How many is different? Answer from ideal Bose gas

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Abstract. How many H\textsubscript{2}O molecules are needed to form water? While the precise answer is not known, it is clear that the answer should be a finite number rather than infinity. We revisit with care the ideal Bose gas confined in a cubic box which is discussed in most statistical physics textbooks. We show that the isobar of the ideal gas zigzags on the temperature-volume plane featuring a \textit{boiling-like} discrete phase transition, provided the number of particles is equal to or greater than a particular value: 7616. This demonstrates for the first time how a finite system can feature a mathematical singularity and realize the notion of ‘Emergence’, without resorting to the thermodynamic limit.

1. Introduction

Emergence is a generic notion that quantitative increase leads to qualitative change. It is often said that the whole is greater than the sum of its parts. It is a key idea in condensed matter physics as well as in statistical physics, such that a classic paper by Anderson goes with the title, \textit{More is different} [1]. Then the question we address in this note is \textit{How many is different?}

To answer the question, we consult the quantum statistical physics where the key quantity is a partition function,

\[ Z = \text{Tr} \left[ e^{-H/(k_B T)} \right]. \tag{1} \]

The energy eigenvalues of the Hamiltonian are generically quantized with respect to the size of the volume. Consequently the partition function depends on both the temperature, \( T \), and the volume, \( V \). Once we know the exact expression of the partition function we may compute all the physical quantities which are typically given by the derivatives of the logarithm of the partition function.

For a finite system, the partition function and the derivatives are all analytic and hence all finite, never diverge. For example, \( C_V \), the specific heat at constant volume is finite: no singularity arises. The conventional way to realize a singularity is then to assume the thermodynamic limit where the volume and the number of particles go to infinity, \( V \rightarrow \infty \), \( N \rightarrow \infty \), while the density, \( N/V \), is kept fixed. In this limit, the partition function may become non-analytic and feature a singular behaviour [2]. It might seem that only infinity system could feature a singularity and realize a discrete phase transition, to coin a phrase, “More is the same: infinitely more is different” [3].

However, strictly speaking, infinite limits are hardly realistic and exist only in theory [4] [5] [6]. Experiments or our daily experiences, like the boiling water in the kitchen, do appear not just

1 Sabbatical leave of absence.
to mimic but actually to manifest discrete phase transitions. As a matter of historical fact in 1937, at the Van der Waals memorial meeting the audience could not agree on the question, whether partition function for a finite system could explain a sharp phase transition or not. So the chairman of the session, Kramers, put it to a vote!  

Nevertheless, despite the old controversy, in a modern rather axiomatic approach adopted mainly by mathematicians, phase transitions are defined simply in the thermodynamic limit only, with the “mathematically-natural” conventional answer infinity to the question, How many is different? The present note highlights an alternative finite answer, like $N = 7616$ reported in the works of the author with Sang-Woo Kim and Imtak Jeon [7, 8, 9]. The emphasis is put on physical implications rather than technical derivations.

2. Discrete phase transition of a finite system under constant pressure

A crucial ingredient in our approach to realize a discrete phase transition from a finite system is to keep not the volume but the pressure constant. The temperature derivative at fixed pressure acting on an arbitrary function of $T$ and $V$ reads

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

When this differential operator acts on e.g. the logarithm of the analytic partition function of a finite system, the temperature and the volume derivatives on the right hand side of the equality cannot generate any mathematical singularity. However, when $\partial_V P(T,V)$ vanishes, namely at the ‘spinodal’ points, it can be singular. In fact, the usual argument against the mathematical singularity from a finite system assumes the volume to be fixed. Alternatively, if we fix the pressure constant, a singularity may occur. That is to say, for a finite system, $C_V$ is finite never diverges, but $C_P$ may become singular,

$$C_V \ll \infty \quad \text{versus} \quad C_P = \infty \quad \text{for} \quad N \ll \infty.$$  

Physically, if we fully fill a rigid box with water and heat it up, the temperature will increase but the water hardly evaporates: no discontinuous phase transition to occur in this case. Nevertheless, opening the lid will set the pressure constant or at 1 atm, and the water will surely start to boil at 100 degree Celsius: no need to take the thermodynamic limit!

Our main point is that a singularity or a discrete phase transition may occur even for a finite system, provided we impose the constraint of keeping the pressure constant, rather than fixing the volume or the density. The next question is then the existence of the spinodal points where $\partial_V P(T,V) = 0$. Our claim is that the spinodal curve originates essentially due to the identical nature of particles without need of any extra interactions. As we describe below, a careful study of an ideal Bose gas indeed reveals the spinodal points and hence a boiling-like discrete phase transition for finite $N$.

3. Ideal Bose gas can boil under constant pressure if $N \geq 7616$

We are interested in a canonical partition function, $Z_N(T,V)$, of the ideal Bose gas confined in a cubic box with a definite number of particles, $N$. It is a standard quantum mechanical system discussed in most of statistical physics textbooks, e.g. [10]. We aim to address the precise dependence on $N$. The commonly adopted approximation of the partition function is

$$Z_N \sim \frac{(Z_{N=1})^N}{N!}.$$  

The author is not aware of the result of this ‘democratic’ decision. 

A short video presentation is also available on-line:
http://www.youtube.com/watch?v=rKo0vyGQd6nU&list=FLfVQVYKya2Jpncn5th00MjA&feature=mh_lolz
such that, e.g. the division by $N!$ solves the Gibbs paradox. This approximation gives for a generic derivative,

$$\frac{\partial \ln Z_N}{\partial V} \sim N \frac{\partial \ln Z_{N=1}}{N!},$$

and hence the number of particles appears as an overall parameter corresponding to an extensive quantity. However, the above approximation would be only correct if the $N$ particles occupied always $N$ distinct quantum states. But if some of the particles are in a common state, the division by $N!$ is too much and the approximation requires improvement. In fact, the correction can be organized as a determinant of a certain $N \times N$ matrix, $\Omega_N$, and the exact formula of the canonical partition function can be expressed as

$$Z_N = \text{Det} (\Omega_N) \times \frac{(Z_{N=1})^N}{N!}.$$  

For the details we refer the readers to [7, 8]. The point is that with the exact expression, $N$ is no longer a strictly-extensive parameter: physical quantities depend non-linearly on the number of particles. Especially a thermodynamic instability and hence zigzagging of the isobar on $(T,V)$-plane emerge provided the number of particles is equal to or greater than 7616 [7].

**Figure 1.** A supercomputer-powered numerical analysis on the exact partition function reveals that a thermodynamically unstable region emerges on $(T,V)$-plane when $N \geq 7616$.

In the figures above, utilizing the scale symmetry of the system, we set dimensionless quantities:

$$\phi = -\left(\frac{V^2}{Nk_B T}\right) \partial_V P, \quad \theta_T = k_B T \left(\frac{V}{N}\right)^{\frac{3}{2}} \left(\frac{2m}{\pi^2 \hbar^2}\right)^{\frac{3}{2}}, \quad \theta_P = V \left(\frac{P^2}{\pi^2 \hbar^2}\right)^{\frac{3}{2}} \left(\frac{2m}{\pi^2 \hbar^2}\right)^{-\frac{3}{2}}.$$  

**Figure 2.** The isobar of the ideal Bose gas zigzags on $(T,V)$-plane when $N \geq 7616$, which features a boiling-like discrete phase transition.
Further, for $N \gg 7616$, the supercooling ($\ast$) and the superheating ($\ast\ast$) points are analytically [9],

\[
\begin{align*}
T^\ast_P / T^\text{BEC}_P &\simeq 1 + \frac{1}{50} \left(\frac{\pi^{15}}{15}\right)^{\frac{1}{2}} (T^\text{BEC}_P)^{\frac{3}{2}} N^{-\frac{1}{4}}, && T^{\ast\ast}_P / T^\text{BEC}_P \simeq 1 + \frac{1}{50} \left(\frac{\pi^{15}}{15}\right)^{\frac{1}{2}} (T^\text{BEC}_P)^{\frac{3}{2}} N^{-\frac{1}{4}}, \\
V^\ast_P &\simeq (T^\text{BEC}_P / T^\text{BEC}_P)^{\frac{3}{2}} \left( N + \frac{7}{8} T^\text{BEC}_V N^{\frac{2}{3}} \ln N \right), && V^{\ast\ast}_P \simeq 8 \left(\frac{15}{\pi}\right)^{\frac{3}{2}} (T^\text{BEC}_P)^{-\frac{3}{2}} N^{\frac{1}{4}}, \\
T^\ast_V &\simeq T^\text{BEC}_V \left( 1 + \frac{7}{8} T^\text{BEC}_V N^{-\frac{1}{3}} \ln N \right), && T^{\ast\ast}_V \simeq 4 \left(\frac{15}{\pi}\right)^{\frac{3}{2}} N^{-\frac{1}{6}}, \\
\end{align*}
\]

where $T^\text{BEC}_P$ and $T^\text{BEC}_V$ denote the “BEC” constants,

\[
T^\text{BEC}_P = \left(\frac{64}{\pi^4}\right)^{\frac{1}{2}} \left[\zeta\left(\frac{3}{2}\right)\right]^{-\frac{2}{3}} \simeq 1.02781, \quad T^\text{BEC}_V = \frac{4}{\pi} \left[\zeta\left(\frac{3}{2}\right)\right]^{-\frac{2}{3}} \simeq 0.671253.
\]

### 4. Discussion

The above boiling-like discrete phase transition is an emergent phenomenon of the finitely many bosonic identical particles, which we ab initio derived from the first principles in statistical physics. The singularity is due to the spinodal curve that also sharply defines the phase diagram itself [8], c.f. [11].

Our results seem to suggest that, a generic liquid-gas phase transition occurs essentially due to the identical nature of particles rather than additional interactions.

The critical number 7616 can be viewed as a quantum mechanically determined characteristic of ‘cube’, the geometric shape of the box. Boxes of different shapes will have their own critical numbers. For example, for ‘sphere’ it is 10458.

It will be experimentally challenging to find a corresponding critical number for each molecule in Nature. We believe there must be a finite definite answer to the question, How many $\text{H}_2\text{O}$ molecules are needed to form water that features boiling phenomenon with zigzagged isobar?

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