

Existence of a critical point in the phase diagram of the ideal relativistic neutral Bose gas

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Abstract. We explore the phase transitions of the ideal relativistic neutral Bose gas confined in a cubic box, without assuming the thermodynamic limit nor continuous approximation. While the corresponding non-relativistic canonical partition function is essentially a one-variable function depending on a particular combination of temperature and volume, the relativistic canonical partition function is genuinely a two-variable function of them. Based on an exact expression for the canonical partition function, we performed numerical computations for up to 10^5 particles. We report that if the number of particles is equal to or greater than a critical value, which amounts to 7616, the ideal relativistic neutral Bose gas features a spinodal curve with a critical point. This enables us to depict the phase diagram of the ideal Bose gas. The consequent phase transition is first order below the critical pressure or second order at the critical pressure. The exponents corresponding to the singularities are $1/2$ and $2/3$, respectively. We also verify the recently observed ‘Widom line’ in the supercritical region.

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1. Introduction

A spinodal curve, by definition, consists of points in a phase diagram where the isothermal volume derivative of pressure vanishes [1, 2]:

$$\partial_V P(T, V) = 0. \quad (1)$$

The curve corresponds to the border line between thermodynamic stable and unstable regions, $\partial_V P(T, V) < 0$ and $\partial_V P(T, V) > 0$, respectively [3]. Moreover, if it exists, the spinodal curve amounts to a first-order phase transition under constant pressure. The temperature derivative at fixed pressure acting on an arbitrary physical quantity, which is a function of temperature and volume, is given by the chain rule of calculus:

$$\left. \frac{\partial}{\partial T} \right|_P = \left. \frac{\partial}{\partial T} \right|_V - \left[\frac{\partial_T P(T, V)}{\partial_V P(T, V)} \right] \left. \frac{\partial}{\partial V} \right|_T. \quad (2)$$

On the spinodal curve, the denominator of the second term vanishes, and the temperature derivative of a generic physical quantity along the isobar diverges [4]. This provides a possible mechanism for a finite system to manifest genuine mathematical singularities, without taking the thermodynamic limit [5].

If we fill a rigid box with water to full capacity and heat the box, the temperature will increase but the water hardly evaporates. According to a well-known standard argument against the emergence of a singularity from a finite system that is based on the analytic property of the canonical partition function [3], no discontinuous phase transition should occur. Nevertheless, opening the lid will set the pressure as constant or at 1 atm, and the water will surely start to boil at 100 °C. The point is that the usual finiteness of physical quantities in a canonical ensemble is for the case of keeping the volume fixed. Once we switch to the alternative constraint of keeping the pressure constant, a first-order phase transition featuring genuine mathematical singularities may arise from a system possessing a finite number of physical degrees. The question is then the existence of the spinodal curve.

In our previous work [4], we investigated the thermodynamic instability of the ideal non-relativistic Bose gas confined in a cubic box, based on an exact expression for the corresponding canonical partition function. The result was that if the number of particles is equal to or greater

than a certain critical value⁴ that turns out to be 7616, the ideal Bose gas subject to the Dirichlet boundary condition indeed reveals thermodynamic instability characterized by a pair of spinodal curves and consequently undergoes a first-order phase transition under constant pressure. The two spinodal curves are identified as the supercooling and the superheating of the ideal Bose gas,

$$\begin{aligned} k_B T_{\text{supercool}} &= \tau_p^* \times [\pi^2 \hbar^2 / (2m)]^{3/5} P^{2/5}, \\ k_B T_{\text{superheat}} &= \tau_p^{**} \times [\pi^2 \hbar^2 / (2m)]^{3/5} P^{2/5}, \end{aligned} \quad (3)$$

where k_B is the Boltzmann constant, m is the mass of the particle, P is an arbitrary given pressure and τ_p^* and τ_p^{**} are dimensionless constants the numerical values of which depend on the number of particles, N , as follows [4]:

N	τ_p^*	τ_p^{**}
7616	1.054 369 4113	1.054 369 4116
10^4	1.052 70	1.052 77
10^5	1.041 0	1.042 4
10^6	1.034	1.036

Between the two temperatures on the isobar, every physical quantity zigzags or becomes triple valued, implying the existence of three different phases during the discontinuous phase transition. This includes the volume as well as the number of particles occupying the ground state. Hence, the corresponding first-order phase transition coincides with the Bose–Einstein condensation (BEC) in both the coordinate and the momentum spaces. This result is comparable with the well-known BEC temperature of the ideal non-relativistic Bose gas in the thermodynamic limit:

$$k_B T_{\text{conti. approx.}} = [2\pi \hbar^2 / m]^{3/5} [P / \zeta(5/2)]^{2/5} \simeq 1.0278 \times [\pi^2 \hbar^2 / (2m)]^{3/5} P^{2/5}, \quad (4)$$

where ζ is the Riemann zeta function. In standard textbooks, e.g. [3], [6]–[9], this temperature is typically obtained by treating the ground state separately and applying the continuous approximation to all the rest of the excited states. From the comparison of equations (3) and (4), it appears that the continuum limit smooths out some details of the thermodynamic quantum structure.

In this paper, we generalize our previous work to the relativistic case. We investigate the spinodal curve of the ideal relativistic quantum gas of neutral bosons confined in a cubic box subject to the Dirichlet boundary condition. While the non-relativistic canonical partition function is essentially a one-variable function depending on a particular combination of temperature and volume, the relativistic canonical partition function is genuinely a two-variable function of them. We show that *if the number of particles is equal to or greater than the critical number 7616, the ideal relativistic neutral Bose gas features a spinodal curve with a critical point where the supercooling and the superheating lines converge*. Further, we verify the recently observed ‘Widom line’ [10] emanating from the critical point as the crossover between

⁴ The number 7616 can be regarded as the characteristic number of a cube. For a sphere we obtain the critical number 10 458.

liquid-like and gas-like behaviour in the supercritical region [11] (see also [12] and [13]). The critical number coincides with that of the non-relativistic system and hence the present paper confirms our previous numerical results [4].

The main motivation for us to consider the relativistic ideal Bose gas in this paper as a generalization of the non-relativistic system we studied previously is, by letting the corresponding canonical partition function be a two-variable function, to observe a more intriguing phase diagram such as a critical point and the Widom line. After all, quantum mechanics and relativity are two cornerstones of modern physics. For pioneering earlier works on the ideal relativistic Bose gas—via the continuous approximation—see [14]–[17]. For a recent discussion, see [18] and references cited therein. In the present paper, we restrict ourselves to neutral bosons. The inclusion of anti-bosons, as in [19]–[21], will be treated separately elsewhere [22].

The rest of the paper is organized as follows. In section 2, we present a model-independent analysis of a canonical ensemble. We first review three different expressions for the canonical partition function of generic non-interacting identical bosonic particles. We then, simply by assuming the existence of a spinodal curve, show that under constant pressure, first-order phase transitions feature singularities of exponent $1/2$, while second-order phase transitions have the critical exponent $2/3$. Section 3 is exclusively devoted to the ideal relativistic neutral Bose gas confined in a cubic box. After analysing non-relativistic and ultra-relativistic limits, we present our numerical results. When the number of particles is equal to or greater than 7616, the ideal relativistic Bose gas reveals a spinodal curve with a critical point. We draw the corresponding phase diagram. Section 4 summarizes our results with comments.

2. General analysis

2.1. The canonical partition function: a review

When a single particle system is completely solvable, each quantum state is uniquely specified by a set of good quantum numbers, which we simply denote here by a vector notation, \vec{n} . With the corresponding energy eigenvalue $E_{\vec{n}}$ and $\beta = 1/(k_B T)$, we define for each positive integer a ,

$$\lambda_a := \sum_{\vec{n}} e^{-a\beta E_{\vec{n}}}, \quad (5)$$

where the sum is over all the quantum states. In particular, when $a = 1$, λ_a coincides with the canonical partition function of the single particle.

For an N -body system composed of the non-interacting identical bosonic particles above, we may write the corresponding canonical particle function in three different ways:

- As first obtained by Matsubara [23] and Feynman [24],

$$Z_N = \sum_{m_a} \prod_{a=1}^N (\lambda_a)^{m_a} / (m_a! a^{m_a}), \quad (6)$$

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

- By a recurrence relation first derived by Landsberg [25],

$$Z_N = \left(\sum_{k=1}^N \lambda_k Z_{N-k} \right) / N, \quad (7)$$

where we set $Z_0 = 1$.

- From [4],

$$Z_N = \det(\Omega_N) (Z_1)^N / N!, \quad (8)$$

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

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

In particular, every diagonal entry is unity.

The first expression (6) implies that, compared with the ideal Boltzmann gas, the ideal Bose gas has a higher probability for the particles to occupy the same quantum state [4]. The last expression (8) is useful for us to see when the canonical partition function reduces to the conventional approximation [26]:

$$Z_N \longrightarrow (Z_1)^N / N!, \quad (9)$$

which would only be valid if all the particles occupied distinct states, as in the high temperature limit. Indeed, in this limit we have $\lambda_1 \rightarrow \infty$. Hence, $\det(\Omega_N) \rightarrow 1$ and the reduction (9) holds.

According to the Hardy–Ramanujan estimation, the number of possible partitions grows exponentially like $e^{\pi\sqrt{2N/3}}/(4\sqrt{3}N)$, and this would make any numerical computation based on expression (6) practically hard for large N . Among the three above, the recurrence relation (7) provides the most efficient scheme of N^2 order computation.

2.2. Critical and non-critical exponents: universal results

When the energy eigenvalue of the single particle system E_n (5) depends on volume, the canonical partition function depends on temperature and volume and so does the pressure:

$$P(T, V) = k_B T \partial_V \ln Z_N(T, V). \quad (10)$$

We consider, at least locally⁵, inverting $P(T, V)$ to express the temperature as a function of P and V like $T(P, V)$. Plugging this expression into $\partial_V P(T, V)$, let us define a quantity Φ as a function of P and V :

$$\Phi(P, V) := - \partial_V P(T', V) \Big|_{T' \rightarrow T(P, V)}. \quad (11)$$

As we change the volume keeping the pressure constant, Φ indicates whether the thermodynamic instability develops or not on the isobar. With the minus sign in front, now negative Φ corresponds to the thermodynamic instability.

⁵ Since the vanishing of $\partial_V T(P, V)$ implies the divergence of $\partial_T V(P, T)$, inverting $P(T, V)$ to express the volume as a function of P and T is not conceivable close to the spinodal curve, as we see shortly from relation (14).

In a similar fashion to (2), we write

$$\left. \frac{\partial}{\partial V} \right|_P = \left. \frac{\partial}{\partial V} \right|_T + \Phi \partial_P T(P, V) \left. \frac{\partial}{\partial T} \right|_V, \quad (12)$$

from which it is straightforward to obtain

$$\partial_V \Phi(P, V) = -\partial_V^2 P(T, V) - \Phi \partial_P T(P, V) \partial_T \partial_V P(T, V), \quad (13)$$

and relate the first and second volume derivatives of $T(P, V)$ to $\Phi(P, V)$ as

$$\begin{aligned} \partial_V T(P, V) &= \Phi \partial_P T(P, V), \\ \partial_V^2 T(P, V) &= \partial_V \Phi(P, V) \partial_P T(P, V) + \Phi \partial_P \partial_V T(P, V). \end{aligned} \quad (14)$$

Further, on the spinodal curve ($\Phi = 0$)—if it exists—we have

$$\left. \frac{dT}{dV} \right|_{\Phi=0} = -\frac{\partial_V^2 P(T, V)}{\partial_T \partial_V P(T, V)}. \quad (15)$$

Now the critical point can be defined as follows. At the critical pressure $P = P_c$, the system is generically stable, i.e. $\Phi > 0$, except at only one point that is the critical point. This implies that the critical pressure line is tangent to the spinodal curve, such that at the critical point, Φ and $\partial_V \Phi$ vanish:

$$\Phi(P_c, V_c) = 0, \quad \partial_V \Phi(P_c, V_c) = 0. \quad (16)$$

Moreover, from (11), (13) and (14), these two conditions are equivalent to

$$\partial_V P(T_c, V_c) = 0, \quad \partial_V^2 P(T_c, V_c) = 0 \quad (17)$$

and also to

$$\partial_V T(P_c, V_c) = 0, \quad \partial_V^2 T(P_c, V_c) = 0. \quad (18)$$

Equation (17) corresponds to the usual definition of the critical point as an inflection point in the critical isotherm on a (P, V) plane [3]. With (15), equation (17) implies that the critical point is an extremal point on the spinodal curve. On the other hand, equation (18) implies that the expansion of $T(P, V)$ near the critical point on the critical isobar starts from the cubic order in $V - V_c$ (for related earlier works, see [27] and references cited therein):

$$T(P_c, V) - T_c = \frac{1}{6}(V - V_c)^3 \partial_V^3 T(P_c, V_c) + \text{higher orders}. \quad (19)$$

Clearly, this leads to the following critical exponent:

$$V/V_c - 1 \sim |T/T_c - 1|^\beta, \quad \beta = 1/3. \quad (20)$$

Similarly, from (13) and (17), the expansion of Φ on the critical isobar starts from the quadratic order in $V - V_c$ such that

$$\Phi(P_c, V) \sim (V/V_c - 1)^2 \sim |T/T_c - 1|^{2/3}. \quad (21)$$

Thus, from (2), any physical quantity given by the temperature derivative along the critical isobar diverges with the universal exponent $2/3$. This includes the critical exponent of the specific heat per particle under constant pressure:

$$C_P \sim |T/T_c - 1|^{-\alpha}, \quad \alpha = 2/3. \quad (22)$$

On the other hand, since the specific heat per particle at constant volume is finite for any finite system, the corresponding critical exponent is trivial:

$$C_V = \text{finite}, \quad \text{i.e. } \alpha = 0. \quad (23)$$

Note that our conclusion does not exclude the possibility for C_V to develop a peak. We merely point out that the peak will be smoothed out if it is sufficiently zoomed in. Further, from (21), the inverse of Φ gives the critical exponent of the isothermal compressibility on the critical isobar:

$$\kappa_T := -V^{-1} \partial_P V(P_c, T) \sim |T/T_c - 1|^{-\gamma}, \quad \gamma = 2/3. \quad (24)$$

Finally, from (17), we also obtain an *isothermal* critical exponent at the critical temperature, $T = T_c$:

$$P/P_c - 1 \sim |V/V_c - 1|^\delta, \quad \delta = 3. \quad (25)$$

On a generic isobar below the critical pressure, $P < P_c$, the thermodynamic instability given by $\Phi(P, V) < 0$ appears naturally over an interval in volume and hence in temperature as well. The two ends then correspond to a supercooling point and a superheating point. At these points Φ vanishes and between them Φ is negative, as depicted in figure 1 from the van der Waals equation of state as an example⁶:

$$\left[(P/P_c) + 3(V_c/V)^2 \right] \left[(V/V_c) - \frac{1}{3} \right] = \frac{8}{3}(T/T_c). \quad (26)$$

It is crucial to note that the volume assumes triple values between the supercooling and the superheating temperatures at constant pressure less than P_c .

In the derivation of the critical exponents above, we tacitly assumed $\partial_V^2 \Phi(P_c, V_c) \neq 0$. In fact, the equivalence among (16), (17) and (18) generalizes up to an arbitrary order, say n : for all $k = 1, 2, \dots, n$, the vanishing of $\partial_V^k P(T, V)$ is equivalent to that of $\partial_V^k T(P, V)$ as well as that of $\partial_V^{k-1} \Phi(P, V)$. Hence, if the first non-vanishing multiple volume derivative of Φ occurs at the order n as $\partial_V^n \Phi(P_c, V_c) \neq 0$, the exponents in (20), (22), (24) and (25) assume the general values:

$$\alpha = \gamma = \frac{n}{n+1}, \quad \beta = \delta^{-1} = \frac{1}{n+1}. \quad (27)$$

Clearly these satisfy the following ‘scaling laws’ [3, 29]:

$$\begin{aligned} \text{Rushbrooke : } & \alpha + 2\beta + \gamma = 2, \\ \text{Widom : } & \gamma = \beta(\delta - 1). \end{aligned} \quad (28)$$

In particular, the case of $n = 1$ corresponds to the first-order phase transition at non-critical, supercooling and superheating points. Even at these points our analysis shows the existence of the universal exponent:

$$\alpha = \beta = \gamma = \delta^{-1} = \frac{1}{2}, \quad (29)$$

which agrees with the mean field theory result [30] (see also [31]). Around the supercooling or superheating point in figure 1, the constant pressure lines can be approximated by a parabola straight up or down, respectively. The possibilities of $n \geq 3$ correspond to exceptional critical points.

In the next section, we show that the ideal relativistic quantum gas of neutral bosons indeed features a spinodal curve similar to figure 1.

⁶ For a modern exposition of van der Waals forces, see e.g. [28].

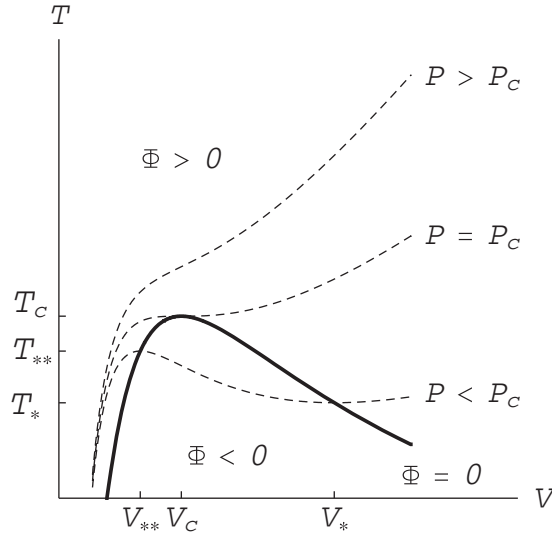


Figure 1. The van der Waals equation of state. The dashed lines are constant pressure lines of three different values, and the thick solid line is the spinodal curve satisfying $\Phi = -\partial_V P(T, V) = 0$. When $P < P_c$ the constant pressure line crosses the spinodal curve twice, at the supercooling 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.

3. The ideal relativistic neutral Bose gas

3.1. Algebraic analysis

Hereafter, exclusively for the ideal relativistic neutral Bose gas, we focus on N particles with mass m , confined in a box of dimension d and length $L \equiv V^{1/d}$. Hard, impenetrable walls impose the Dirichlet boundary condition⁷.

With *positive* integer valued good quantum numbers,

$$\vec{n} = (n_1, n_2, \dots, n_d), \quad (30)$$

the spatial momentum is quantized as $\vec{p} = \pi \hbar \vec{n} / L$, such that the single particle Boltzmann factor in (5) assumes the form

$$e^{-\beta E_{\vec{n}}} = \exp(-\mathcal{T}^{-1} \sqrt{1 + \vec{n} \cdot \vec{n}} \mathcal{V}^{-2/d}). \quad (31)$$

Here we have introduced, for simplicity of notation and the forthcoming analysis, *dimensionless temperature*:

$$\mathcal{T} := k_B T / (mc^2), \quad (32)$$

⁷ We recall that nevertheless enforcing the periodic or Neumann boundary condition leads to thermodynamic instability at low temperature close to absolute zero for arbitrary N [4].

as well as *dimensionless volume*:

$$\mathcal{V} := [mc/(\pi\hbar)]^d V. \quad (33)$$

The canonical partition function is then a two-variable function of them, $Z_N(\mathcal{T}, \mathcal{V})$. We further define *dimensionless pressure* by

$$\mathcal{P} := [(\pi\hbar)^d / (m^{d+1} c^{d+2})] P = \mathcal{T} \partial_{\mathcal{V}} \ln Z_N(\mathcal{T}, \mathcal{V}), \quad (34)$$

and a dimensionless indicator of the thermodynamic instability, as for Φ in (11):

$$\phi := -(1/N) \mathcal{V}^2 \partial_{\mathcal{V}}^2 \ln Z_N(\mathcal{T}, \mathcal{V}). \quad (35)$$

Other physical quantities we are particularly interested in this paper are specific heats per particle at constant volume or under constant pressure:

$$\begin{aligned} C_V &= (k_B/N) [(\mathcal{T} \partial_{\mathcal{T}})^2 + \mathcal{T} \partial_{\mathcal{T}}] \ln Z_N(\mathcal{T}, \mathcal{V}), \\ C_P &= C_V - k_B \mathcal{T} [\partial_{\mathcal{T}} \mathcal{P}(\mathcal{T}, \mathcal{V})]^2 / [N \partial_{\mathcal{V}} \mathcal{P}(\mathcal{T}, \mathcal{V})]. \end{aligned} \quad (36)$$

Non-relativistic limit. The non-relativistic limit corresponds to the limit of low temperature and large volume with $\mathcal{T} \mathcal{V}^{2/d}$ held fixed. For larger volume, the Boltzmann factor (31) reduces to that of the non-relativistic particle, up to the shift of the energy by mc^2 :

$$e^{-\beta E_{\vec{n}}} \rightarrow e^{-\beta [mc^2 + \vec{p} \cdot \vec{p} / (2m)]} = e^{-1/\mathcal{T} - \vec{n} \cdot \vec{n} / (2\mathcal{T} \mathcal{V}^{2/d})}. \quad (37)$$

Physical quantities such as ϕ , C_V and C_P become one-variable functions depending on the single variable $\mathcal{T} \mathcal{V}^{2/d}$, or alternatively $\mathcal{T} \mathcal{P}^{-2/(d+2)}$ [4]. The constant energy shift is irrelevant to them. Furthermore, at extremely low temperature only the ground state energy matters and the canonical partition function reduces to

$$Z_N \rightarrow e^{-\beta N E_0} = \exp(-N \mathcal{T}^{-1} \sqrt{1+d} \mathcal{V}^{-2/d}). \quad (38)$$

Hence close to absolute zero temperature, we obtain

$$N/\mathcal{P} = \mathcal{V}^{1+1/d} \sqrt{d + \mathcal{V}^{2/d}}, \quad (39)$$

and also

$$\phi = \infty, \quad C_V = 0, \quad C_P = 0. \quad (40)$$

For large volume, equation (39) further leads to $\mathcal{V} = (N/\mathcal{P})^{d/(d+2)}$ and this agrees with [4]. Apparently the volume assumes a finite value at absolute zero temperature, essentially due to the Heisenberg uncertainty principle. It is worthwhile to recall

$$PV = Nk_B T, \quad \phi = 1, \quad C_V/k_B = d/2, \quad C_P/k_B = 1 + d/2, \quad (41)$$

in the large $\mathcal{T} \mathcal{V}^{2/d}$ limit of the non-relativistic case [4]. Note that the first relation is equivalent to $\mathcal{P} \mathcal{V} = N \mathcal{T}$.

Ultra-relativistic limit. The ultra-relativistic limit corresponds to the limit of high temperature and small volume with $\mathcal{T} \mathcal{V}^{1/d}$ held fixed. At sufficiently high temperature, highly excited states dominate and from (9) the canonical partition function reduces to $(Z_1)^N / N!$, where the Boltzmann factor also reduces as

$$e^{-\beta E_{\vec{n}}} \rightarrow e^{-\beta c |\vec{p}|} = \exp[-|\vec{n}| / (\mathcal{T} \mathcal{V}^{1/d})]. \quad (42)$$

Consequently, the canonical partition function and the physical quantities such as ϕ , C_V and C_P become one-variable functions depending on the single variable $\mathcal{T}\mathcal{V}^{1/d}$ or alternatively from (34) and (42) on $\mathcal{T}\mathcal{P}^{-1/(d+1)}$.

Moreover, for large $\mathcal{T}\mathcal{V}^{1/d}$ we may safely assume the continuous approximation to obtain [32]

$$Z_N(\mathcal{T}, \mathcal{V}) \propto (\mathcal{V}\mathcal{T}^d)^N, \quad (43)$$

which implies in the large $\mathcal{T}\mathcal{V}^{1/d}$ limit, cf (41):

$$PV = Nk_B T, \quad \phi = 1, \quad C_V/k_B = d, \quad C_P/k_B = 1 + d. \quad (44)$$

3.2. Numerical results

Here, we present our numerical results on the ideal relativistic neutral Bose gas confined in a cubic box, i.e. $d = 3$, at generic temperature and volume, performed by a supercomputer (SUN B6048). Our analysis is based on the recurrence relation (7) and the previous work [4]⁸.

Emergence of a spinodal curve (figure 2). As N grows, ϕ develops a valley of local minima, which eventually assumes negative values if $N \geq 7616$.

Specific heat per particle under constant pressure (figures 3–5). During the first-order phase transition under constant pressure that is less than the critical value, the volume and hence every physical quantity are triple valued between the supercooling and the superheating temperatures. We focus here on C_P , the specific heat per particle under constant pressure. For the explicit behaviour of other quantities, see our earlier work [4].

Phase diagram of the ideal relativistic neutral Bose gas for $N = 10^5$ (figure 6).

Our numerical results of the critical point are listed below for some selected N :

N	\mathcal{T}_c	\mathcal{V}_c/N	\mathcal{P}_c
7616	$3.665\,1475 \times 10^{-5}$	$9.510\,401 \times 10^5$	$2.015\,1967 \times 10^{-11}$
10^4	0.149 54	3.133	0.027 02
10^5	1.738	0.025 2	53.1

which gives

N	$\mathcal{T}_c(\mathcal{V}_c/N)^{2/3}$	$\mathcal{T}_c\mathcal{P}_c^{-2/5}$	$\mathcal{T}_c(\mathcal{V}_c/N)^{1/3}$	$\mathcal{T}_c\mathcal{P}_c^{-1/4}$
7616	0.354 4519	0.695 6079	$3.604\,329 \times 10^{-3}$	$1.729\,865 \times 10^{-2}$
10^4	0.320 2	0.634 0	0.218 8	0.368 8
10^5	0.149	0.355	0.510	0.644

⁸ The numerical computation inevitably requires a momentum cutoff as for $\vec{n} \cdot \vec{n}$, which generically deforms the result at high temperature. We choose mutually different, sufficiently large values of the cutoff, such that we maintain at least for some interval of temperature the high temperature behaviour (44), and report only the cutoff-independent results (cf [33, 34]).

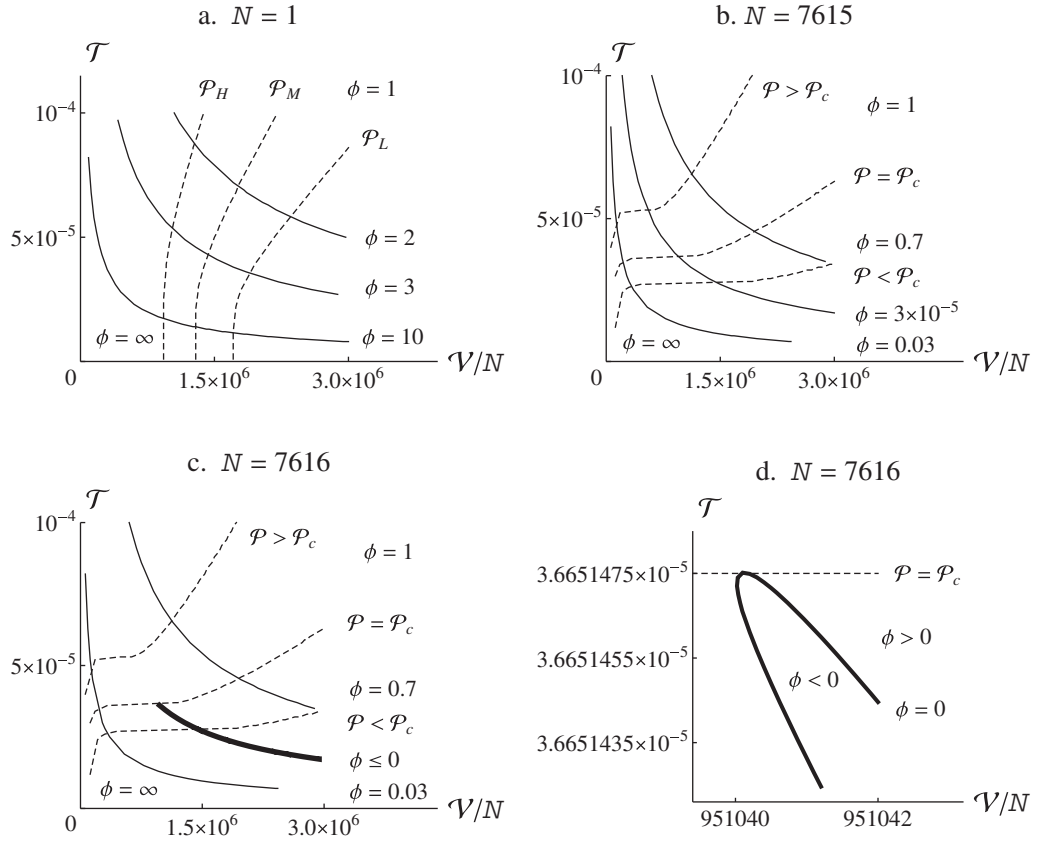


Figure 2. Constant pressure lines and spinodal curve. Dashed, thin solid or thick solid lines denote the constant pressure, constant ϕ or spinodal curve, respectively. Close to the origin of the $(\mathcal{T}, \mathcal{V}/N)$ plane, ϕ diverges, and in the opposite infinite limit, ϕ converges to unity. When $N = 1$ (figure 2(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. Figure 2(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 figure 2(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, $N = 7616$.

Comparison with the non-relativistic results in [4] indicates that the critical point of $N = 7616$ is in the non-relativistic region, while those of $N = 10^4$ and $N = 10^5$ are not.

4. Summary and comments

In summary, as seen from figures 3 and 6, the ideal relativistic neutral Bose gas divides the $(\mathcal{T}, \mathcal{V}/N)$ phase diagram into three parts:

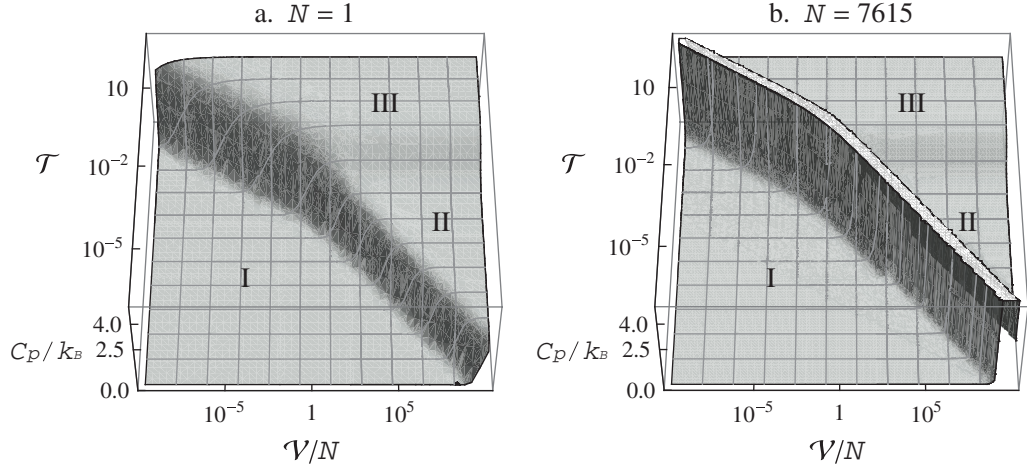


Figure 3. 3D image of C_P on the $(\mathcal{T}, \mathcal{V}/N)$ plane for $N = 1$ and $N = 7615$. The plane decomposes into three parts: phase **I** with $C_P \simeq 0$, phase **II** with $C_P \simeq 2.5k_B$ and phase **III** with $C_P \simeq 4k_B$. When $N = 1$, the transitions are monotonic and smooth.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

- Phase **I**: condensate with $C_P \simeq 0$ (40),

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

- Phase **II**: non-relativistic gas with $C_P \simeq 2.5k_B$ (41),

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

- Phase **III**: ultra-relativistic gas with $C_P \simeq 4k_B$ (44),

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

Equivalently, the $(\mathcal{P}, \mathcal{T})$ phase diagram splits into three parts:

- Phase **I**: $\{(\mathcal{P}, \mathcal{T}) \mid \mathcal{T} \lesssim \mathcal{P}^{2/5} \text{ and } \mathcal{T} \lesssim \mathcal{P}^{1/4}\}$.
- Phase **II**: $\{(\mathcal{P}, \mathcal{T}) \mid \mathcal{T} \gtrsim \mathcal{P}^{2/5} \text{ and } \mathcal{T} \lesssim 1\}$.
- Phase **III**: $\{(\mathcal{P}, \mathcal{T}) \mid \mathcal{T} \gtrsim \mathcal{P}^{1/4} \text{ and } \mathcal{T} \gtrsim 1\}$.

Here \lesssim and \gtrsim mean rough inequalities up to constants of the order of unity.

When $N = 1$, the transitions are all smooth and monotonic along any isobar. As N increases, a valley in ϕ , and hence a range of peaks in C_P , develops along the boundary of the condensate phase **I**. In particular, when $N = 7616$, the valley of ϕ assumes negative values and a spinodal curve with a critical point emerges along the boundary of phase **I** starting from absolute zero temperature. Beyond the critical point it is the Widom line that divides phase **I** and phase **III**. As N further increases, the critical point moves along the Widom line toward the ultra-relativistic higher temperature region. For the transition between the non-relativistic

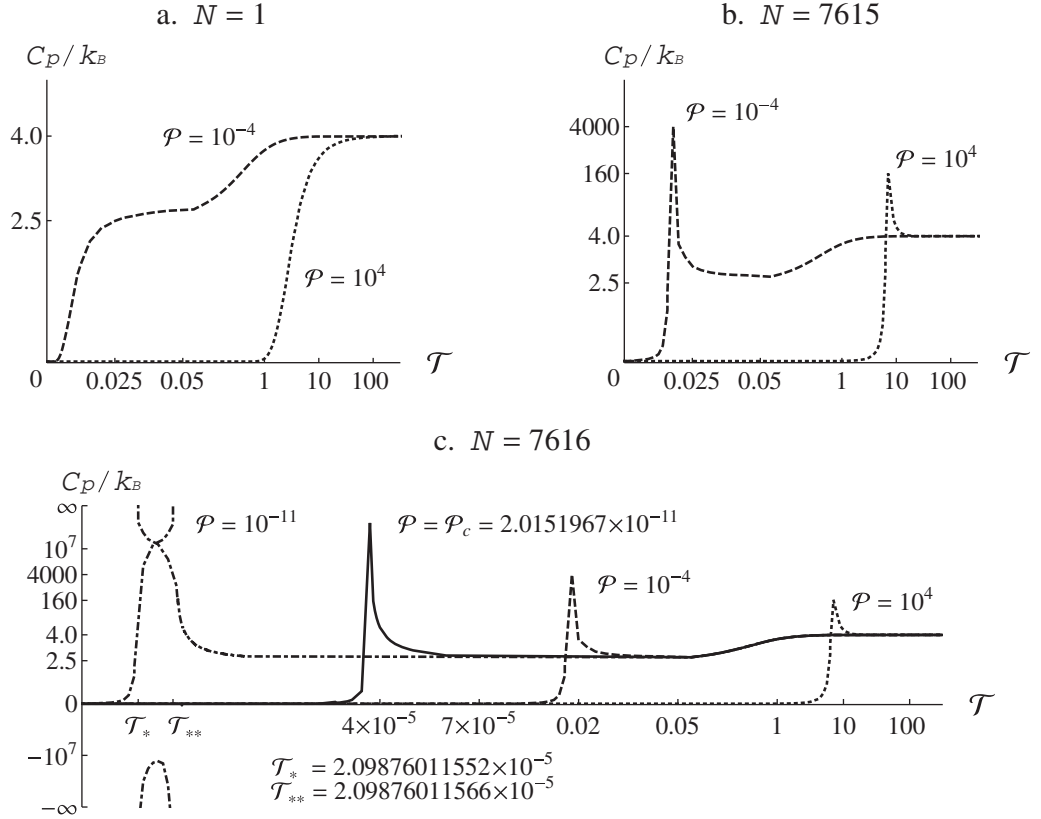


Figure 4. C_P for various N and P . For $N = 1$, C_P is monotonically increasing from zero to $4k_B$ on any isobar. Under sufficiently low pressure, it assumes the intermediate value of $2.5k_B$ as in equation (41). As N increases, C_P develops a peak on each isobar. In particular, when $N \geq 7616$ and $P < P_c$, it diverges both to the plus and minus infinities at the supercooling point $T = T_*$ as well as at the superheating point $T = T_{**}$. At the critical point $T = T_c = 3.6651475 \times 10^{-5}$, it diverges only positively. For $P > P_c$, the specific heat features a single finite peak, which can be identified as the Widom line.

and ultra-relativistic gas phases **II** and **III** there is no latent heat involved. The spinodal curve sharply defines the phase diagram. The consequent phase transition is first order below the critical pressure or second order at the critical pressure. The exponents corresponding to the singularities are $1/2$ and $2/3$, respectively. The presence of both supercooling and superheating characterizes the first-order phase transition.

The resulting equation of state from the spinodal curve of the relativistic ideal gas resembles the van der Waals equation of state, which is derived by assuming both repulsive potential at short distance and attractive potential at long distance. It is well known that the effective statistical interaction of the ideal Bose gas is attractive [3]. Our result seems to suggest a more intriguing structure. The fact that the volume is finite at absolute zero temperature seems also to indicate a repulsive interaction at short distance related to the Heisenberg uncertainty principle.

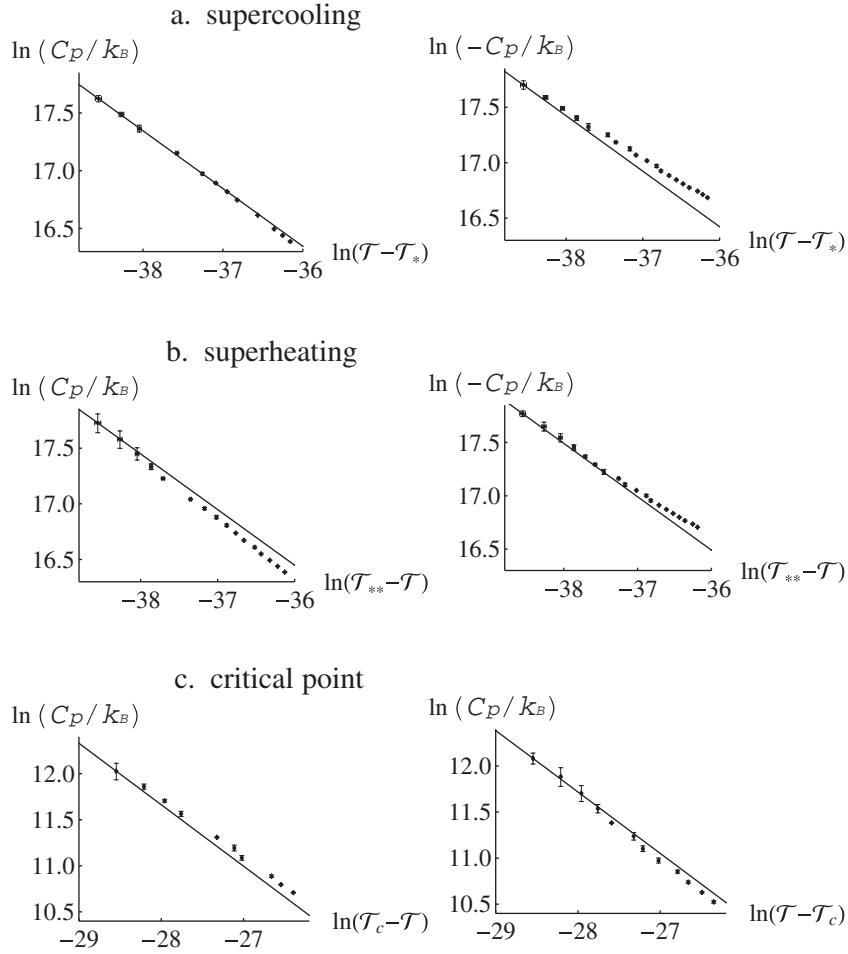


Figure 5. Critical and non-critical exponents. Our numerical data confirm the singular behaviour of the specific heat C_P anticipated in section 2.2: above the supercooling point, $C_P \sim \pm(\mathcal{T} - \mathcal{T}_*)^{-1/2}$ (figure 5(a)); below the superheating point, $C_P \sim \pm(\mathcal{T}_{**} - \mathcal{T})^{-1/2}$ (figure 5(b)); and around the critical point, $C_P \sim |\mathcal{T} - \mathcal{T}_c|^{-2/3}$ (figure 5(c)). The numerical data are for $N = 7616$, $\mathcal{P} = 5.000\,170\,056\,40 \times 10^{-12}$ (figures 5(a) and (b)) or $\mathcal{P}_c = 2.015\,1967 \times 10^{-11}$ (figure 5(c)). The error bars originate from the numerical uncertainty beyond these digits. The straight lines correspond to the theoretical slopes, $-1/2$ (figures 5(a) and (b)) or $-2/3$ (figure 5(c)).

An interesting open question is whether the critical point converges or not in the phase diagram as $N \rightarrow \infty$. If not, one may also wonder whether there exists another critical number in N for the emergence of a spinodal curve from the ultra-relativistic canonical partition function (42). We have verified for up to $N = 10^6$ that the ultra-relativistic canonical partition function does not feature any spinodal curve, although ϕ develops a local minimum.

Although in this work we have focused on the relativistic generalization of the non-relativistic ideal Bose gas and have obtained a non-trivial phase diagram with a critical point and Widom line, it is natural to expect that other generalizations that involve extra

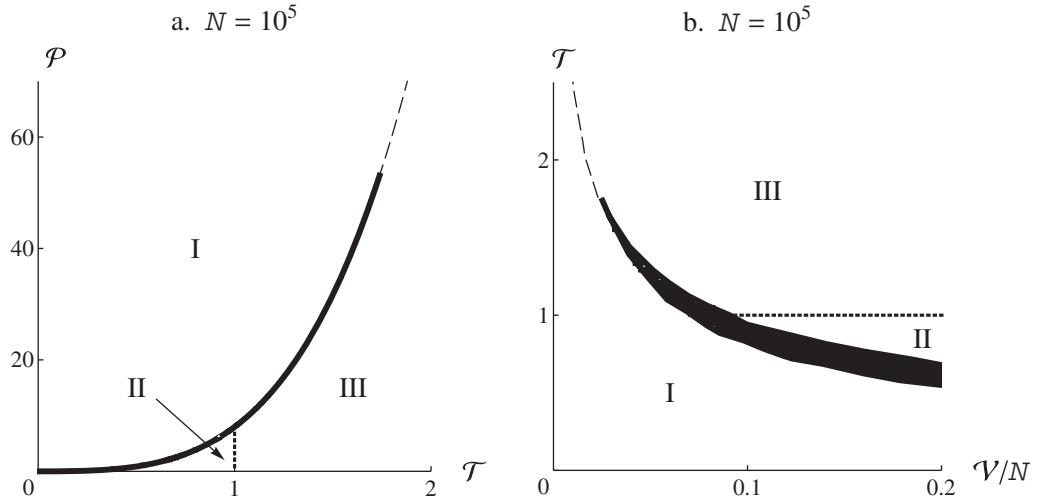


Figure 6. Phase diagram for $N = 10^5$ on the $(\mathcal{P}, \mathcal{T})$ and $(\mathcal{T}, \mathcal{V}/N)$ planes. The thick solid line, dashed line and dotted line correspond to the spinodal curve (including its inside), the Widom line (a range of finite peaks in C_P that also coincide with the valley 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 $C_P \simeq 2.5k_B$ and phase III of $C_P \simeq 4k_B$. On the top of the solid line, there exists a critical point. As N increases, the critical point moves towards the 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.

dimensionful parameters, e.g. trapping potentials, may also lead to qualitatively similar or even more intriguing phase diagrams.

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