TECHNICAL NOTE

First and Second Derivatives of the Chemical Potential for Noninteracting Particles

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Abstract
Both the first and the second derivatives of the chemical potential with respect to the temperature, for any system of noninteracting bosons, are shown to be negative. For noninteracting fermions, these derivatives can be either negative or positive, but for generic spectra they are both negative at higher temperatures.

Keywords Noninteracting bosons · Chemical potential

1 Introduction

In the grand canonical treatment of a system of non-interacting indistinguishable particles, the number of particles and the chemical potential are related by [1, 2]

$$N = \sum_i \frac{1}{\exp\left(\frac{e_i - \mu}{kT}\right) \pm 1},$$

(1)

where the plus sign refers to fermions and the minus sign to bosons. In the case of bosons, if the energy spectrum is such that a transition to a Bose–Einstein condensate takes place at some temperature T_c [3], then the discussion that follows applies only above this temperature. The class of systems of noninteracting particles is much broader and richer than the ideal gases, which involve very definite spectra that depend on the dimension of the space considered. Several approaches to the calculation of the chemical potential, μ, given the temperature, T, the number of particles, N and the one-particle energies, $e_1 \leq e_2 \leq e_3 \leq \cdots$, have very recently been reviewed by Cowan [4], who presented explicit expressions and detailed plots for the

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chemical potentials of ideal Fermi, Bose and Maxwell gases in one, two and three dimensions.

In Sect. 2, it is demonstrated that for a system of noninteracting fermions the first and the second derivatives of the chemical potential with respect to the temperature can be either positive or negative at low temperature. In the former case, both become negative (first the second derivative, then the first) as the temperature rises. In Sects. 3 and 4, it is shown that for any system of noninteracting bosons both the first and the second derivative of the chemical potential with respect to the temperature are always negative.

2 The First and Second Derivatives of the Chemical Potential for Noninteracting Fermions

For an ideal Fermi gas, the Sommerfeld expansion yields a vanishing first derivative of the chemical potential, at $T \to 0$. At the same limit, the second derivative is positive for the one-dimensional and negative for the three-dimensional free electron gas, breaking down in two dimensions [4]. More generally, the Sommerfeld expansion yields [5]

$$\mu = \epsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)},$$

where $g(\epsilon)$ is the energy-density of states. Hence, the sign of the second derivative of the chemical potential at very low temperatures depends on the sign of $g'(\epsilon_F)$, being negative when the density of states in the vicinity of the Fermi energy increases with increasing energy, which is the more commonly expected behavior in three-dimensional systems.

The results presented by Cowan [4] indicate that for the one-dimensional ideal Fermi gas the chemical potential starts from $T = 0\,\mathrm{K}$ by rising, with positive second derivative, towards a maximum. This is not the case for the two- and three-dimensional ideal Fermi gases, for which both the first and second derivatives of the chemical potential with respect to the temperature are always negative.

Kuntsevich et al. [6] measured $\left(\frac{\partial \mu}{\partial T}\right)_n$ for (interacting) two-dimensional electron systems, observing positive $\left(\frac{\partial \mu}{\partial T}\right)_n$ at 3 K, in a Si MOS sample.

At higher temperatures, the chemical potentials of both fermion and boson systems approach the Maxwell–Boltzmann chemical potential, decreasing without bound. A fermionic chemical potential that initially increases upon increasing the temperature, with a positive second derivative, must go through a maximum, with an inflection point preceding it. Hence, first the second derivative, then the first, turn negative.

For the ideal Bose gas, the plots presented by Cowan [4] suggest that the chemical potential is always a decreasing $\left(\frac{\partial \mu}{\partial T} \leq 0\right)$ and concave $\left(\frac{\partial^2 \mu}{\partial T^2} \leq 0\right)$ function of the temperature. The same properties were reported by Wang et al. [7] for a finite

number of noninteracting bosons in a box with Dirichlet or periodic boundary conditions, as well as for approximately quartically confined bosons [8].

3 First Derivative of the Chemical Potential for Non-interacting Particles

If the total number of particles is constant, then

$$\frac{\mathrm{d}N}{\mathrm{d}T} = \frac{1}{kT^2} \sum_i \left[(e_i - \mu) + T\left(\frac{\partial \mu}{\partial T}\right) \right] f_i = 0, \tag{2}$$

where

$$f_i = \frac{\exp\left(\frac{e_i - \mu}{kT}\right)}{\left(\exp\left(\frac{e_i - \mu}{kT}\right) \pm 1\right)^2}.$$

Equation (2) can be written in the form

$$T\left(\frac{\partial \mu}{\partial T}\right) = \mu - \langle e \rangle, \tag{3}$$

where $\langle e \rangle = \frac{\sum_i e_i f_i}{\sum_i f_i}$. We note that $f_i > 0$, when $0 < T < \infty$, for all i. Hence, the sum on the right hand side is higher than the sum obtained by replacing all e_i by e_1, the lowest energy, yielding $\langle e \rangle > e_1$.

3.1 Bosons

In the case of bosons $\mu < e_1$, to guarantee that all the occupancies

$$n_i = \frac{1}{\exp\left(\frac{e_i - \mu}{kT}\right) - 1}$$

are non-negative.

On the other hand, we concluded above, from Eq. (3), that

$$T\left(\frac{\partial \mu}{\partial T}\right) < \mu - e_1,$$

It follows that $\frac{\partial \mu}{\partial T} < 0$.

An expression that is equivalent to Eq. (3) for the bosonic case was presented by Hu et al. [9], but the universal negativity of $\frac{\partial \mu}{\partial T}$ was not pointed out, although the numerical calculations reported there, for a 3D harmonic spectrum, are in agreement with this fact. A different expression [10], derived in a similar context, does

not appear to be able to be brought into a form in which the negativity of $\frac{\partial \mu}{\partial T}$ is manifested.

3.2 Fermions

In this case, at low temperatures $\mu > e_1$ (assuming that $N > 1$). A definite sign for $\frac{\partial \mu}{\partial T}$ cannot be concluded.

4 Second Derivative of the Chemical Potential for Non-interacting Particles

We will now examine the second derivative of the chemical potential with respect to the temperature (at constant N and V).

Differentiating Eq. (3) with respect to T, we obtain

$$-T\frac{\partial^2 \mu}{\partial T^2} = \frac{1}{\sum_i f_i} \sum_i \left(e_i - \mu + T\frac{\partial \mu}{\partial T} \right) \frac{\partial f_i}{\partial T}. \tag{4}$$

4.1 Bosons

For a system of non-interacting bosons,

$$f_i = \frac{\exp[\beta(e_i - \mu)]}{\{\exp[\beta(e_i - \mu)] - 1\}^2} = \frac{1}{4\left(\sinh\left(\frac{e_i - \mu}{2kT} \right) \right)^2}.$$

We obtain

$$\frac{\partial f_i}{\partial T} = \frac{1}{4kT^2} \frac{\cosh\left(\frac{e_i - \mu}{2kT} \right)}{\left(\sinh\left(\frac{e_i - \mu}{2kT} \right) \right)^3} \left(e_i - \mu + T\frac{\partial \mu}{\partial T} \right). \tag{5}$$

Substituting Eq. (5) in Eq. (4), we obtain

$$-T\frac{\partial^2 \mu}{\partial T^2} = \frac{1}{\sum_i f_i} \sum_i \left(e_i - \mu + T\frac{\partial \mu}{\partial T} \right)^2 \frac{1}{4kT^2} \frac{\cosh\left(\frac{e_i - \mu}{2kT} \right)}{\left(\sinh\left(\frac{e_i - \mu}{2kT} \right) \right)^3}. \tag{6}$$

Since all the terms on the right-hand side are positive, it follows that

$$\frac{\partial^2 \mu}{\partial T^2} < 0.$$

An expression for $\frac{\partial^2 \mu}{\partial T^2}$, for the bosonic case, was presented by Hu et al. [9], in a form that does not reveal its universal negativity. The expression for this second derivative presented in [10] is similarly mute about its universal negativity.

4.2 Fermions

For fermions,

$$f_i = \frac{\exp[\beta(e_i - \mu)]}{\{\exp[\beta(e_i - \mu)] + 1\}^2} = \frac{1}{4\left(\cosh\left(\frac{e_i - \mu}{2kT}\right)\right)^2}.$$

We obtain

$$\frac{\partial f_i}{\partial T} = \frac{1}{4kT^2} \frac{\sinh\left(\frac{e_i - \mu}{2kT}\right)}{\left(\cosh\left(\frac{e_i - \mu}{2kT}\right)\right)^3} \left(e_i - \mu + T\frac{\partial \mu}{\partial T}\right),$$

which, upon substitution in (4) yields

$$-T\frac{\partial^2 \mu}{\partial T^2} = \frac{1}{\sum_i f_i} \sum_i \left(e_i - \mu + T\frac{\partial \mu}{\partial T}\right)^2 \frac{1}{4kT^2} \frac{\sinh\left(\frac{e_i - \mu}{2kT}\right)}{\left(\cosh\left(\frac{e_i - \mu}{2kT}\right)\right)^3}.$$

Since $\sinh\left(\frac{e_i - \mu}{2kT}\right)$ is negative for $e_i - \mu < 0$, the sign of $\frac{\partial^2 \mu}{\partial T^2}$ can be positive, in particular when the contribution of the low-lying energies is dominant (i.e., at low temperatures).

5 Conclusion

Both the first and the second derivatives of the chemical potential of any system of non-interacting indistinguishable bosons have been shown to be negative, at all temperatures. For fermions, the low temperature behavior of the chemical potential depends on the slope of the density of states at the Fermi energy, but the high temperature behavior is generically similar to that of bosons (both approaching Maxwellian behavior).

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