qquad C_P = \infty$$

- Since we know the source of the singularity,

$$\left.\frac{\partial}{\partial T}\right|_P = \left.\frac{\partial}{\partial T}\right|_V - \left[\frac{\partial_T P(T,V)}{\partial_V P(T,V)}\right] \left.\frac{\partial}{\partial V}\right|_T$$

we can easily obtain the exponents of the singularities, considering

$$\partial_V P(T_*, V_*) = 0 \iff \partial_V T(P_*, V_*) = 0$$

such that

$$T(P_*, V) - T_* = \tfrac{1}{2}(V - V_*)^2 \partial_V^2 T(P_*, V_*) + \text{higher orders}$$

and

$$V/V_* - 1 \sim |T/T_* - 1|^\beta, \qquad \beta = \tfrac{1}{2}$$

$$\left.\frac{\mathrm{d}V}{\mathrm{d}T}\right|_P \sim |T/T_* - 1|^{-1/2}$$

Universal Exponents on Isobars :

- Isobar crossing the spinodal curve (superheating/cooling), the singularity has the exponent, **1/2** ,

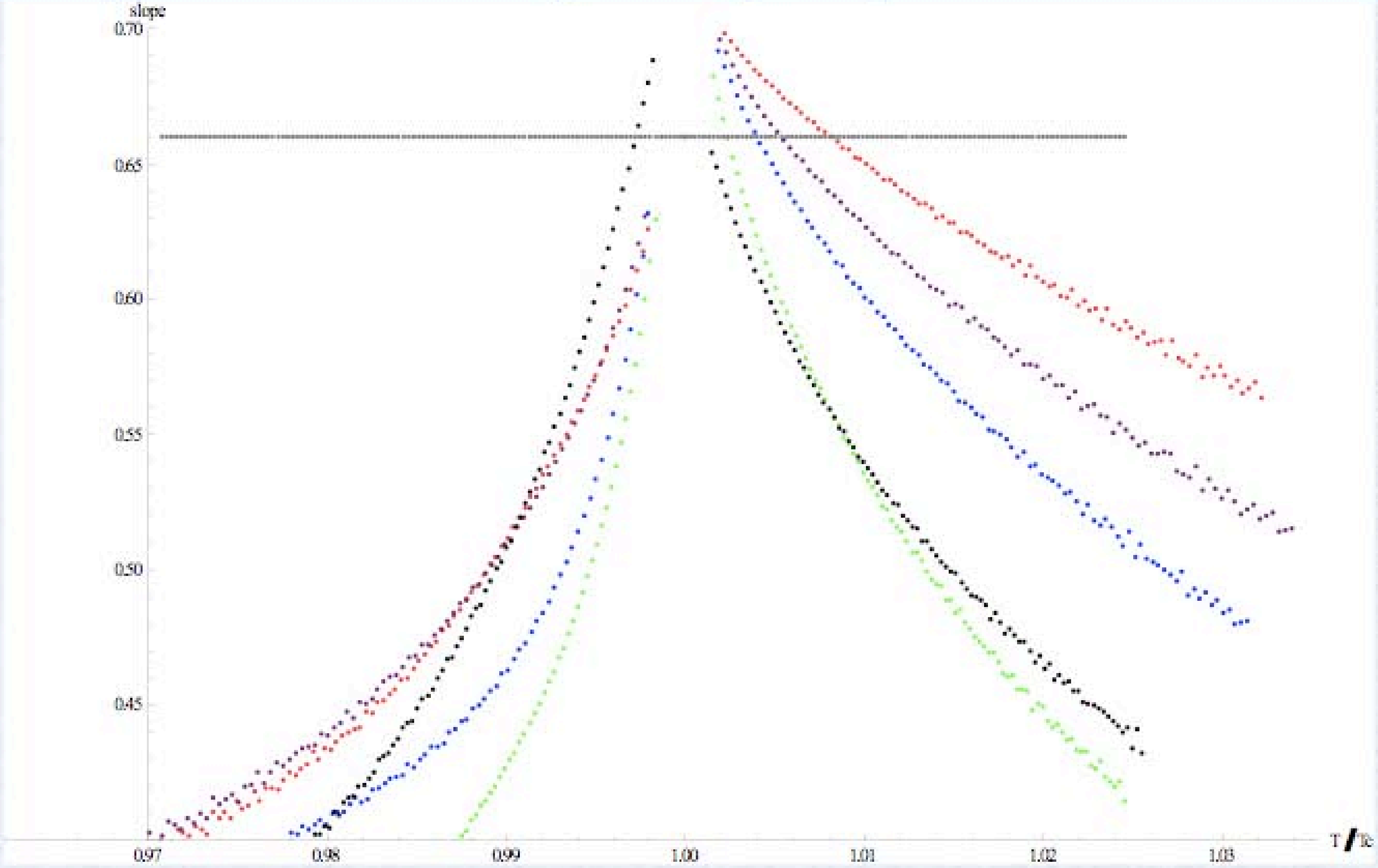
$$C_P \sim |T/T_* - 1|^{-1/2}$$

- Isobar touching the spinodal curve (critical point), the singularity has the exponent, **2/3** ,

$$C_P \sim |T/T_c - 1|^{-2/3}$$

NIST Data

Critical point for Liquid-gas phase transition



Red line = Carbon dioxide
Green line = Propane
Blue line = Ethane
Purple line = Ethene
Black line = Propene

x−axis : $\frac{T}{T_c}$ rescaled , y−axis : slope $= -\frac{\ln(C_{p\,n+1}) - \ln(C_{p\,n})}{\ln(|T_{n+1} - T_c|) - \ln(|T_n - T_c|)}$

Our Main Point Nr. 1

- ✓ The usual finiteness of a canonical ensemble is for the case of keeping the volume fixed.

- ✓ Once we switch to the alternative constraint of keeping the pressure constant, discrete phase transition featuring mathematical singularities may arise from a system with finite number of physical degrees.

The real question is then ...

the existence of the spinodal curve :

$$\partial_V P(T,V) = 0$$

* Note its expression :

$$\partial_V P = \beta\langle\, (\partial_V E - \langle \partial_V E \rangle)^2 \,\rangle - \langle \partial_V^2 E \rangle$$

- Take van der Waals equation, as an *ad hoc* example,

$$[(P/P_c) + 3(V_c/V)^2][(V/V_c) - \tfrac{1}{3}] = \tfrac{8}{3}(T/T_c)$$

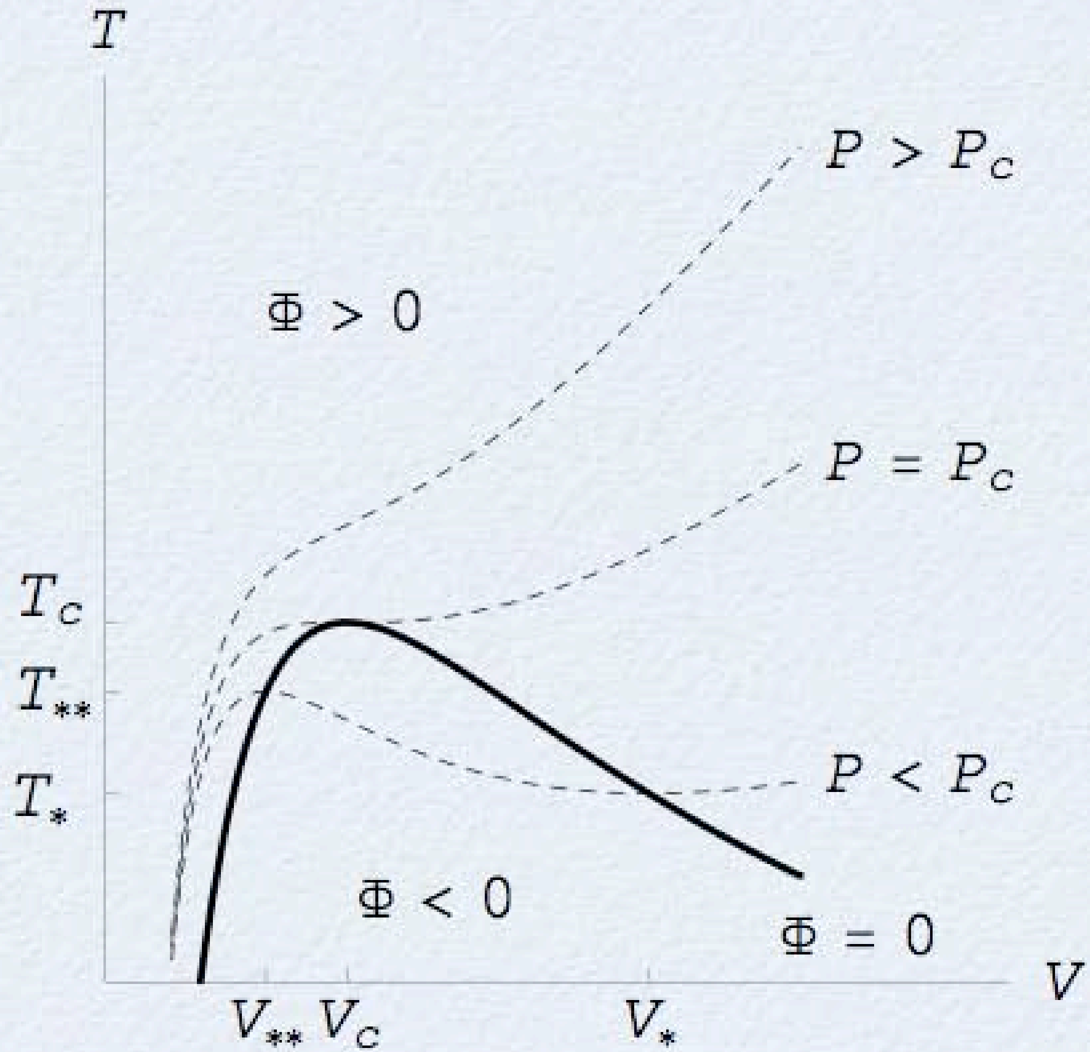


Figure 1: **Van der Waals equation of state**

The dashed lines are constant pressure lines of three different values, and the thick solid line is the spinodal curve satisfying $\Phi = -\partial_V P(T,V) = 0$. When $P < P_c$ the constant pressure line crosses the spinodal curve twice, at the supercooling point (V_*, T_*) and at the superheating point (V_{**}, T_{**}). Between the two temperatures the volume is triple valued. If $P = P_c$ the constant pressure line comes in contact with the spinodal curve only once at the critical point (V_c, T_c). Otherwise, *i.e.* $P > P_c$, the constant pressure line does not undergo thermodynamic instability and hence no first-order phase transition arises. On the spinodal curve the critical point has the highest temperature.

Back to the primary question:

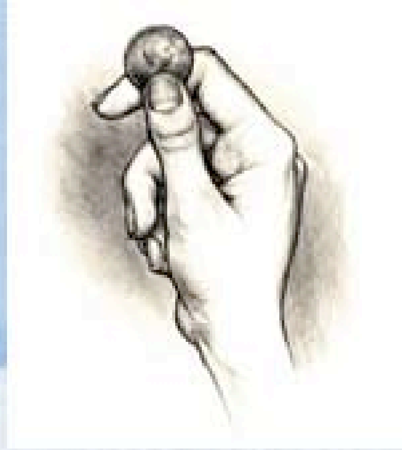
the existence of the spinodal curve,

$$\partial_V P(T,V) = 0 \quad ?$$

Our Main Point Nr. 2

The spinodal curve may originate from the identical nature of particles.

Flipping identical bosonic coins



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The probability is $$\frac{1}{N+1}$$

cf. distinguishable coins: $$\frac{1}{2^N}$$

Ideal Bose Gas

- When a single particle system is completely solvable, each quantum state is uniquely specified by a set of good quantum numbers, $\vec{n}$.

- With the corresponding energy eigenvalue $E_{\vec{n}}$ we define for each positive integer a ,

$$\lambda_a := \sum_{\vec{n}} e^{-a\beta E_{\vec{n}}}$$

If a=1, it amounts to single particle partition function.

- The volume dependence is inside the energy eigenvalues.

Ideal Bose Gas

- From Grand Canonical Partition Function:

$$\mathcal{Z} = \prod_{\vec{n}} \left(1 - \eta e^{-\beta E_{\vec{n}}}\right)^{-1} = \sum_N Z_N \, \eta^N$$

one can read off the Canonical Partition Function.

* But, No compact expression exists.

Three Equivalent Expressions for Canonical Partition Function

1. Matsubara-Feynman

$$Z_N = \sum_{m_a} \prod_{a=1}^{N} (\lambda_a)^{m_a} / (m_a!\, a^{m_a})$$

where the sum is over all the partitions of N, given by non-negative integers m_a with $a = 1, 2, \cdots, N$ satisfying $N = \sum_{a=1}^{N} a\, m_a$.

However, according to the Hardy-Ramanujan's estimation, the number of possible partitions grows exponentially, $e^{\pi\sqrt{2N/3}}/(4\sqrt{3}N)$, and this makes numerical computation practically hard.

Three Equivalent Expressions for Canonical Partition Function

2. Recurrence relation by Landsberg

$$Z_N = \left(\sum_{k=1}^{N} \lambda_k Z_{N-k}\right) / N$$

N^2 order computation

Three Equivalent Expressions for Canonical Partition Function

3. New formula:

$$Z_N = \det(\Omega_N)\,(Z_1)^N/N!$$

where Ω_N is an almost triangularized $N \times N$ matrix of which the entries are defined by

$$\Omega_N[a,b] := \begin{cases} \lambda_{a-b+1}/\lambda_1 & \text{for} \quad b \leq a \\ -a/\lambda_1 & \text{for} \quad b = a+1 \\ 0 & \text{otherwise}\,. \end{cases}$$

Three Equivalent Expressions for Canonical Partition Function

3. New formula:

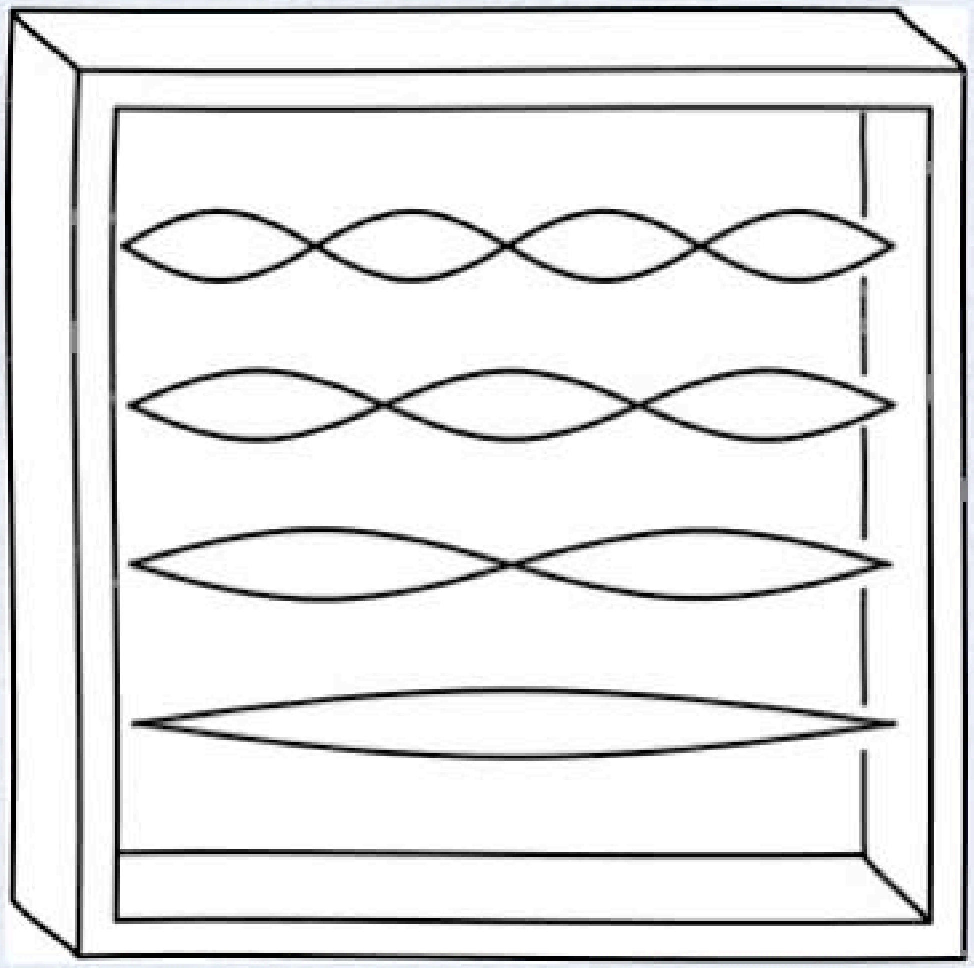
$$Z_N = \det(\Omega_N)\,(Z_1)^N/N!$$

Useful to see the conventional approximation,

$$Z_N \longrightarrow (Z_1)^N/N!$$

valid if all the particles occupied distinct states,
as in high temperature limit, $\det(\Omega_N) \to 1$.

Ideal Bose Gas confined in a Cubic Box



- Length: L
- Volume: $V = L^3$
- Momentum: $\vec{p} = \pi\hbar\vec{n}/L$

Dirichlet boundary condition sets $\vec{n} = (n_1, n_2, n_3)$ to be positive integer valued.

Ideal Bose Gas confined in a Cubic Box

Define dimensionless volume,

$$\mathcal{V} := (mc/\pi\hbar)^3\, V\,,$$

temperature,

$$\mathcal{T} := k_{\mathrm{B}}T/mc^2\,,$$

pressure,

$$\mathcal{P} := \left(\pi^3\hbar^3/m^4c^5\right)P = \mathcal{T}\partial_{\mathcal{V}}\ln Z_N(\mathcal{T},\mathcal{V})\,,$$

and for the spinodal curve,

$$\phi \;:= -(\mathcal{V}^2/N\mathcal{T})\,\partial_{\mathcal{V}}\mathcal{P}(\mathcal{T},\mathcal{V}) = -(1/N)\mathcal{V}^2\partial_{\mathcal{V}}^2\ln Z_N(\mathcal{T},\mathcal{V})\,.$$

Ideal Bose Gas confined in a Cubic Box

- Nonrelativistic gas:

$$e^{-\beta E_{\vec{n}}} = e^{-\vec{n}\cdot\vec{n}/2\mathcal{T}\mathcal{V}^{2/3}} ,$$

Thus,

$$Z_N(\mathcal{T}\mathcal{V}^{2/3}) \quad : \qquad \text{one-variable function} .$$

Jacobi θ_3 function:

$$\lambda_a(q) = \left[\sum_{n=1}^{\infty} q^{an^2}\right]^3 , \qquad q = e^{-1/(\mathcal{T}\mathcal{V}^{2/3})} .$$

Ideal Bose Gas confined in a Cubic Box

- Nonrelativistic gas:

$$e^{-\beta E_{\vec{n}}} = e^{-\vec{n}\cdot\vec{n}/2\mathcal{T}\mathcal{V}^{2/3}} ,$$

Thus,

$$Z_N(\mathcal{T}\mathcal{V}^{2/3}) \quad : \quad \text{one-variable function} .$$

Useful to define two dimensionless temperatures:

$$\mathcal{T}_V := \mathcal{T}(\mathcal{V}/N)^{2/3} = k_{\mathrm{B}}T(V/N)^{2/3}(2m/\left(\pi^2\hbar^2\right)) ,$$

$$\mathcal{T}_P := k_{\mathrm{B}}TP^{-2/5}\left(2m/(\pi^2\hbar^2)\right)^{3/5} \quad : \quad \text{function of } \mathcal{T}_V .$$

• *Low temperature limit*, $\mathcal{T}_V = \mathcal{T}_P = 0$,

$$C_V = C_P = 0 \,, \qquad \phi = \infty \,, \qquad \langle N_0 \rangle = N \,.$$

and the volume reads at absolute zero,

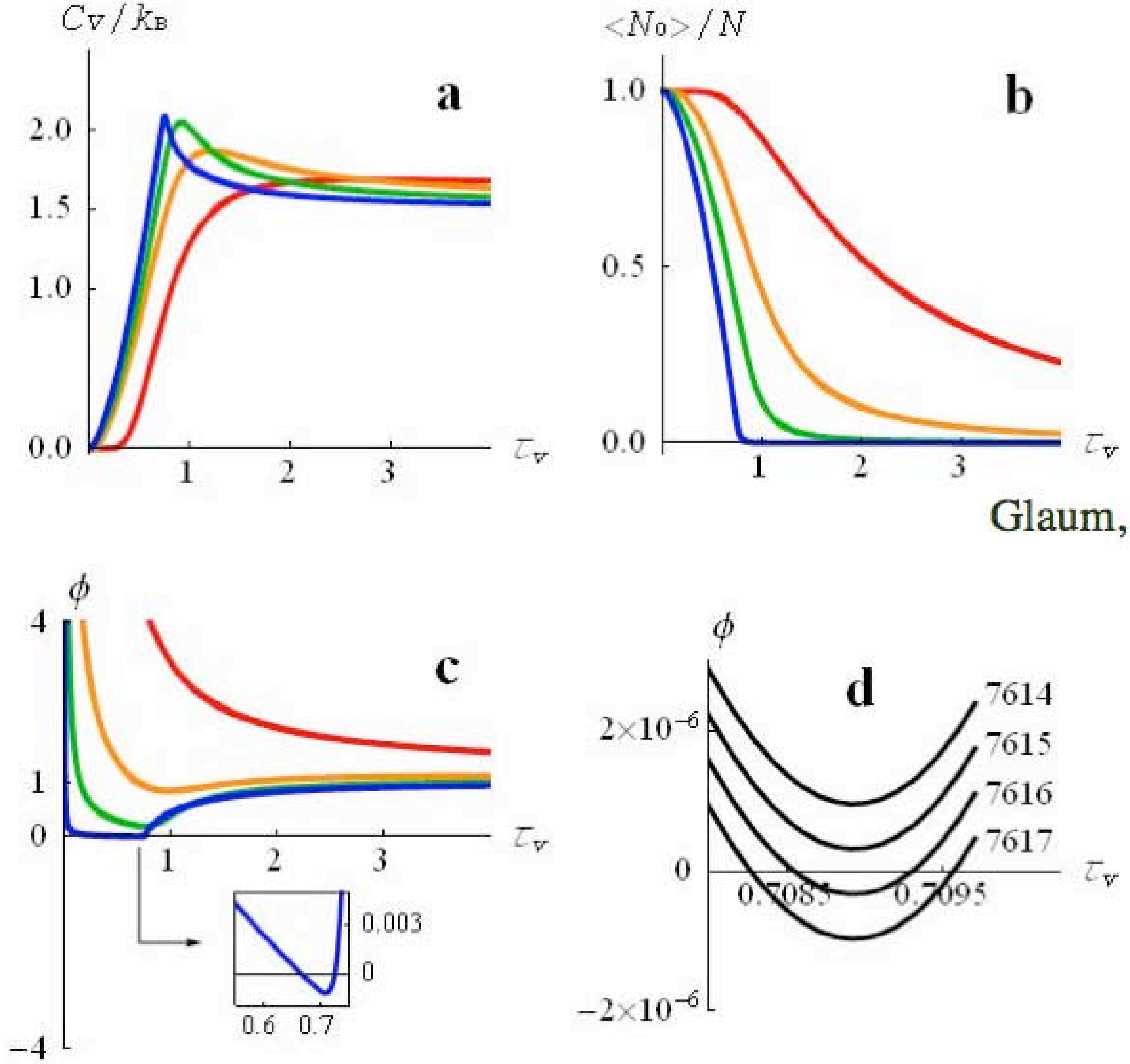
$$V = [N\pi^2\hbar^2/(mP)]^{2/5} \,.$$

This non-zero finiteness is due to the Heisenberg uncertainty principle.

• *High temperature limit*, $\mathcal{T}_V = \mathcal{T}_P = \infty$,

$$C_V/k_{\rm B} = 3/2 \,, \qquad C_P/k_{\rm B} = 5/2 \,, \qquad \phi = 1 \,, \qquad \langle N_0 \rangle = 0 \,, \qquad PV = Nk_{\rm B}T \,.$$

Constant volume curves

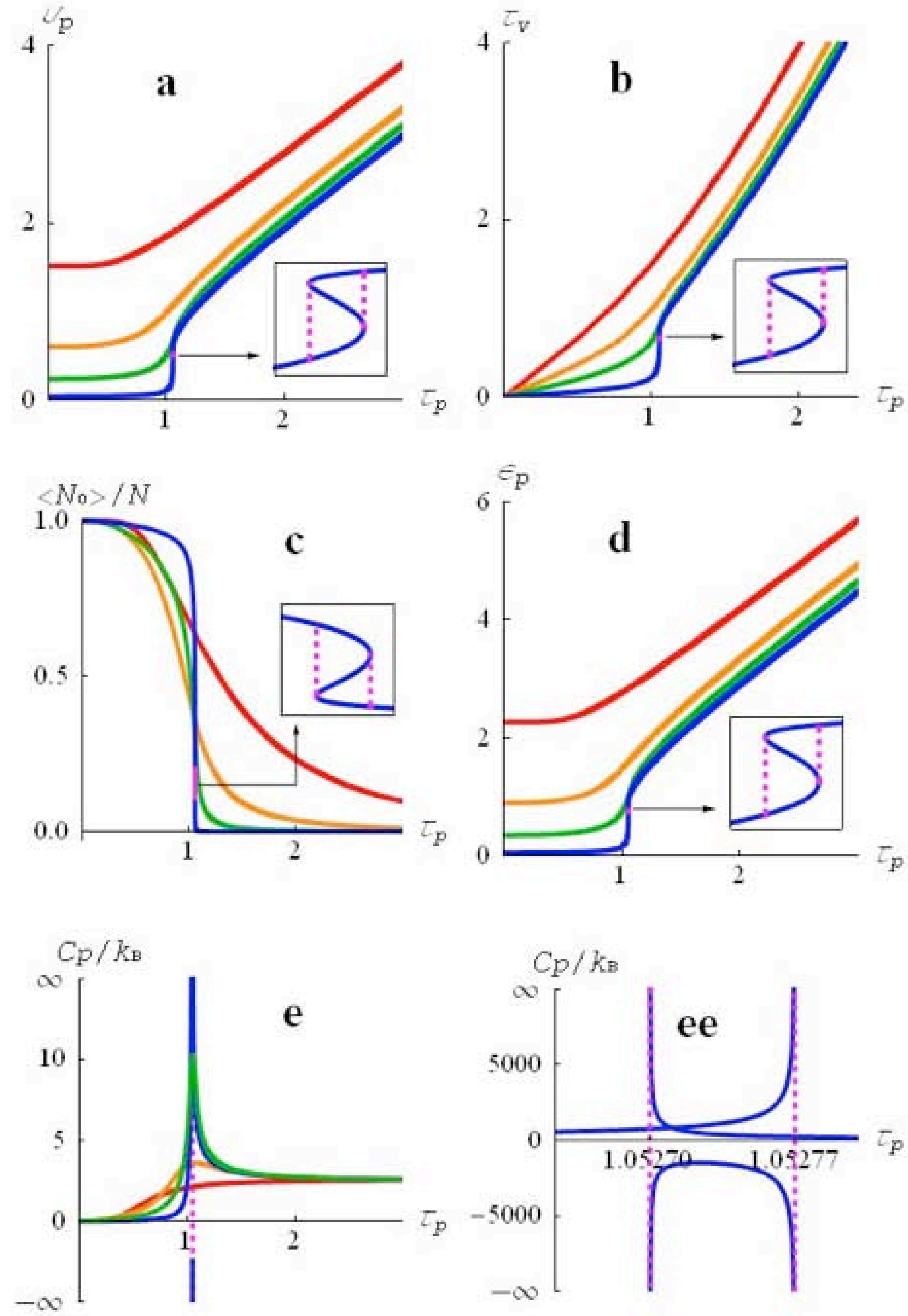


Glaum, Kleinert, Pelster 2007

N = 1, 10, 100, 10000

Constant pressure curves

N = 1, 10, 100, 10000



For $N \geq 7616$, all the physical quantities are triple-valued between the supercooling and the superheating points.

Spinodal curve emerges when $N \geq 7616$!

For $N = 7616$,

$$k_B T_{\rm supercool} \simeq 1.0543694113 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,,$$

$$k_B T_{\rm superheat} \simeq 1.0543694116 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,.$$

For $N = 10^4$,

$$k_B T_{\rm supercool} \simeq 1.05270 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,,$$

$$k_B T_{\rm superheat} \simeq 1.05277 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,.$$

For $N = 10^5$,

$$k_B T_{\rm supercool} \simeq 1.0410 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,,$$

$$k_B T_{\rm superheat} \simeq 1.0424 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,.$$

For $N = 10^6$,

$$k_B T_{\rm supercool} \simeq 1.034 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,,$$

$$k_B T_{\rm superheat} \simeq 1.036 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,.$$

cf. known BEC temperature in the thermodynamic limit:

$$k_B T_{\rm conti.\,approx.} = (\tfrac{2\pi\hbar^2}{m})^{3/5} [P/\zeta(\tfrac{5}{2})]^{2/5} \simeq 1.0278 \times (\tfrac{\pi^2\hbar^2}{2m})^{3/5} P^{2/5}\,.$$

Generalization to the Relativistic Gas

The Boltzmann factor assumes the form:

$$e^{-\beta E_{\vec{n}}} = \exp\Big(-\mathcal{T}^{-1}\sqrt{1+\vec{n}\cdot\vec{n}\,\mathcal{V}^{-2/d}}\,\Big).$$

Thus,

$$Z_N(\mathcal{T},\mathcal{V}) \quad : \quad \text{Two-variable function}$$

Generalization to the Relativistic Gas

- *Low temperature (non-relativistic) limit,* $\mathcal{T} \to 0$,

$$C_V = C_P = 0\,, \qquad \phi = \infty\,, \qquad \langle N_0 \rangle = N\,.$$

- *High temperature limit,* $\mathcal{T} = \infty$,

$$C_V/k_{\rm B} = 3\,, \qquad C_P/k_{\rm B} = 4\,, \qquad \phi = 1\,, \qquad \langle N_0 \rangle = 0\,, \qquad PV = Nk_{\rm B}T\,.$$

cf. Non-relativistic high temperature limit,

$$C_V/k_{\rm B} = 3/2\,, \qquad C_P/k_{\rm B} = 5/2\,, \qquad \phi = 1\,, \qquad \langle N_0 \rangle = 0\,, \qquad PV = Nk_{\rm B}T\,.$$

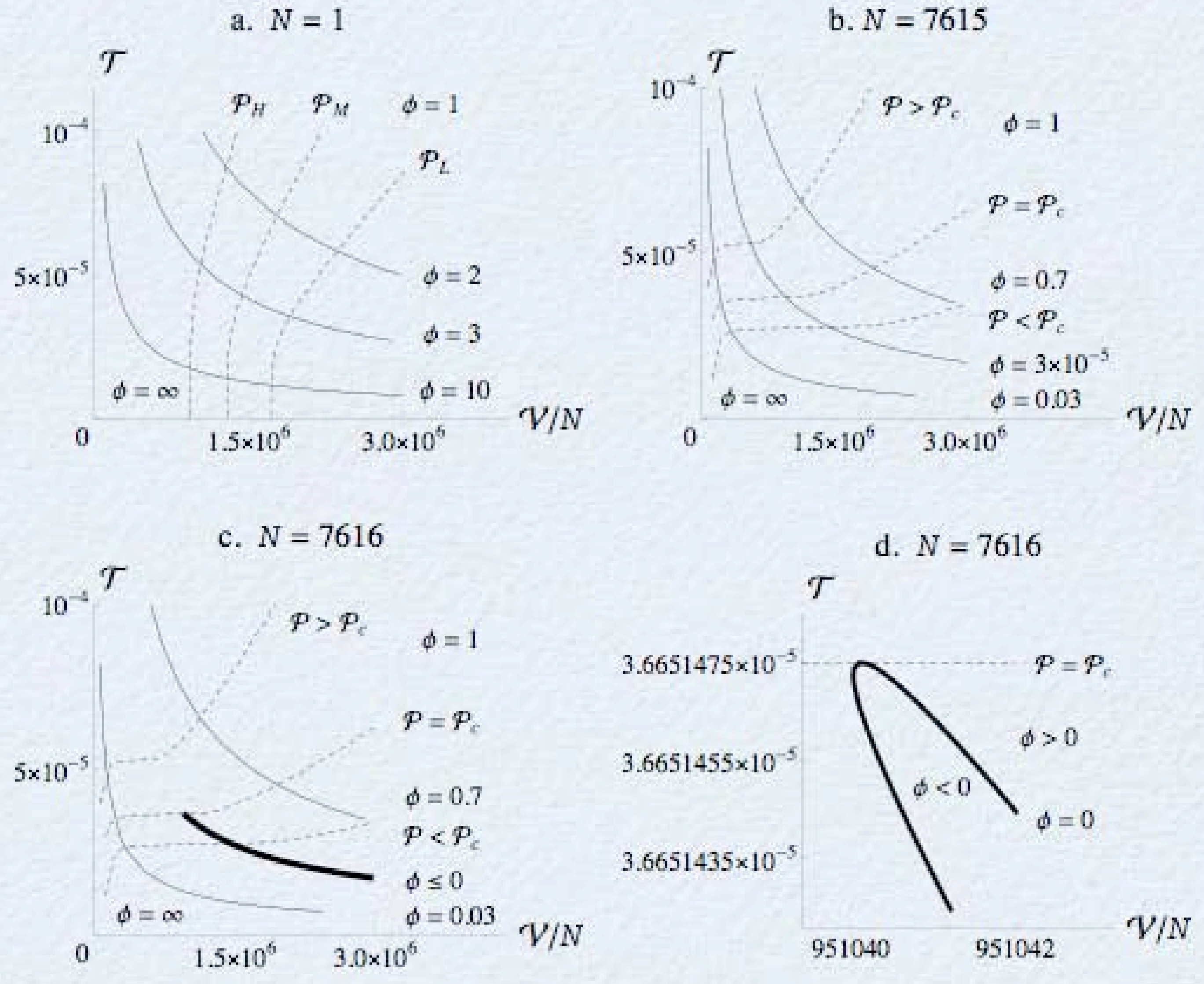


Figure 2: **Constant pressure lines and spinodal curve**
Dashed, thin solid or thick solid lines denote respectively the constant pressure, constant ϕ or spinodal curve. Near to the origin of the $(\mathcal{T}, \mathcal{V}/N)$ plane ϕ diverges and in the opposite infinite limit ϕ converges to unity. When $N = 1$ (Fig. **a** with $\mathcal{P}_L < \mathcal{P}_M < \mathcal{P}_H$), ϕ is monotonically decreasing from ∞ to 1 on arbitrary isobars. As N increases ϕ develops a valley whose height is less than unity. Moreover if $N \geq 7616$ the valley assumes negative values and a spinodal curve emerges. Fig. **d** magnifies the tip of the spinodal curve for $N = 7616$ to manifest a critical point $(\mathcal{T}_c, \mathcal{V}_c/N) = (3.6651475 \times 10^{-5}, 9.510401 \times 10^{5})$. In Fig. **b**, $\mathcal{P}_c$ denotes merely the numerical value, $\mathcal{P}_c = 2.0151967 \times 10^{-11}$, which amounts to the critical pressure in the system with one more particle, $N = 7616$.

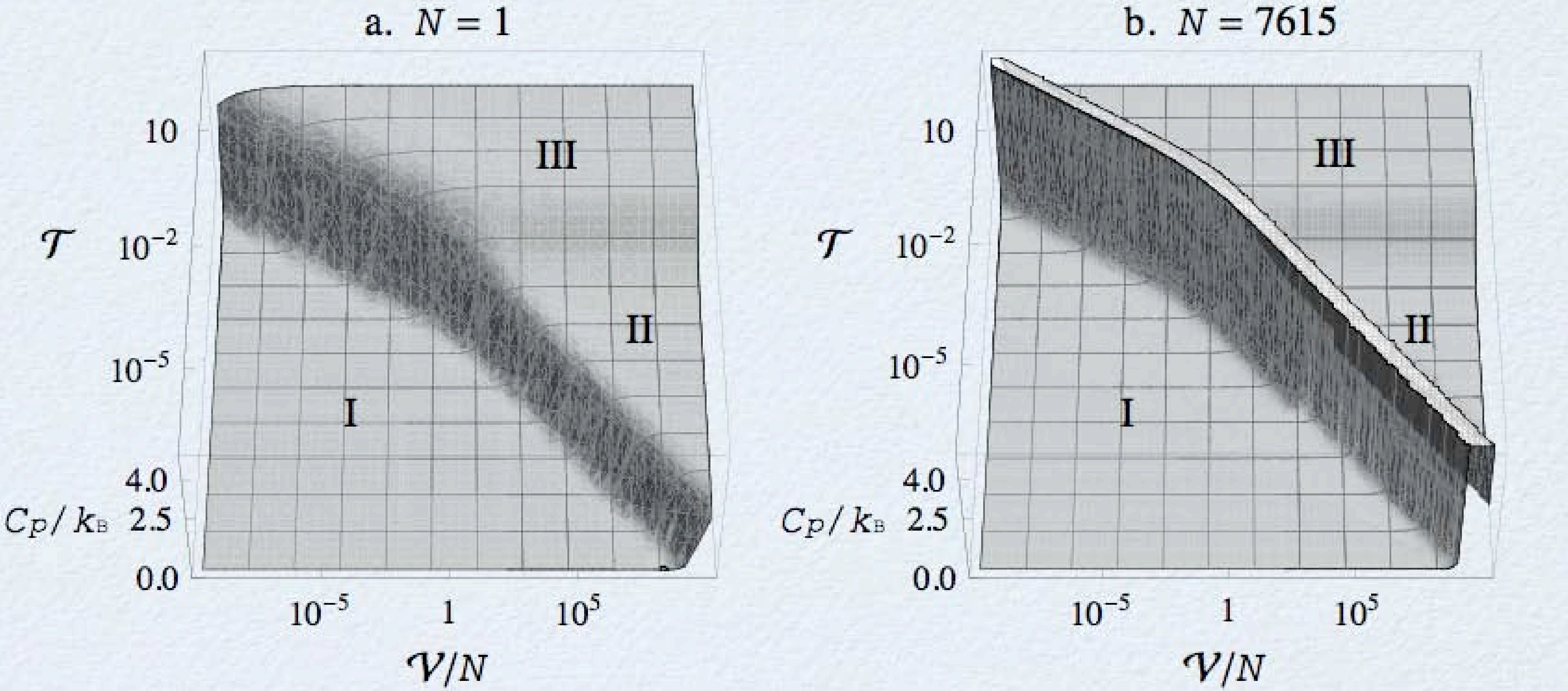


Figure 3: $3D$ **image of** C_P **on** $(\mathcal{T}, \mathcal{V}/N)$ **plane for** $N = 1$ **and** $N = 7615$
The plane decomposes into three parts: phase **I** with $C_P \simeq 0$, phase **II** with $C_P \simeq 2.5k_B$ and phase **III** with $C_P \simeq 4k_B$. When $N = 1$ the transitions are monotonic and smooth. As N grows, at the borders between **I** and **II** as well as between **I** and **III**, a range of peaks emerges which will eventually diverge for $N \geq 7616$. Fig. **b** has been cut at the height of $C_P = 5k_B$, and the actual peak rises up to $C_P \simeq 5.33684 \times 10^6 k_B$.

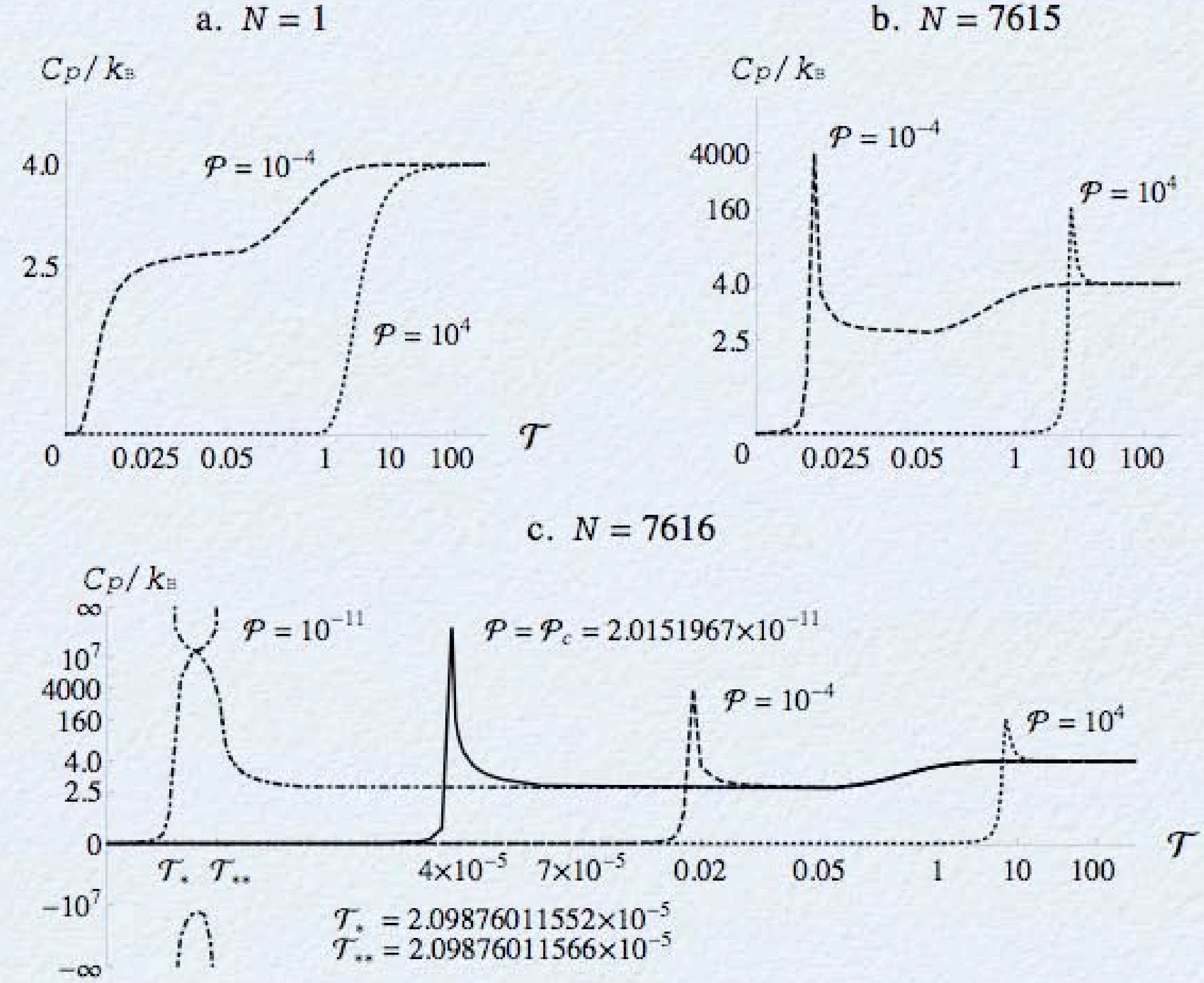


Figure 4: C_P **for various** N **and** $\mathcal{P}$

For $N = 1$, C_P is monotonically increasing from zero to $4k_B$ on any isobar. Under sufficiently low pressure, it assumes the intermediate value of $2.5k_B$ as in Eq.(44). As N increases, C_P develops a peak on each isobar. Especially when $N \geq 7616$ and $\mathcal{P} < \mathcal{P}_c$, it diverges both to the plus and minus infinities at the supercooling point $\mathcal{T} = \mathcal{T}_*$ as well as at the superheating point $\mathcal{T} = \mathcal{T}_{**}$. At the critical point $\mathcal{T} = \mathcal{T}_c = 3.6651475 \times 10^{-5}$, it diverges only positively. For $\mathcal{P} > \mathcal{P}_c$, the specific heat features a single finite peak which corresponds to the Widom line [10, 11]. **G. G. Simeoni *et al.* + P. F. McMillan and H. E. Stanley Nature Phys. 2010**

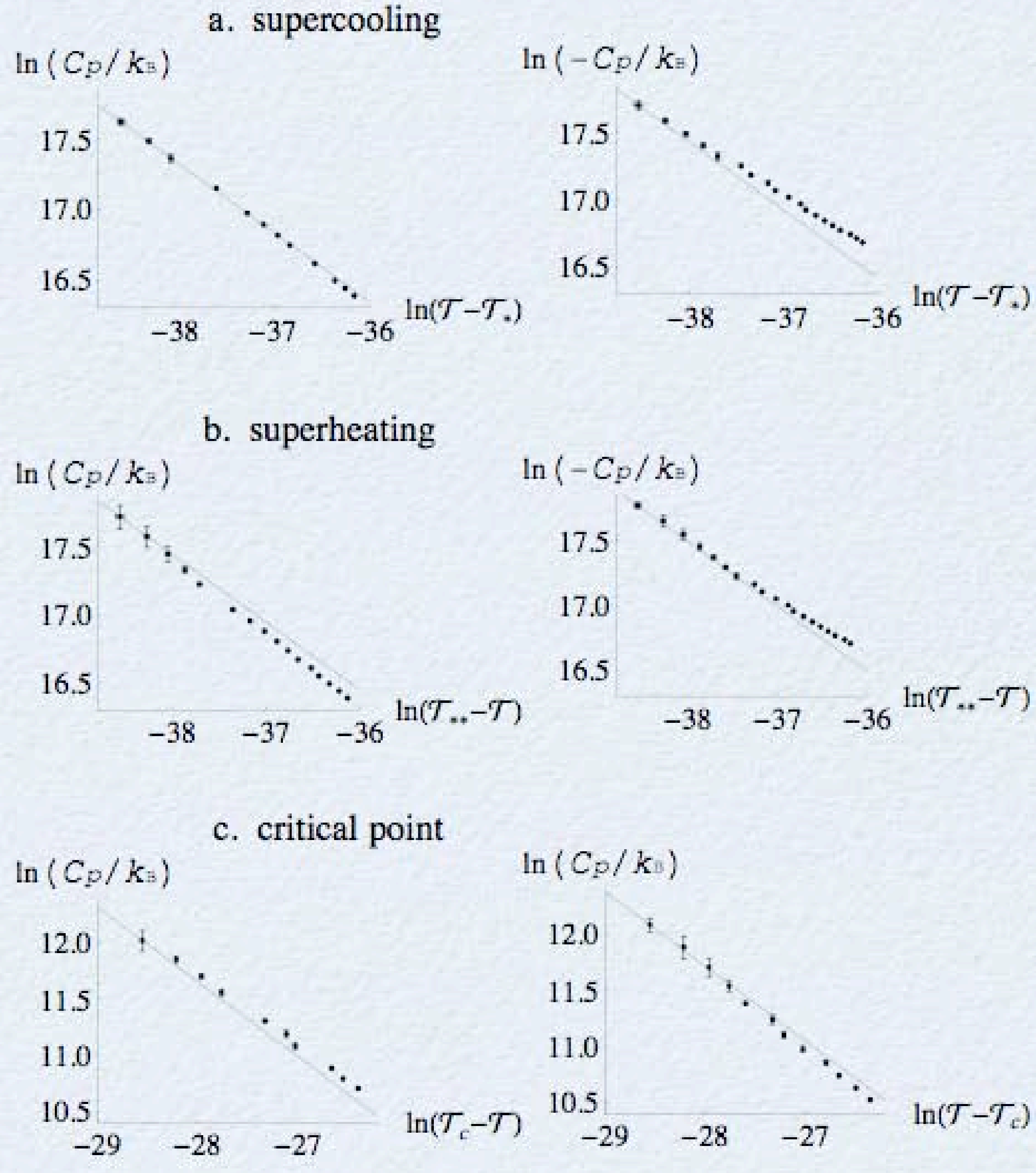


Figure 5: **Critical and noncritical exponents**

Our numerical data confirm the singular behavior of the specific heat C_P anticipated in Sec. 2.2: just above the supercooling point $C_P \sim \pm(\mathcal{T} - \mathcal{T}_*)^{-1/2}$ (Fig. **a**); just below the superheating point $C_P \sim \pm(\mathcal{T}_{**} - \mathcal{T})^{-1/2}$ (Fig. **b**); and around the critical point $C_P \sim |\mathcal{T} - \mathcal{T}_c|^{-2/3}$ (Fig. **c**). The numerical data are for $N = 7616$, $\mathcal{P} = 5.00017005640 \times 10^{-12}$ or $\mathcal{P}_c = 2.0151967 \times 10^{-11}$ such that the error bars are due to the numerical errors maintaining the pressure. The straight lines correspond to the theoretical slopes, $-1/2$ or $-2/3$.

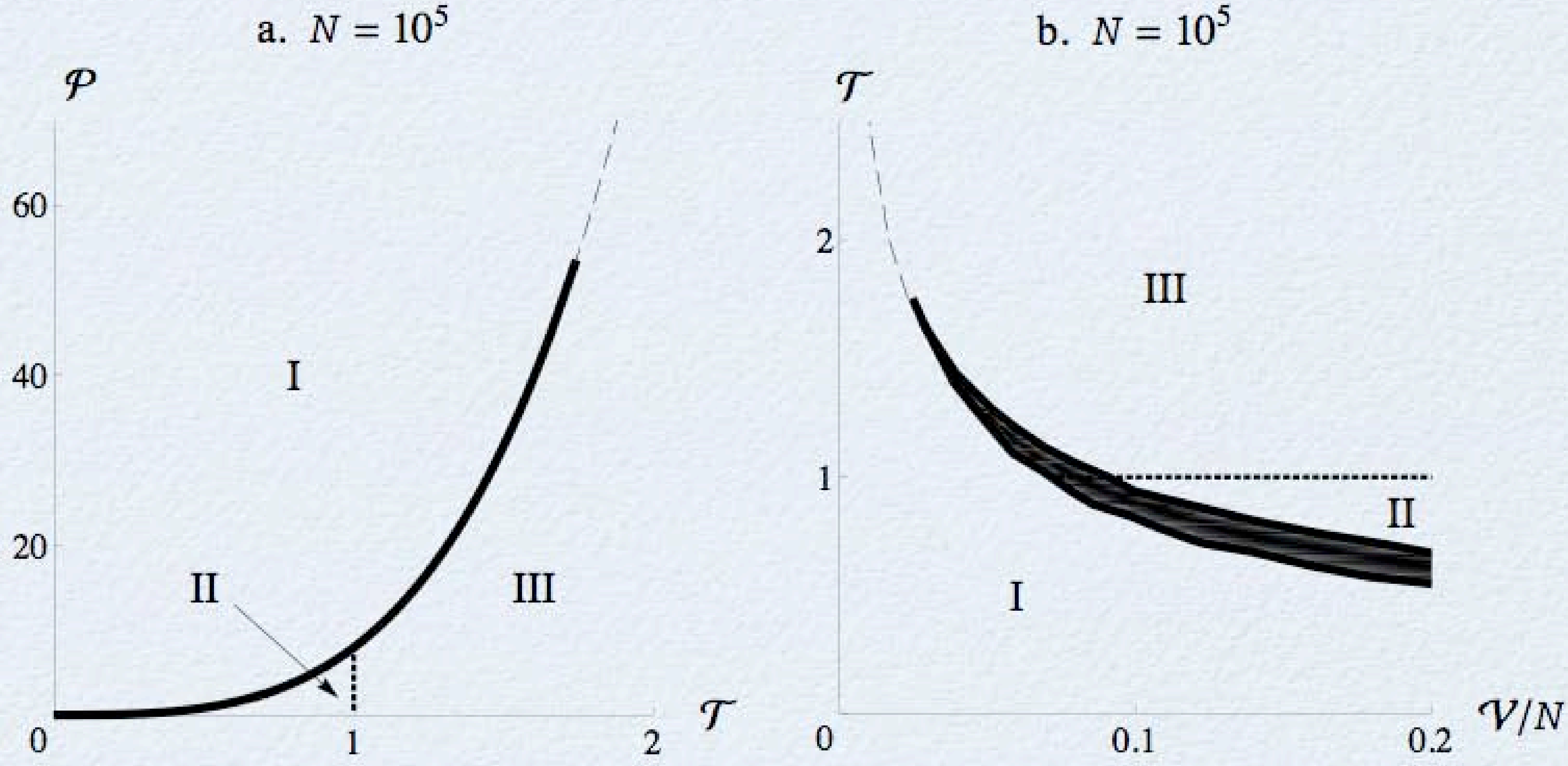


Figure 6: **Phase diagram for $N = 10^5$ on $(\mathcal{P}, \mathcal{T})$ and $(\mathcal{T}, \mathcal{V}/N)$ planes** Thick solid line, dashed line and dotted line correspond to the spinodal curve (including its inside), the Widom line (a range of finite peaks in C_P which also coincides with the valley of ϕ) and the $\mathcal{T} \simeq 1$ line respectively. The lines divide the phase diagram into three parts: phase **I** of $C_P \simeq 0$, phase **II** of $C_P \simeq 2.5k_\mathrm{B}$ and phase **III** of $C_P \simeq 4k_\mathrm{B}$. On the top of the solid line, there exists a critical point. As N increases, the critical point moves toward more ultra-relativistic, higher temperature region along the Widom line keeping $\mathcal{T}_c(\mathcal{V}_c/N)^{1/3}$ and $\mathcal{T}_c\mathcal{P}_c^{-1/4}$ constant.

Three Phases of Ideal Relativistic Bose Gas

- Phase **I**: *condensate* with $C_p \simeq 0$,

$$\Big\{ (\mathcal{T}, \mathcal{V}/N) \ \Big| \ \mathcal{T} \lesssim (N/\mathcal{V})^{1/3} \ \text{ and } \ \mathcal{T} \lesssim (N/\mathcal{V})^{2/3} \Big\}.$$

- Phase **II**: *non-relativistic gas* with $C_p \simeq 2.5 k_{\mathrm{B}}$,

$$\Big\{ (\mathcal{T}, \mathcal{V}/N) \ \Big| \ \mathcal{T} \lesssim 1 \ \text{ and } \ \mathcal{T} \gtrsim (N/\mathcal{V})^{2/3} \Big\}.$$

- Phase **III**: *ultra-relativistic gas* with $C_p \simeq 4 k_{\mathrm{B}}$,

$$\Big\{ (\mathcal{T}, \mathcal{V}/N) \ \Big| \ \mathcal{T} \gtrsim (N/\mathcal{V})^{1/3} \ \text{ and } \ \mathcal{T} \gtrsim 1 \Big\}.$$

Equivalently,

- Condensate phase **I**, $\Big\{ (\mathcal{P}, \mathcal{T}) \ \Big| \ \mathcal{T} \lesssim \mathcal{P}^{2/5} \ \text{ and } \ \mathcal{T} \lesssim \mathcal{P}^{1/4} \Big\}.$
- Non-relativistic gas phase **II**, $\Big\{ (\mathcal{P}, \mathcal{T}) \ \Big| \ \mathcal{T} \gtrsim \mathcal{P}^{2/5} \ \text{ and } \ \mathcal{T} \lesssim 1 \Big\}.$
- Ultra-relativistic gas phase **III**, $\Big\{ (\mathcal{P}, \mathcal{T}) \ \Big| \ \mathcal{T} \gtrsim \mathcal{P}^{1/4} \ \text{ and } \ \mathcal{T} \gtrsim 1 \Big\}.$

Grand Canonical Ensemble

Recall the Grand Canonical Partition Function of the ideal Bose gas,

$$\ln \mathcal{Z}(\varepsilon, \sigma) = -\sum_{\vec{n}\in\mathbb{N}^3} \ln\left(1 - e^{-\varepsilon \vec{n}^2 - \sigma}\right) .$$

$$\varepsilon := \frac{\pi^2 \hbar^2}{2 m k_{\mathrm{B}}} \left(T V^{2/3}\right)^{-1} , \qquad \sigma := -\ln z .$$

$$N(\varepsilon,\sigma) = -\partial_\sigma \ln \mathcal{Z}(\varepsilon,\sigma)\,,$$

$$\mathcal{T}_P(\varepsilon,\sigma) := \left(\tfrac{2m}{\pi^2\hbar^2}\right)^{\frac{3}{5}} k_{\mathrm{B}} T P^{-\frac{2}{5}} = \left[-\tfrac{2}{3}\varepsilon^{\frac{5}{2}}\partial_\varepsilon \ln \mathcal{Z}(\varepsilon,\sigma)\right]^{-\frac{2}{5}}$$

$$\mathcal{V}_P(\varepsilon,\sigma) := \left(\tfrac{2m}{\pi^2\hbar^2} P\right)^{\frac{3}{5}} V = \left[-\tfrac{2}{3}\partial_\varepsilon \ln \mathcal{Z}(\varepsilon,\sigma)\right]^{\frac{3}{5}}$$

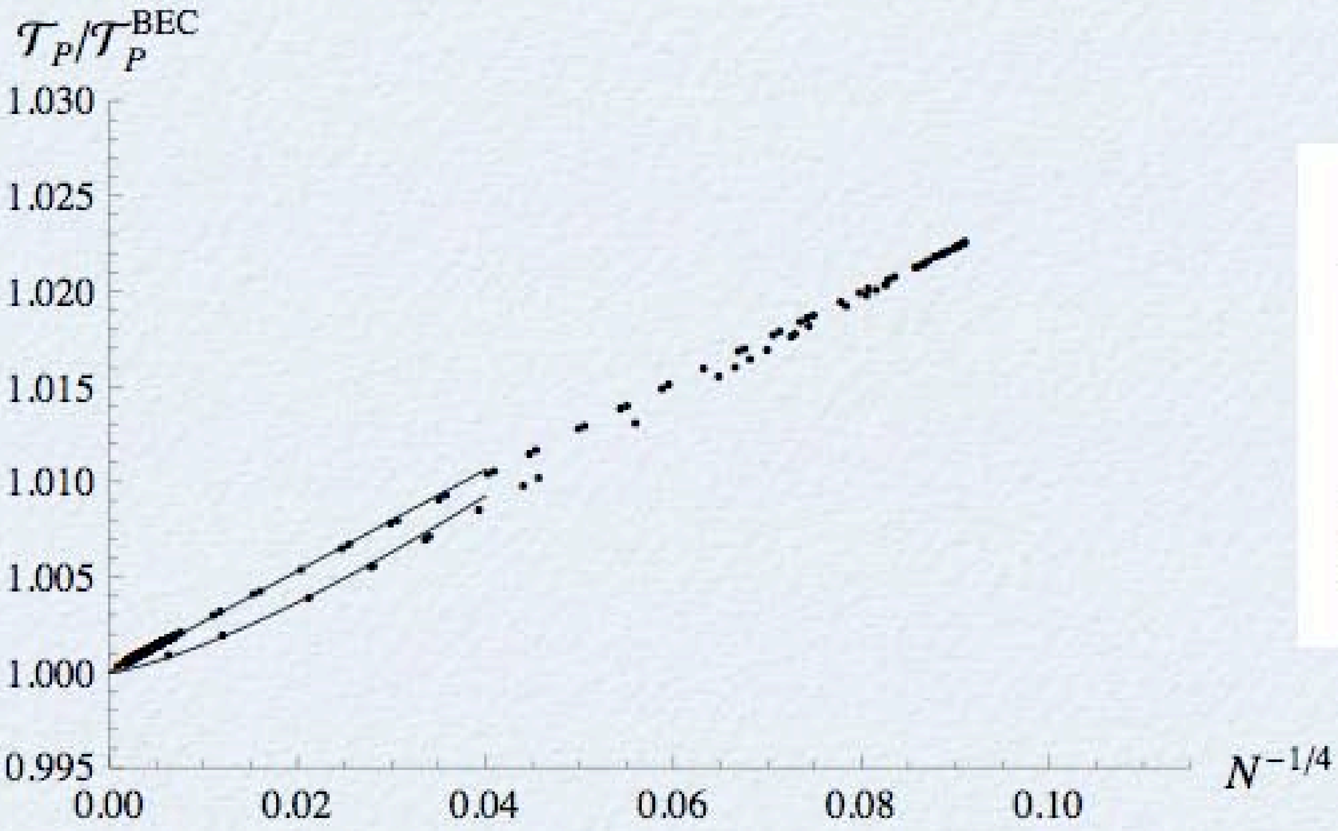


FIG. 1: The supercooling and the superheating spinodal curves on the $(N^{-1/4}, \mathcal{T}_P/\mathcal{T}_P^{\mathrm{BEC}})$-plane (lower and upper curves respectively). The dotted curves are from the numerical computations based on the exact formulae. The solid lines correspond to our analytic approximation for large N. A pair of spinodal curves start to develop at $N = N_c \simeq 14392.4$ ($N_c^{-1/4} \simeq 0.0912991$) which is comparable to the critical number, 7616 from the canonical ensemble.

$(\mathcal{T}_P^{*}, \mathcal{T}_P^{**})$	Grand canonical	Canonical
$N = 10^5$	$(1.041, 1.043)$	$(1.0410, 1.0424)$
$N = 10^6$	$(1.0348, 1.0364)$	$(1.034, 1.036)$

TABLE I: Quantitative agreement between the canonical and the grand canonical results, within 0.1% error.

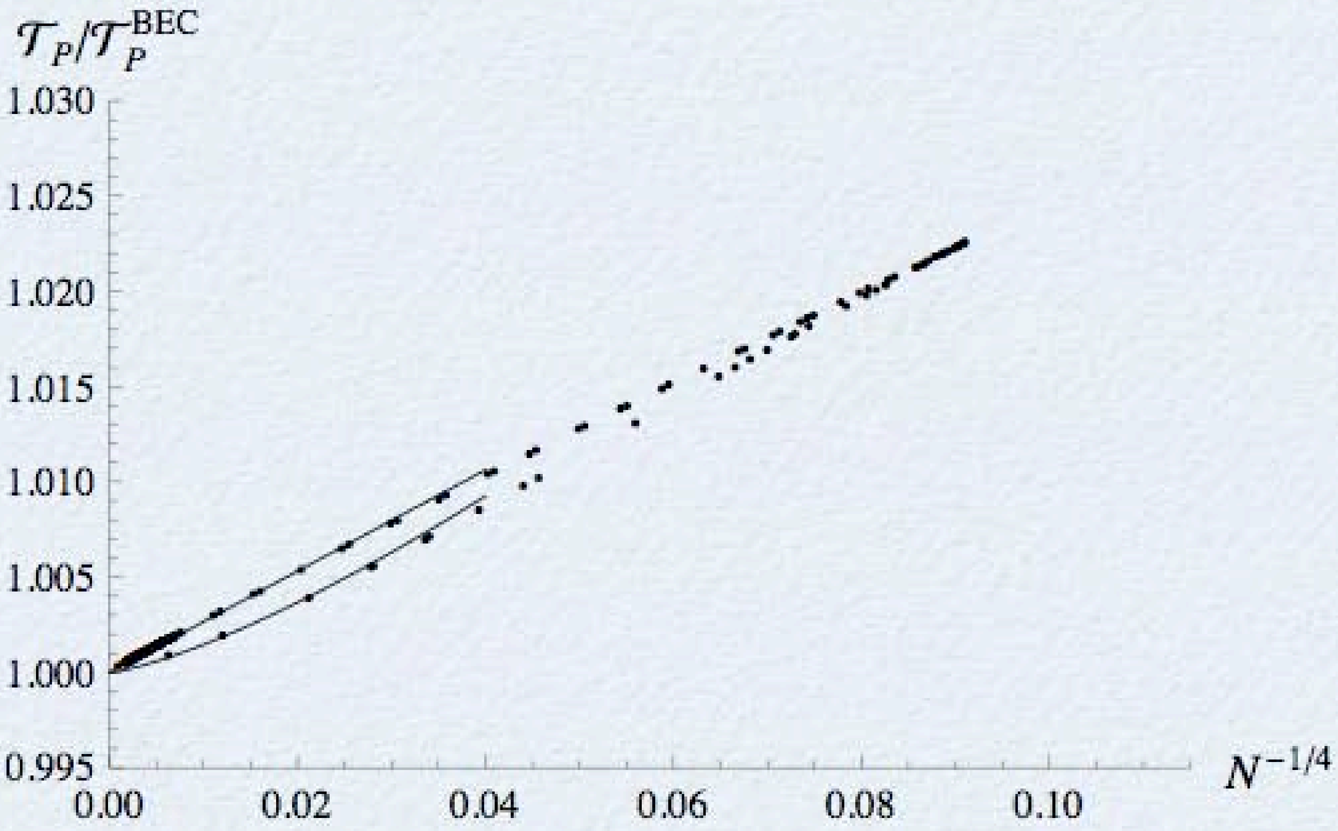


FIG. 1: The supercooling and the superheating spinodal curves on the $(N^{-1/4}, \mathcal{T}_P/\mathcal{T}_P^{\rm BEC})$-plane (lower and upper curves respectively). The dotted curves are from the numerical computations based on the exact formulae. The solid lines correspond to our analytic approximation for large N. A pair of spinodal curves start to develop at $N = N_{\rm c} \simeq 14392.4$ ($N_{\rm c}^{-1/4} \simeq 0.0912991$) which is comparable to the critical number, 7616 from the canonical ensemble.

$*$ *Supercooling spinodal curve*

$$\mathcal{T}_P^{*}/\mathcal{T}_P^{\rm BEC} \simeq 1 + \frac{\pi^3}{60}\left[\left(\mathcal{T}_P^{\rm BEC}\right)^5/\mathcal{T}_\rho^{\rm BEC}\right]^{\frac{1}{2}} N^{-\frac{1}{3}},$$

$$\mathcal{V}_P^{*} \simeq \left(\mathcal{T}_\rho^{\rm BEC}/\mathcal{T}_P^{\rm BEC}\right)^{\frac{3}{2}} \left(N + \frac{\pi}{4}\mathcal{T}_\rho^{\rm BEC} N^{\frac{2}{3}} \ln N\right),$$

$$\mathcal{T}_\rho^{*}/\mathcal{T}_\rho^{\rm BEC} \simeq 1 + \frac{\pi}{6}\mathcal{T}_\rho^{\rm BEC} N^{-\frac{1}{3}} \ln N.$$

$**$ *Superheating spinodal curve*

$$\mathcal{T}_P^{**}/\mathcal{T}_P^{\rm BEC} \simeq 1 + \frac{1}{150}\left(\frac{\pi^{15}}{15}\right)^{\frac{1}{4}} \left(\mathcal{T}_P^{\rm BEC}\right)^{\frac{5}{2}} N^{-\frac{1}{4}},$$

$$\mathcal{V}_P^{**} \simeq 8\left(\frac{15}{\pi^3}\right)^{\frac{3}{4}} \left(\mathcal{T}_P^{\rm BEC}\right)^{-\frac{3}{2}} N^{\frac{3}{4}},$$

$$\mathcal{T}_\rho^{**} \simeq 4\left(\frac{15}{\pi^3}\right)^{\frac{1}{2}} N^{-\frac{1}{6}}.$$

In the above, $\mathcal{T}_P^{\rm BEC}$ and $\mathcal{T}_\rho^{\rm BEC}$ denote two constants,

$$\mathcal{T}_P^{\rm BEC} = \left(\frac{64}{\pi^3}\right)^{\frac{1}{5}} \left[\zeta\left(\tfrac{5}{2}\right)\right]^{-\frac{2}{5}} \simeq 1.02781,$$

$$\mathcal{T}_\rho^{\rm BEC} = \frac{4}{\pi} \left[\zeta\left(\tfrac{3}{2}\right)\right]^{-\frac{2}{3}} \simeq 0.671253,$$

which correspond to the well-known Bose-Einstein condensation temperatures.

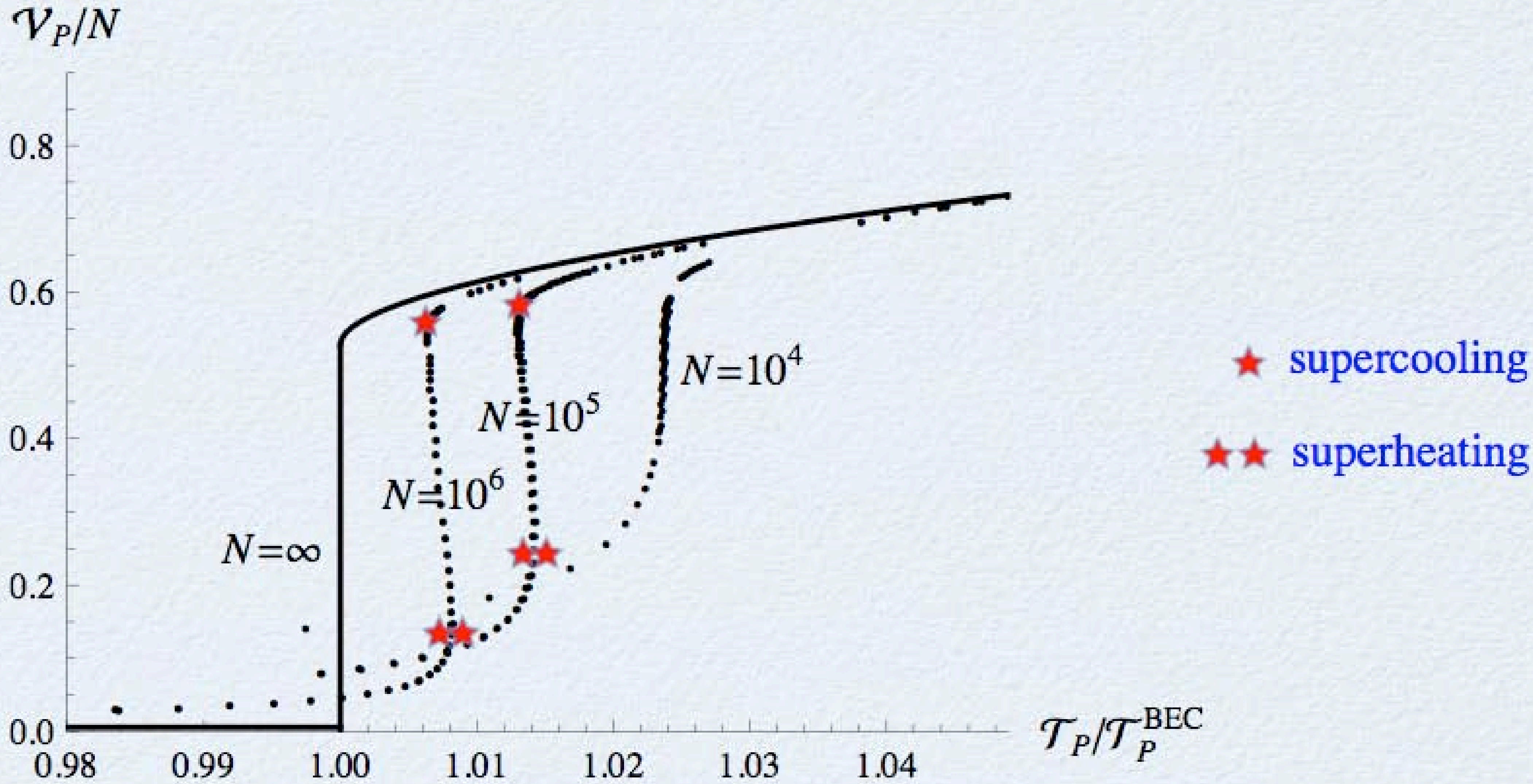


FIG. 2: Isobar curves on the $(\mathcal{T}_P/\mathcal{T}_P^{\mathrm{BEC}}, \mathcal{V}_P/N)$-plane. They zigzag featuring '$\mathcal{S}$-shape' if $14393 \leq N < \infty$.

- The ratio of the two volumes,

$$\mathcal{V}_P^*/\mathcal{V}_P^{**} \simeq \left(\tfrac{\pi}{15}\right)^{\frac{3}{4}} \left[\zeta(\tfrac{3}{2})\right]^{-1} N^{\frac{1}{4}} \simeq 0.118511 \times N^{\frac{1}{4}}\,,$$

enables us to estimate the discrete volume expansion rate at the liquid-gas type phase transition.

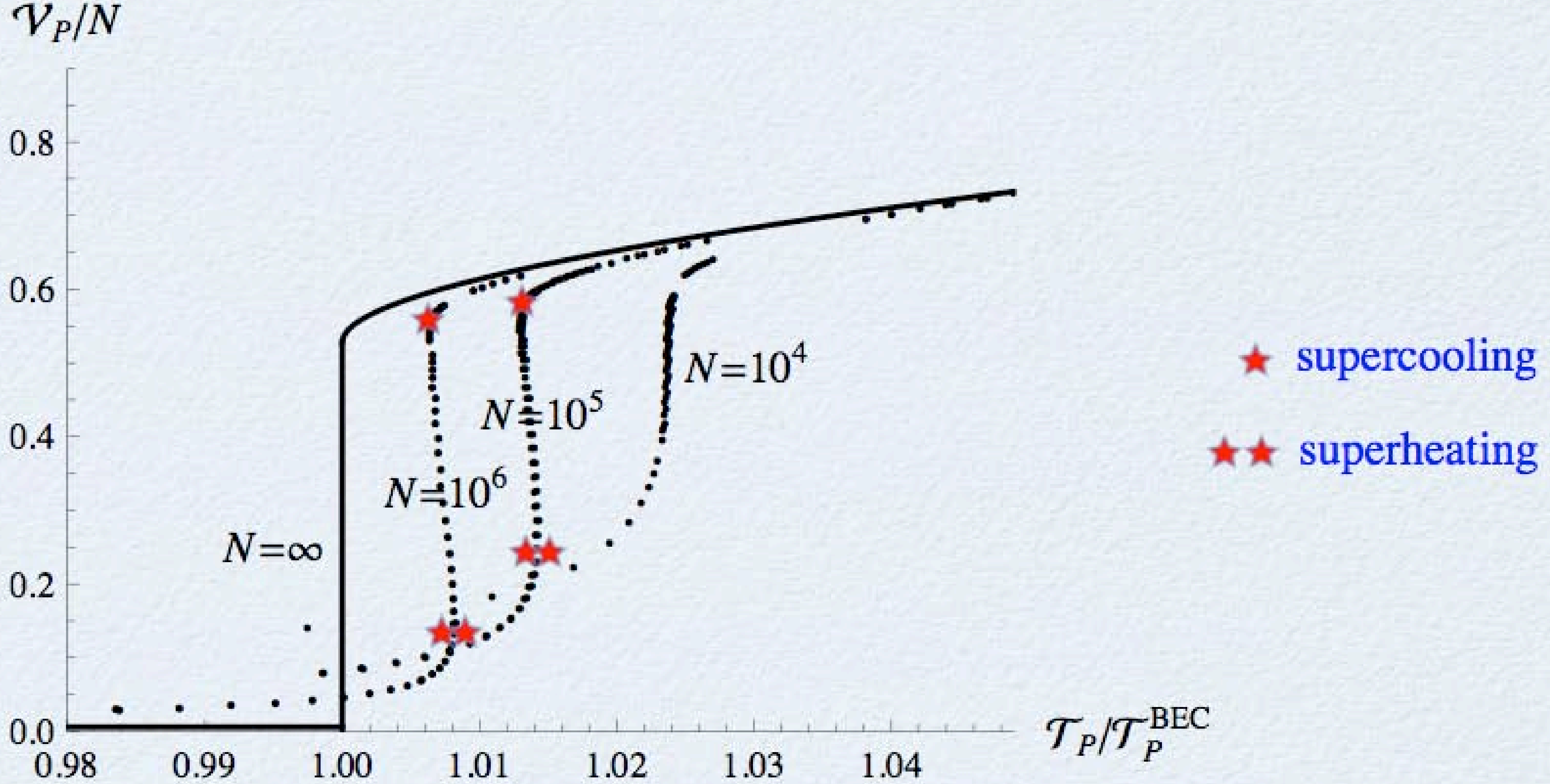


FIG. 2: Isobar curves on the $(\mathcal{T}_P/\mathcal{T}_P^{\rm BEC}, \mathcal{V}_P/N)$-plane. They zigzag featuring '$\mathcal{S}$-shape' if $14393 \leq N < \infty$.

- For the Avogadro's number, $N_{\rm A} \simeq 6.02214 \times 10^{23}$, the volume expansion rate reads $\mathcal{V}_P^{*}/\mathcal{V}_P^{**} \simeq 104399$.

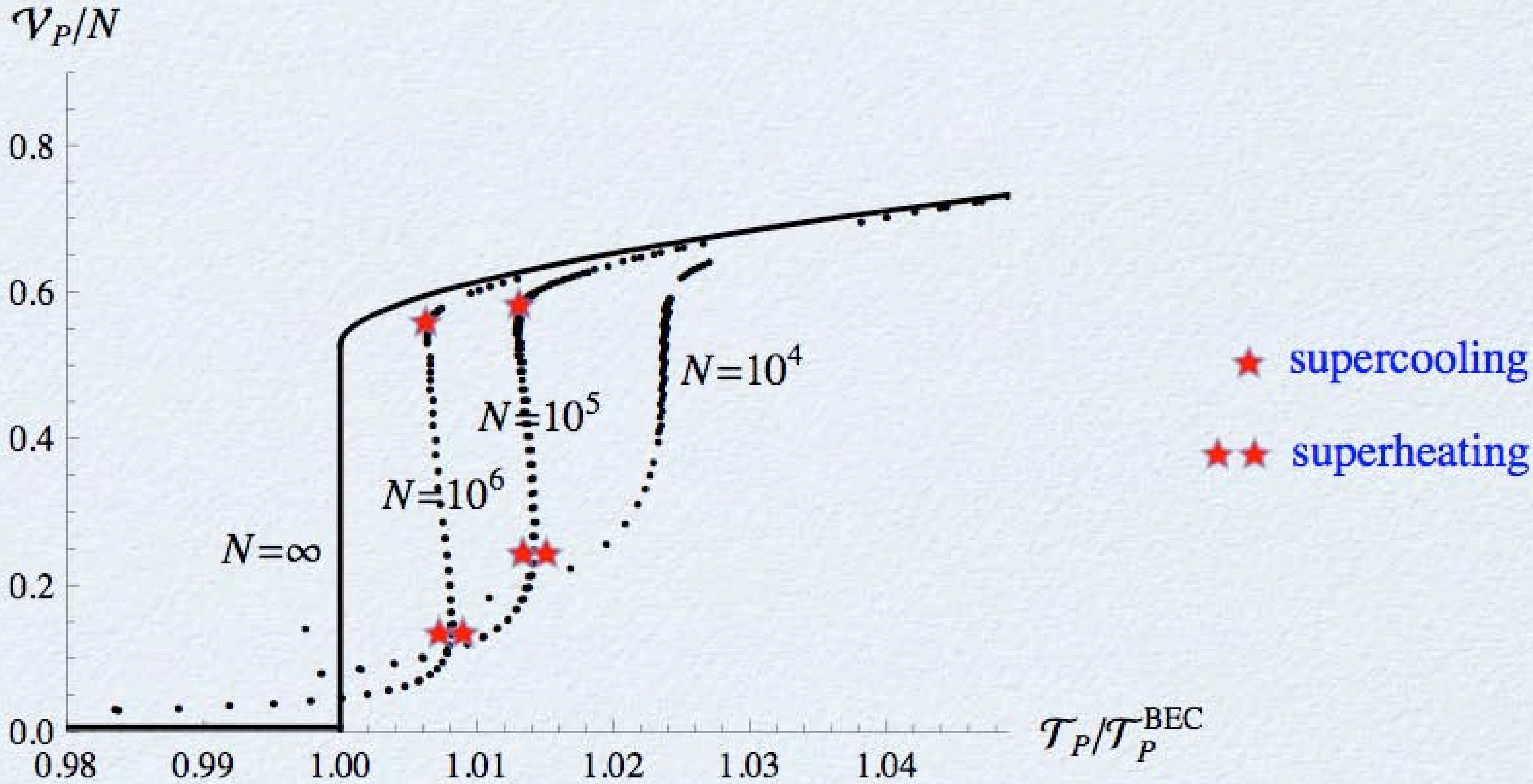


FIG. 2: Isobar curves on the $(\mathcal{T}_P/\mathcal{T}_P^{\rm BEC}, \mathcal{V}_P/N)$-plane. They zigzag featuring '$\mathcal{S}$-shape' if $14393 \leq N < \infty$.

- Thus, the ideal Bose gas made up of the Avogadro's number of particles expands its volume discretely about 10^5 times during the liquid-gas transition-like phase transition.
- This is a genuine *finite effect* of the Avogadro's number, which cannot be seen directly in the thermodynamic limit.

Concluding Remarks

- Keeping the pressure constant, discrete phase transition arises for finite ideal Bose gas system with

  $N \geq 7616$ (Canonical) or $N \geq 14393$ (Grand canonical).

- This is an emergent phenomenon of the finitely many bosonic identical particles, which we *ab initio* derived from the first principles in statistical physics.

Concluding Remarks

- The singularity is due to the spinodal curve that sharply defines the phase diagram.

- Presence of both the supercooling and the superheating characterizes the first-order phase transition.

- Between the supercooling and superheating temperatures every physical quantity zigzags or becomes triple valued, implying the existence of three different states during the liquid-gas transition-like discontinuous phase transition.

Concluding Remarks

Relativistic ideal gas:

- The spinodal curve defines the phase diagram having a critical point.
- The consequent phase transition is first-order below the critical pressure or second-order at the pressure.
- The exponents of the singularities are 1/2 and 2/3 respectively.
- The equation of state of the ideal relativistic Bose gas resembles the Van der Waals equation of state.

Concluding Remarks

- Recall the similarity between the permutation symmetry of the identical particle indices and the gauge symmetry in QFT:

  Both correspond to nonphysical symmetry.

  - ✓ Although the former is discrete
    while the latter is continuous,
    the latter may include the former as a subgroup.

Concluding Remarks

- The description of identical particles appears closely related to a low energy strong coupling limit of Yang-Mills matrix models.

- The potential therein is given by matrix commutator squared, multiplied by a coupling constant.

- Hence, in a strong coupling limit in order to maintain the energy finite, all the matrices should commute each other and become simultaneously diagonalizable, so that their eigenvalues are effectively only the remaining physical degrees.

- The unbroken gauge symmetry then corresponds to the permutation of the eigenvalues and can be identified as the permutation symmetry of the identical particle indices.

Concluding Remarks

- The critical number 7616 can be taken as a characteristic number of `cube', the geometric shape of the box.
- Boxes of different shapes will have different critical numbers.
- For a sphere, we get $N = 10458$ as for the critical number of particles.
- Thus, our scheme provides a novel algorithm to assign a characteristic number to a closed 2D manifold.

Concluding Remarks

- Generically, for a stable matter $\partial_V P$ is negative.

- What we show by taking ideal Bose gas as an exactly solvable model is an explicit demonstration that,

  if there are sufficiently, yet finitely, many **identical** bosonic particles, it can be positive.

Concluding Remarks

- It will be therefore interesting and crucial to see, to what extent interactions can alter this.

- If not much (weak interaction), one first-order phase transition, accompanying discontinuous volume change like the liquid-gas transition, should occur essentially due to the identical nature of particles - *indistinguishability*.

Concluding Remarks

- It will be also experimentally challenging to find a corresponding critical number for each molecule to manifest a discontinuous phase transition or its liquid-gas transition under constant pressure.

- **How many H_2O molecules are needed to form water that features boiling phase transition?**

- A criterion for the first-order phase transition is to observe the supercooling and the superheating phenomena.

If we take the thermodynamic limit...

- one may convert the discrete sum into an integral,
- $\ln(Z)$ becomes linear in volume,
- consequently, no spinodal curve is seen.

Taking thermodynamic limit implies ...

- From the combination,

$$\frac{\hbar^d}{V}$$

we note

$$V \rightarrow \infty \quad \Longleftrightarrow \quad \hbar \rightarrow 0$$

Taking thermodynamic limit implies ...

- ☑ Naive thermodynamic limit reduces to the classical limit.
- ☑ Quantum effect may be lost !!!
- ☑ Essentially, taking derivatives and taking the thermodynamic limit do not commute.

⇒ Implication to QFT

Concluding Remarks

- Back to the question: ``How Many is Different?"

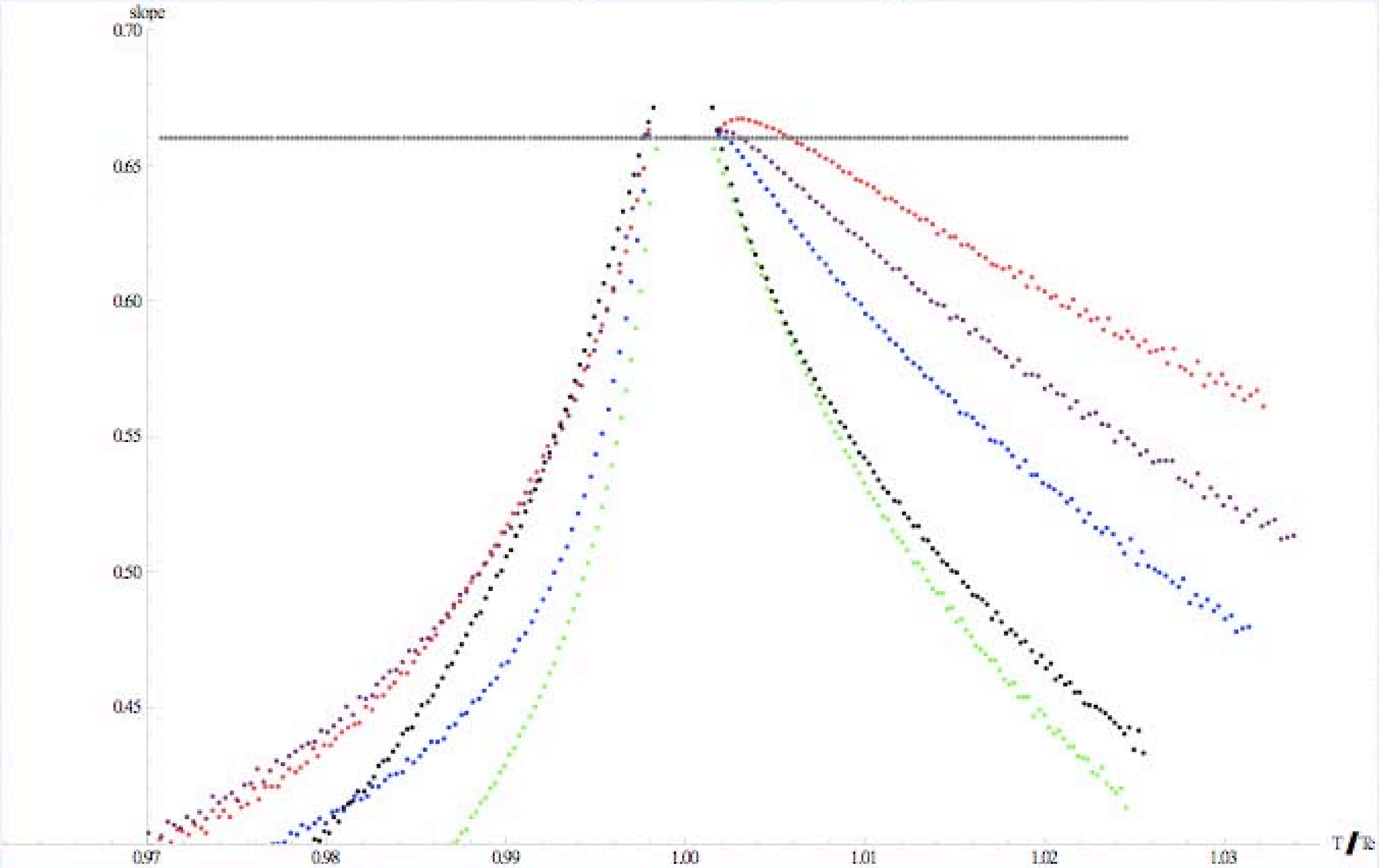
Our answer is finite as 7616 or 14393, etc.

Thank you.

The End

NIST Data

Critical point for Liquid-gas phase transition



Red line = Carbon dioxide, $T_c = 304.162K$
Green line = Propane, $T_c = 369.849K$
Blue line = Ethane, $T_c = 305.357K$
Purple line = Ethene, $T_c = 282.379K$
Black line = Propene, $T_c = 365.555K$

x−axis : $\frac{T}{T_c}$ rescaled , y−axis : slope = $-\frac{\ln(C_{p\,n+1}) - \ln(C_{p\,n})}{\ln(|T_{n+1} - T_c|) - \ln(|T_n - T_c|)}$

Concluding Remarks

- It will be experimentally challenging to find a corresponding critical number for each molecule to manifest a discontinuous phase transition or its liquid-gas transition under constant pressure.

- A criterion for the first-order phase transition is to observe the supercooling and the superheating phenomena.

Thank you.