

On quantum statistics for ensembles with a finite number of particles

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Abstract. The well-known Bose–Einstein and Fermi–Dirac quantum distributions can be considered as stationary solutions of kinetic equations for the mean occupation numbers in an ideal gas of an arbitrary finite number of identical particles.

1. Introduction

In recent years, with experimental advances in the deep cooling of dilute gases [1–3] and with the achievement of Bose–Einstein condensation [4, 5], it has become a necessity to apply quantum statistics to ensembles of a relatively small (of order 1000–1,000,000) number of particles, when the thermodynamic limit cannot be justifiably used and when, in addition, the discrete structure of energy levels should be taken into account [6–31].

The average number of particles in a state of energy E_k in an ideal gas being in contact with a thermostat is given by

$$n_k = \frac{1}{\exp[(E_k - \mu)/T] \pm 1}, \quad (1)$$

where T is the temperature (in energy units), and μ is the chemical potential defined by the condition

$$\sum_k n_k = N. \quad (2)$$

Here, N is the total number of particles in the system, and the + (–) sign refers to the Fermi (Bose) statistics. As is known, this distribution is asymptotically exact for a canonical ensemble in the thermodynamic ($N \rightarrow \infty$) limit (see, for

example, Refs [32, 33]). For systems with a finite number of particles, this distribution is approximate and corresponds to the grand canonical ensemble model, in which the conservation of the number of particles according to condition (2) is obeyed on the average.

In the present note we point out that distribution (1) is a stationary solution of the kinetic equations for the average occupations in an ideal gas consisting of an arbitrary finite number of particles. In so doing, we make no use of the general kinetic equation for the density matrix and restrict ourselves to only the kinetic (or balance) equations for average occupations. Notice that while kinetic equations for density matrix with due account of the interparticle interaction have been repeatedly discussed for application to quantum statistics [35–42], their analysis for finite systems in the canonical, let alone microcanonical, ensembles remain an intriguing open question. This article, of course, is not intended to solve the problem but rather to discuss some methodological aspects. As well as illustrating the general point that the equilibrium distribution is a stationary solution of the kinetic equations (see, for example, paper [34] and references therein), we will reveal the correspondence between the way these distributions are approximated (specifically, by the grand canonical or microcanonical ensembles) and what form the corresponding kinetic equations take.

2. Kinetic equation for average occupations in the grand canonical ensemble

As is known, the establishment of thermodynamic equilibrium in a system does not depend on exactly how particles interact with the thermostat, nor on how strong this interaction is. Note that we will consider the gas to be ideal and its constituent particles as mutually noninteracting.

The interaction operator between an ideal gas of identical particles and a thermostat will be here presented as the sum of interaction operators for each particle, with one-particle operators being considered identical.

We will limit the discussion to $k \rightarrow k \pm 1$ transitions between the neighboring states of a single particle due to its interaction with a thermostat of temperature T . Denoting the

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probabilities of such transitions by $w_{k,k+1}$ and $w_{k,k-1}$, the detailed balance principle can be expressed as

$$\exp\left[-\frac{E_k}{T}\right] w_{k,k-1} = \exp\left[-\frac{E_{k-1}}{T}\right] w_{k-1,k}. \quad (3)$$

The transition probabilities per unit time between the multi-particle states

$$|\dots n_{k-1}, n_k, n_{k+1}, \dots\rangle \rightarrow |\dots n_{k-1} + 1, n_k - 1, n_{k+1}, \dots\rangle$$

can be written as follows using the wave function symmetry of a system of identical particles:

$$W_{k,k-1} = w_{k,k-1} n_k (1 \mp n_{k-1}), \quad (4)$$

where the upper (lower) sign refers to the Fermi–Dirac (Bose–Einstein) statistics.

Denoting the number of particles in state k by n_k , the probability that this number in a time Δt will increase by one is given by

$$(W_{k-1,k} + W_{k+1,k}) \Delta t. \quad (5)$$

Similarly, the probability that the number of particles in state k will decrease in a time Δt by one is

$$(W_{k,k-1} + W_{k,k+1}) \Delta t. \quad (6)$$

Therefore, the average quantum mechanical change in the number of atoms in this state in a time Δt is

$$\Delta n_k = -(W_{k,k-1} + W_{k,k+1}) \Delta t + (W_{k-1,k} + W_{k+1,k}) \Delta t. \quad (7)$$

As a result, the time derivative is

$$\dot{n}_k = \lim_{\Delta t \rightarrow 0} \frac{\Delta n_k}{\Delta t} = -(W_{k,k-1} + W_{k,k+1}) + (W_{k-1,k} + W_{k+1,k}). \quad (8)$$

Using formula (4), we obtain

$$\begin{aligned} \dot{n}_k = & -w_{k,k-1} n_k (1 \mp n_{k-1}) - w_{k,k+1} n_k (1 \mp n_{k+1}) \\ & + w_{k+1,k} n_{k+1} (1 \mp n_k) + w_{k-1,k} n_{k-1} (1 \mp n_k). \end{aligned} \quad (9)$$

This equation for the rate of change in the number of particles in k state is valid under the assumption that the initial state of the system was one with definite (integer) occupation numbers. We will assume further on that the right-hand side of Eqn (9) can be *independently (statistically)* averaged over the occupation numbers of *different* states, allowing equation (9) to be considered as kinetic equations for the *average occupation numbers*.

Summing the left-hand and right-hand sides of Eqn (9), one readily obtains the law of conservation of the average number of particles:

$$\sum_k \dot{n}_k = 0. \quad (10)$$

This means that equations (9) correspond to the grand canonical ensemble model.

By using the relationship

$$1 \mp \frac{1}{n_k} = \mp \exp\left[\frac{E_k - \mu}{T}\right], \quad (11)$$

which follows from Eqn (1), it is readily shown that distributions (1) represent a stationary solution of equations (9). That this is indeed the case is easily seen by substituting Eqn (1) into the right-hand side of Eqn (9). The inverse statement also appears to be substantive: kinetic equations can be represented in the form (9) if their stationary solutions are identical to distributions (1).

Kinetic equations (9) should be modified if there are degenerate energy levels in the system. Assuming the level E_k to be g_k -fold degenerate and summing the left-hand and right-hand sides of the equations referring to the same energy value, we arrive at

$$\begin{aligned} \dot{n}_k = & \frac{1}{g_k} \left[-w_{k,k-1} n_k (1 \mp n_{k-1}) - w_{k,k+1} n_k (1 \mp n_{k+1}) \right. \\ & \left. + w_{k+1,k} n_{k+1} (1 \mp n_k) + w_{k-1,k} n_{k-1} (1 \mp n_k) \right]. \end{aligned} \quad (9a)$$

Now k subscript numerates energy levels, but n_k , as before, denotes the occupation of one state of a given level. Equation (2) for the chemical potential in this case becomes

$$\sum_k g_k n_k = N. \quad (2a)$$

The results so obtained can be assessed for their accuracy by comparing what three different approaches — the grand canonical ensemble approximation (corresponding to the stationary solution of the kinetic equation), the thermodynamic limit approximation, and the exact recurrence method [30] — predict for average occupation numbers in the Bose–Einstein condensate of an ideal gas of 1000 bosons in an isotropic harmonic trap (see Table 1).

Here, temperature is expressed in units of critical temperature T_c as obtained in the thermodynamics limit. It will be recalled that for an isotropic harmonic trap $E_k = (3/2 + k) \hbar \omega$, where ω is the natural frequency of the harmonic trap, $g_k = (k+1)(k+2)/2$, and $T_c \approx \hbar \omega (N/1.202)^{1/3}$. The last column of the table gives the average occupation numbers of a Bose–Einstein condensate in the thermodynamic limit: $n_{0\text{tl}} = N(1 - T^3/T_c^3)$.

Table 1. Ground state occupation in an isotropic harmonic trap calculated using a grand canonical ensemble (n_0), the exact recurrence method ($n_{0\text{rec}}$), and the thermodynamic limit ($n_{0\text{tl}}$) for 1000 Bose particles.

T/T_c	n_0	$n_{0\text{rec}}$	$n_{0\text{tl}}$
0.1	996.8	996.8	999
0.2	982.2	982.2	992
0.3	950.8	950.7	973
0.4	896.8	896.6	936
0.5	814.4	813.8	875
0.6	697.4	696.5	784
0.7	540.5	538.7	657
0.8	338.1	334.5	488
0.9	93.8	80.3	27.1
1.0	5.95	5.81	0
1.1	2.21	2.21	0
1.2	1.25	1.26	0
1.3	0.82	0.83	0

3. Doppler cooling

A well-known method of cooling a gas is by irradiating it with monochromatic light which is red-shifted relative to an atomic resonance transition — a method which is commonly referred to as Doppler cooling [1–3]. Let us demonstrate that the application of Doppler cooling is equivalent to immersing the gas into a fixed-temperature thermostat.

Consider the model of a one-dimensional harmonic trap.

The probability of light absorption per unit time by an atom with the quantum vibrational number k changing by unity can be written out as

$$w_{k,k\pm 1} = \frac{a_{k,k\pm 1}}{(\omega_0 \pm \omega - \omega_L)^2 + \Gamma^2/4}. \tag{12}$$

Here, the $+$ ($-$) sign corresponds to k being increased (decreased) by unity, the constants $a_{k,k\pm 1} = a_{k\pm 1,k}$ are proportional to the laser field intensity, Γ is the radiative width of the excited electronic state of the atom, and ω is the natural frequency of the harmonic trap. It will be further assumed that the return to the ground electronic state does not, on average, change the vibrational quantum number. If $\Delta = \omega_0 - \omega_L > 0$, i.e., the laser frequency is shifted to the red side of the resonance frequency, then absorption events that decrease the quantum number have a higher probability than transitions increasing it, with the consequence that the absorption of light will result in lowering the atomic vibrational energy — which is cooling.

Using Eqn (12) for the probability, we obtain

$$\frac{w_{k+1,k}}{w_{k,k+1}} = \frac{(\Delta + \omega)^2 + \Gamma^2/4}{(\Delta - \omega)^2 + \Gamma^2/4}. \tag{13}$$

For $\omega \ll \Delta$, one finds

$$\begin{aligned} \frac{w_{k+1,k}}{w_{k,k+1}} &= \frac{(\Delta + \omega)^2 + \Gamma^2/4}{(\Delta - \omega)^2 + \Gamma^2/4} \approx \frac{\Delta^2 + \Gamma^2/4 + 2\Delta\omega}{\Delta^2 + \Gamma^2/4 - 2\Delta\omega} \\ &\approx 1 + \frac{4\Delta\omega}{\Delta^2 + \Gamma^2/4} \approx \exp\left[\frac{4\Delta\omega}{\Delta^2 + \Gamma^2/4}\right] = \exp\left[\frac{\hbar\omega}{T_{\text{eff}}}\right], \end{aligned} \tag{14}$$

where

$$T_{\text{eff}} = \hbar \frac{\Delta^2 + \Gamma^2/4}{4\Delta}. \tag{15}$$

Relation (14) expresses detailed balance at temperature T_{eff} . The minimum value of temperature is obtained for mismatch $\Delta = \Gamma/2$ and equals $T_{\text{min}} = \hbar\Gamma/4$, the equilibration process itself being described by equations (9). It can be said that by exposing the system to lower frequency radiation than the resonance-produced radiation, we place it into a thermostat at a temperature given by Eqn (15). It is this thermostat which realizes the so-called optical molasses technique [2]. It should be noted that, unlike the standard experimental setup, the Doppler cooling of a trapped gas does not, in principle, require the use of colliding beams.

4. A grand microcanonical ensemble

Next, we will show that an isolated system of an arbitrary finite number of particles also allows distributions (1) to be obtained as stationary solutions of the corresponding kinetic equations. To make things more tractable, only the Bose–

Einstein statistics will be considered. The proof for the Fermi–Dirac statistics is similar.

The relaxation of an isolated system to thermodynamic equilibrium occurs via the interaction between the particles. Importantly, this interaction can be of any arbitrary nature provided only that, as a result of a sequence of transitions, any pair of the system’s states is connected by the interaction. In what follows, the interparticle interaction is assumed to be weak and its effect on quantum states changing and energy levels negligible.

Because it is necessary to ensure energy conservation law for interparticle interactions in an isolated system, we will consider a special model of a one-dimensional harmonic trap, whose feature of equidistant energy levels allows for satisfying this requirement in a simple and clear way. The interparticle interaction operator can also be taken in the harmonic approximation as a nondiagonal quadratic form in particle coordinates. To first order in perturbation theory, such interaction describes transitions in which one particle moves to the upper (lower) neighboring level, whereas another particle moves to the lower (upper) neighboring level. To this model should, of course, be added the transverse relaxation of the states being considered. Assuming the matrix elements of the nondiagonal quadratic form to be all equal to each other and choosing an appropriate time scale, the system of kinetic equations for this process simplifies to

$$\begin{aligned} \dot{n}_k &= -n_k(n_{k-1} + 1)k \sum_{p=1, p \neq k, p \neq k+1, p \neq k-1} n_{p-1}(n_p + 1) \\ &\times p - n_k(n_{k+1} + 1)(k + 1) \sum_{p=0, p \neq k, p \neq k+1, p \neq k-1} n_{p+1}(n_p + 1) \\ &\times (p + 1) + n_{k+1}(n_k + 1)(k + 1) \sum_{p=1, p \neq k, p \neq k+1, p \neq k+2} n_{p-1} \\ &\times (n_p + 1)p + n_{k-1}(n_k + 1)k \sum_{p=0, p \neq k, p \neq k-1, p \neq k-2} n_{p+1} \\ &\times (n_p + 1)(p + 1). \end{aligned} \tag{16}$$

The above set of equations ensures the laws of conservation of the average number of particles and of the average energy, thus satisfying requirements for the grand canonical ensemble. To check the law of conservation of the average number of particles, namely

$$\sum_s \dot{n}_s = 0, \tag{17}$$

note that corresponding to each term of the type $-n_k(n_{k+1} + 1)n_p(n_{p-1} + 1)$ in the equation for \dot{n}_k is a similar term but with the sign ‘+’ in the equation for \dot{n}_{p-1} . The sum $\sum_s \dot{n}_s$ is therefore zero.

The law of conservation of average energy can be expressed in the form

$$\sum_s s\dot{n}_s = 0 \tag{18}$$

and can be verified as follows. The combination

$$(k + 1)n_k(n_{k+1} + 1)pn_p(n_{p-1} + 1) \tag{19}$$

appears only in the four terms of this sum: with \dot{n}_k multiplied by $-k$; with \dot{n}_{k+1} multiplied by $(k + 1)$; with \dot{n}_p multiplied by

$-p$, and with \dot{n}_{p-1} multiplied by $p-1$. Summing these factors yields zero, thus proving the validity of Eqn (18).

Let us show that, similarly to the case of a grand canonical ensemble, equations (16) have as their stationary solution the Bose–Einstein distribution

$$n_k = \frac{1}{\exp[(k-\mu)/T] - 1}. \quad (20)$$

Here, the temperature T and the chemical potential μ are in units of $\hbar\omega$, with ω the natural frequency of the harmonic trap. It is assumed that the chemical potential is reckoned from the ground state energy.

Introducing notations

$$\begin{aligned} \tilde{w}_{k,k-1} &= k \sum_{p=1, p \neq k, p \neq k+1, p \neq k-1} n_{p-1}(n_p+1)p, \\ \tilde{w}_{k,k+1} &= (k+1) \sum_{p=0, p \neq k, p \neq k+1, p \neq k-1} n_{p+1}(n_p+1)(p+1), \end{aligned} \quad (21)$$

$$\tilde{w}_{k+1,k} = (k+1) \sum_{p=1, p \neq k, p \neq k+1, p \neq k+2} n_{p-1}(n_p+1)p,$$

$$\tilde{w}_{k-1,k} = k \sum_{p=0, p \neq k, p \neq k-1, p \neq k-2} n_{p+1}(n_p+1)(p+1),$$

equations (16) take the following form, similar to Eqn (9):

$$\begin{aligned} \dot{n}_k &= -n_k(n_{k-1}+1)\tilde{w}_{k,k-1} - n_k(n_{k+1}+1)\tilde{w}_{k,k+1} \\ &+ n_{k+1}(n_k+1)\tilde{w}_{k+1,k} + n_{k-1}(n_k+1)\tilde{w}_{k-1,k}. \end{aligned} \quad (22)$$

It is easy to show using Eqns (20) and (21) that the coefficients $\tilde{w}_{k,k-1}$ and $\tilde{w}_{k-1,k}$ are related in the same way as $w_{k,k-1}$ and $w_{k-1,k}$ in Eqn (9):

$$\tilde{w}_{k-1,k} = \tilde{w}_{k,k-1} \exp\left(-\frac{1}{T}\right). \quad (23)$$

This is sufficient to argue that, as shown in Section 3, distribution (20) is a stationary solution to kinetic equations (16). For a degenerate system, kinetic equations (16) can be modified similarly to equations (9a).

To illustrate the application of the Bose–Einstein distribution to an isolated system of a finite number of particles, let us consider a system of a million bosons in an isotropic harmonic trap and determine how its chemical potential and the occupation of the ground state (i.e., of the Bose–Einstein condensate) depend on temperature. Equation (2a) in this case takes the form

$$\sum_{k=0,1,2,\dots} \frac{(1/2)(k+1)(k+2)}{\exp[(k-\mu)/T] - 1} = N. \quad (24)$$

Table 2 lists the results obtained from Eqn (24) by an easy-to-use solution technique. The last column of the table gives the average energy value per degree of freedom, calculated as

$$\varepsilon = \frac{1}{2} + \frac{1}{3N} \sum_{k=0,1,2,\dots} \frac{(1/2)k(k+1)(k+2)}{\exp[(k-\mu)/T] - 1}. \quad (25)$$

Comparing the first and last columns of the table can, for a specified initial energy, determine the steady state temperature to which the isolated system relaxes.

Table 2. Chemical potential and occupation number of the ground state as a function of temperature for a grand microcanonical ensemble of 10^6 Bose particles in an isotropic harmonic trap.

T	μ	n_0	$\varepsilon - 1/2$
50	-0.000 059 3	843,400	6.916
80	-0.000 217	368,600	44.89
90	-0.000 864	104,100	71.60
93	-0.007 334	12,680	81.49
94	-1.293	72.178	83.71
95	-3.530	26.416	85.04
100	-15.793	5.845	91.16

5. Conclusion

The above analysis shows that the Fermi–Dirac and Bose–Einstein distributions for an ideal gas of an arbitrary finite number of particles can be interpreted as the stationary solutions of the proposed kinetic equations.

It is to be noted again that our kinetic equations are of an approximate nature, because their derivation involves averaging over the occupation numbers of different states. This approximation corresponds to the grand canonical and grand microcanonical ensemble models. At the same time, comparison with exact results for a canonical ensemble of even a relatively small (1000) number of Bose particles shows (see Table 1) that the obtained stationary solutions are quite accurate for noticeable departures from the thermodynamic limit approximation.

By solving kinetic equations (9) or (21) with arbitrary initial equations, it is possible to demonstrate the evolution of how thermodynamic equilibrium is established and, in particular, how, in the case of a Bose gas, the Bose–Einstein condensate forms. A still better picture of the process can be achieved with the aid of statistical test methods (Monte Carlo simulation) using transition probabilities of type (4) without averaging over occupation numbers.

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