

# Elementary Thermodynamics of Trapped Particles

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## Abstract

I develop simple thermodynamic relations for a collection of noninteracting classical particles confined in a harmonic trap. The volume of such a trap is not a good thermodynamic variable, so conventional expressions of the first law of thermodynamics and the ideal gas law must be modified. I use the frequency of oscillations about the minimum of the trap as an external parameter characterizing the confinement, and derive elementary relations between particle number, temperature, energy, oscillation frequency, and a generalized pressure, that are analogous to conventional thermodynamic relations for an ideal gas in a rigid volume. I also discuss heat capacities for trapped particles.

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## I. INTRODUCTION

The derivation of the ideal gas law is covered in essentially every modern text on thermodynamics and statistical mechanics. This law applies to non-interacting classical particles in a rigid container, and expresses the familiar relationship

$$PV = NkT \tag{1}$$

between the pressure  $P$ , volume  $V$ , number of particles  $N$ , and the temperature  $T$ ;  $k$  is the Boltzmann constant. It is also shown that the energy of of an ideal gas is given by

$$E = \frac{3}{2}NkT. \tag{2}$$

Recent experiments on cooled neutral atoms (which have ultimately led to observations of Bose-Einstein condensation) have been performed in atom traps which in the ideal case have confining potentials of infinite range. Thus volume is not an appropriate thermodynamic variable. It is instructive to consider how the familiar elementary relations of Eqs. (1) and (2) must be modified in these circumstances.

In this paper I consider atoms in isotropic harmonic confining potentials. For particles of mass  $m$  and energy  $E$  confined by a one-dimensional harmonic potential with angular oscillation frequency  $\omega$ , the amplitude of oscillation is  $\sqrt{2E/(m\omega^2)}$ . This suggests using the frequency of oscillation about the minimum of the trap as the externally determined parameter characterizing the confinement of the particles in the trap, and in this note I consider the development of thermodynamic relations which involve  $\omega$  rather than the volume  $V$ .

I follow the approach used in several modern texts to derive the ideal gas law (see, for example, [1–4]). The canonical ensemble partition function is derived in a semi-classical manner, i.e., using information about the spacing and degeneracy of quantized energy levels, and the partition function is then used in combination with the first law of thermodynamics to derive relationships between the thermodynamic variables.

## II. FUNDAMENTAL EQUATIONS

The first law of thermodynamics is an articulation of the work-energy theorem. For a gas in a volume  $V$  this is expressed as

$$\Delta E = \Delta Q - P\Delta V. \quad (3)$$

Although the volume isn't a relevant parameter for particles in a trap, the confining potential can do work on the particles when it is altered. We can express this idea in a modification of the first the first law,

$$\Delta E = \Delta Q + \mathcal{P}\Delta\omega, \quad (4)$$

in which  $\mathcal{P}$  is a "pressure" for which I will derive an expression below. (I use the term "pressure" loosely; this quantity does not have the dimensions of force per unit area.) Note that I have chosen the sign of the second term to be positive in Eq. (4), reflecting the fact that an increase in  $\omega$  corresponds to an increase in the strength of the confinement, which increases the density of the particles and effectively compresses them.

The conventional arguments leading to the definition of the Helmholtz free energy

$$F = E - TS \quad (5)$$

are not affected by the change from confinement in a rigid volume to confinement in a trap. Combining the modified first law with the definition of free energy leads to the relationship

$$dF = -S dT + \mathcal{P} d\omega, \quad (6)$$

which implies

$$\mathcal{P} = + \left( \frac{\partial F}{\partial \omega} \right)_{T,N} \quad (7)$$

and

$$S = - \left( \frac{\partial F}{\partial T} \right)_{\omega,N}. \quad (8)$$

The relationship between the Helmholtz free energy and the partition function is based on general arguments regarding entropy, so that for particles in a trap it is still true that

$$F(T, \omega, N) = -kT \ln Z(T, \omega, N). \quad (9)$$

### III. EXPLICIT PARTITION FUNCTION AND CONSEQUENCES

The partition function for a single particle in a harmonic trap is

$$\begin{aligned}
 Z_1 &= \sum_i e^{-\beta \epsilon_i} \\
 &\longrightarrow \int_0^\infty f(\epsilon) e^{-\beta \epsilon} d\epsilon \\
 &= \int_0^\infty \frac{\epsilon^2}{2(\hbar\omega)^3} e^{-\beta \epsilon} d\epsilon \\
 &= \left( \frac{kT}{\hbar\omega} \right)^3.
 \end{aligned} \tag{10}$$

In the derivation above I have assumed that  $kT \gg \hbar\omega$  and converted the discrete sum into an integral, and I have used the density of states  $f(\epsilon)$  appropriate for a harmonic oscillator potential. Using standard arguments, the partition function for  $N$  non-interacting particles in a dilute gas is

$$\begin{aligned}
 Z &= \frac{1}{N!} [Z_1(T, \omega)]^N \\
 &\simeq \left( \frac{e}{N} \right)^N \left( \frac{kT}{\hbar\omega} \right)^{3N}
 \end{aligned} \tag{11}$$

where in the last line I have used Stirling's approximation for large  $N$ .

The Helmholtz free energy is thus

$$\begin{aligned}
 F &= -kT \ln Z \\
 &= -NkT \ln \left[ \frac{e}{N} \left( \frac{kT}{\hbar\omega} \right)^3 \right].
 \end{aligned} \tag{12}$$

The “pressure”  $\mathcal{P}$  is given by

$$\begin{aligned}
 \mathcal{P} &= + \left( \frac{\partial F}{\partial \omega} \right)_{T, N} \\
 &= \frac{3NkT}{\omega},
 \end{aligned} \tag{13}$$

which gives the analog to the ideal gas law for the trapped particles:

$$\mathcal{P}\omega = 3NkT. \tag{14}$$

The energy of the particles is

$$\begin{aligned}
 E &= - \left( \frac{\partial \ln Z}{\partial \beta} \right)_{N, \omega} \\
 &= 3NkT,
 \end{aligned} \tag{15}$$

which combined with Eqs. (13) shows that

$$E = \mathcal{P}\omega. \quad (16)$$

The linear relationship between energy and oscillation frequency is to be expected given the fact that energy of each quantized single-particle energy level is of the form  $m\hbar\omega$  (where  $m$  is an integer).

#### IV. COMMENT ON HEAT CAPACITY

For conventional ideal gases the heat capacity at constant volume is

$$C_V = \left(\frac{\partial E}{\partial T}\right) = \frac{3}{2}Nk, \quad (17)$$

and this is related to the heat capacity at constant pressure  $C_P$  by the familiar equation

$$C_P - C_V = P \left(\frac{\partial V}{\partial T}\right)_P = Nk. \quad (18)$$

For trapped particles the heat capacity at constant  $\omega$  is

$$C_\omega = \left(\frac{\partial E}{\partial T}\right) = 3Nk. \quad (19)$$

This makes sense because the translational motion of each particle contributes  $3k/2$  to the heat capacity, and the potential energy of the three-dimensional harmonic oscillator confining potential contributes an additional  $3k/2$ . The difference between the heat capacities at constant  $\omega$  and at constant  $\mathcal{P}$  is

$$\begin{aligned} C_P - C_\omega &= -P \left(\frac{\partial \omega}{\partial T}\right)_P \\ &= -3Nk. \end{aligned} \quad (20)$$

This means that

$$C_P = 0. \quad (21)$$

In other words, the energy needed to raise the temperature of the particles by  $\Delta T$  all comes from the work done on the particles by the increase in  $\omega$  that is necessary to keep  $\mathcal{P} = E/\omega$  constant.

## V. CONCLUSION

For particles trapped in smoothly varying long-range potentials volume is not an appropriate thermodynamic variable. Thermodynamics can, however, be developed using other parameters characterizing the confinement of the particles. In this paper I have considered particles in isotropic harmonic traps, and I have used the frequency of oscillations about the minimum of the trap as the confinement parameter analogous to  $V$ . I have derived the analog to the ideal gas law for this simple case, and also formulas for appropriate heat capacities. These simple relations can be used to solve many thermodynamic problems for trapped particles that are analogous to problems for gases in containers with rigid walls that are posed in introductory texts. Generalizations to anisotropic traps and more complicated potentials are certainly possible, and would make good student projects.

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