

# Classical Thermodynamics of Particles in Harmonic Traps

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## Abstract

I develop simple thermodynamic relations for a collection of non-interacting classical particles confined in an isotropic harmonic trap. The volume occupied by the particles in such a trap is not well-defined and pressure varies with position, indicating that the thermodynamic relations should be expressed in terms of more appropriate variables. I use the effective spring constant of the trap as a state variable, and show that the conjugate state variable is proportional to the ensemble average of the mean squared displacement of particles from the center of the trap. New thermodynamic relations are derived in terms of these variables, including the equation of state, the dependence of the internal energy on temperature, as well as expressions for the entropy and heat capacities. I also consider cyclic thermodynamic processes in a harmonically confined gas.

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## I. INTRODUCTION

The equation of state for a gas for  $N$  non-interacting particles in a rigid volume  $V$  is derived in essentially every modern text on thermodynamics and statistical mechanics, yielding the familiar ideal gas law

$$pV = NkT, \tag{1}$$

where  $p$  and  $T$  are the pressure and temperature of the gas and  $k$  is Boltzmann's constant. It is also standard textbook material to derive expressions for the internal energy  $U$ , entropy  $S$ , and heat capacities,  $C_V$  and  $C_p$ . The recent flurry of experimental and theoretical work on cooled neutral atoms confined in external potentials has highlighted an important system of weakly interacting particles that are confined in a manner that does not conform to the conditions of the usual introductory treatments of thermodynamics. The density and pressure vary with position within such atom traps and the volume of the gas is not well defined, and it is an instructive exercise to see how standard textbook statements of thermodynamic relationships like the first law of thermodynamics and the ideal gas law must be modified in this context. Although much of the recent work on trapped atoms has been driven by an interest in the ultracold regime in which quantum statistics plays an important role, the focus of this paper will be in the realm of classical thermodynamics.

I consider a fixed number of atoms in an idealized isotropic harmonic confining potential of infinite extent. The restoring force is given by

$$\mathbf{F}_{\text{trap}} = -br \hat{\mathbf{r}}, \tag{2}$$

where  $\mathbf{r}$  is the displacement of a particle from the minimum of the trap, and  $b$  is an effective spring constant. I show that the effective spring constant of the trap and the mean squared displacement of the particles from the minimum of the trap can serve as state variables for this gas, and I develop simple thermodynamic relations in terms of these variables. These relations include expressions for the first law of thermodynamics, the equation of state, internal energy, entropy, and heat capacities. I also consider cyclic thermodynamic processes for harmonically confined gases. The main results are collected in Table 1.

## II. FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is an articulation of the work-energy theorem, and for conventionally confined particles work is done on the fluid when external forces act on the walls of the container to change its volume, yielding

$$\Delta U = Q - p\Delta V. \quad (3)$$

For a system of harmonically trapped particles there is no surface on which to apply external forces, but the environment can perform compression work on the system of “atoms plus trap” by changing the effective spring constant, so I choose to use  $b$  as a thermodynamic variable characterizing the confinement of the particles. This means that the expression for the compressive work done on the gas must change from  $-p\Delta V$  to something of the form  $\mathcal{A} db$ , where  $\mathcal{A}$  is a quantity with dimensions of area that must be determined. With this change the first law becomes

$$\Delta U = Q + \mathcal{A} \Delta b. \quad (4)$$

Note that the sign of the second term in Eq. (4) is positive, reflecting the fact that an increase in the spring constant corresponds to a stronger confinement of the gas and an increased density, thereby that positive work is being done on the gas.

As a first step in the determination of an expression for the new quantity  $\mathcal{A}$ , I consider a single one-dimensional oscillator with constant mass  $m$  and slowly varying spring constant  $b$ . The equation of motion for this oscillator is identical in form to the time-independent Schrödinger equation for a particle in a potential that varies slowly in space. Direct application of the WKB approximation that is familiar from quantum mechanics<sup>1</sup> gives

$$x(t) \simeq A_0 \frac{\sqrt{\omega(0)}}{\sqrt{\omega(t)}} \exp\left(i \int_0^t \omega(t') dt'\right). \quad (5)$$

This is an oscillation with a slowly varying amplitude that decreases as  $1/\sqrt[4]{b}$ . The energy of the oscillator is

$$E(t) \simeq \frac{1}{2} m A_0^2 \omega(0) \omega(t), \quad (6)$$

giving the differential relationship

$$dE = \frac{1}{4} \left( \frac{A_0^2 \omega(0)}{\omega(t)} \right) db. \quad (7)$$

The term in parentheses is the square of the instantaneous amplitude, which I rewrite for convenience in terms of the average over one cycle of the square of the displacement, giving

$$dE = \frac{1}{2} \bar{x}_{\text{rms}}^2 db. \quad (8)$$

For a three-dimensional oscillator this relationship becomes

$$dE = \frac{1}{2} (\bar{x}_{\text{rms}}^2 + \bar{y}_{\text{rms}}^2 + \bar{z}_{\text{rms}}^2) db = \frac{1}{2} r_{\text{rms}}^2 db, \quad (9)$$

and for  $N$  particles in a trap we have

$$\begin{aligned} dE &= \sum_{i=1}^N \frac{1}{2} (r_{\text{rms}}^2)_i db \\ &= \frac{1}{2} N \langle r^2 \rangle db, \end{aligned} \quad (10)$$

where  $\langle r^2 \rangle$  represents the ensemble average of the mean squared displacement of the particles from the center of the trap. The increased energy of the trapped particles must be the result of work that is done to effect the change in the spring constant, so the factor  $\mathcal{A}$  in the compression work term of the first law is

$$\mathcal{A} = \frac{1}{2} N \langle r^2 \rangle. \quad (11)$$

In the following I will often express relations in terms of  $\langle r^2 \rangle$  instead of the extensive variable  $\mathcal{A}$  because of the obvious connection of the quantity  $\langle r^2 \rangle$  to the size of the gas cloud. For example, the first law of thermodynamics for  $N$  non-interacting particles in a trap can be written as

$$\Delta U = Q + \frac{1}{2} N \langle r^2 \rangle \Delta b. \quad (12)$$

It should be noted that knowledge of  $\langle r^2 \rangle$  for a gas of particles in thermodynamic equilibrium in a harmonic trap is sufficient to determine the density distribution of the particles. In thermal equilibrium the spatially varying density in the trap is proportional to  $\exp(-br^2/2kT)$ , which depends on the single ratio  $b/T$ . Knowledge of any moment of this distribution fixes this ratio, and thus all moments are determined.

### III. EQUATIONS OF STATE AND INTERNAL ENERGY

To derive the equations of state of a trapped gas, I parallel the treatment of the conventional ideal gas that is given in several modern texts.<sup>2-5</sup> In these treatments the ideal gas

law is derived from the Helmholtz free energy expressed in terms of the canonical ensemble partition function.

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

$$F = U - TS \quad (13)$$

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

$$dF = -S dT + \mathcal{A} db, \quad (14)$$

which implies

$$\mathcal{A} = + \left( \frac{\partial F}{\partial b} \right)_{T,N} \quad (15)$$

and

$$S = - \left( \frac{\partial F}{\partial T} \right)_{b,N}. \quad (16)$$

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

$$F(T, b, N) = -kT \ln Z(T, b, N). \quad (17)$$

The partition function for a single particle is the sum of the Boltzmann factors over all of the single-particle states. If we make the assumption that the level spacing is small compared to thermal energies, i.e.,  $\beta \equiv 1/kT \ll \hbar\omega$ , the sum can be approximated with an integral, yielding

$$Z_1 = \sum_i e^{-\beta\epsilon_i} \longrightarrow \int_0^\infty f(\epsilon) e^{-\beta\epsilon} d\epsilon, \quad (18)$$

where  $f(\epsilon)$  is the density of states. Inserting the density of states for a three-dimensional harmonic potential<sup>6</sup> gives

$$\begin{aligned} Z_1 &= \int_0^\infty \frac{\epsilon^2}{2(\hbar\omega)^3} e^{-\beta\epsilon} d\epsilon \\ &= \left( \frac{kT}{\hbar\omega} \right)^3. \end{aligned} \quad (19)$$

Using standard arguments, the partition function for  $N$  non-interacting particles in a dilute gas is

$$Z = \frac{1}{N!} [Z_1(T, \omega)]^N$$

$$\simeq \left(\frac{e}{N}\right)^N \left(\frac{kT}{\hbar\omega}\right)^{3N} \quad (20)$$

where I use Stirling's approximation for large  $N$ . The Helmholtz free energy is thus

$$\begin{aligned} F &= -kT \ln Z \\ &= -NkT \ln \left[ \frac{e}{N} \left(\frac{kT}{\hbar\omega}\right)^3 \right]. \end{aligned} \quad (21)$$

The formula for the free energy given in Eq. (21) can now be used to derive thermodynamic expressions for the variables  $\mathcal{A}$  and  $S$  using Eqs. (15) & (16). For  $\mathcal{A}$  we have

$$\begin{aligned} \mathcal{A} &= + \left(\frac{\partial F}{\partial b}\right)_{T,N} = \left(\frac{\partial F}{\partial \omega}\right)_{T,N} \frac{d\omega}{db} \\ &= \frac{3NkT}{2b}. \end{aligned} \quad (22)$$

Combining this expression for  $\mathcal{A}$  in terms of thermodynamic variables with Eq. (11) derived by considering the work done on the particles gives the analog to the ideal gas law for the trapped particles

$$\mathcal{A}b = \frac{3}{2}NkT, \quad (23)$$

or equivalently,

$$\langle r^2 \rangle b = 3kT. \quad (24)$$

The entropy  $S$  is given by

$$S = - \left(\frac{\partial F}{\partial T}\right)_{b,N} = Nk \left\{ \ln \left[ \frac{e}{N} \left(\frac{U}{3\hbar\omega}\right)^3 \right] + 3 \right\}. \quad (25)$$

This is an analog of the Sackur-Tetrode equation<sup>2</sup> giving the entropy of an ideal gas in a rigid volume.

The internal energy can also be derived from the partition function:

$$\begin{aligned} U &= - \left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,\omega} \\ &= 3NkT. \end{aligned} \quad (26)$$

This result could be anticipated by considering the equipartition of energy among the translational degrees of freedom and the potential energy stored in the three-dimensional ‘‘springs’’ of the trap.

	Rigid Volume	Harmonic Trap
First Law	$\Delta U = Q - p\Delta V$	$\Delta U = Q + \mathcal{A}\Delta b$ or $\Delta U = Q + \frac{1}{2}N\langle r^2 \rangle \Delta b$
Equation of State	$pV = NkT$	$\mathcal{A}b = \frac{3}{2}NkT$ or $\langle r^2 \rangle b = 3kT$
Internal Energy	$U = \frac{3}{2}NkT$	$U = 3NkT$
Entropy	$S = Nk \left\{ \ln \left[ \frac{V}{N} \left( \frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$	$S = Nk \left\{ \ln \left[ \frac{e}{N} \left( \frac{U}{3\hbar\omega} \right)^3 \right] + 3 \right\}$
Heat Capacities	$C_V = \frac{3}{2}Nk$ and $C_p = C_V + Nk$	$C_b = 3Nk$ and $C_{\mathcal{A}} = C_b - \frac{3}{2}Nk$
Adiabatic Process	$pV^\gamma = \text{constant}$  $\left( \gamma = \frac{C_p}{C_V} \rightarrow \frac{5}{3} \right)$	$\mathcal{A}b^{\gamma'} = \text{constant}$ or $\langle r^2 \rangle b^{\gamma'} = \text{constant}$  $\left( \gamma' = \frac{C_{\mathcal{A}}}{C_b} \rightarrow \frac{1}{2} \right)$

TABLE I: Comparison of thermodynamic relations for non-interacting gases confined in rigid volumes and confined in harmonic traps with effective spring constant  $b$ .

#### IV. CYCLIC THERMODYNAMIC PROCESSES

Although harmonically trapped gases do not provide a practical means for converting heat into work, it is still an instructive pedagogical exercise to consider cyclic processes. In Fig. 1, I illustrate a reversible cycle that is analogous to the familiar Carnot cycle. Note that the state variables I have chosen result in a change in interpretation from conventional  $p$ - $V$  diagrams: the work done by the gas is positive when paths in  $\langle r^2 \rangle$ - $b$  space are traversed in the direction of *decreasing* spring constant  $b$ . The equation of state given in Eq. (23) or Eq. (24) shows that isotherms for harmonically trapped gases are still hyperbolas. For adiabatic processes the combination of the equation of state with the first law given by

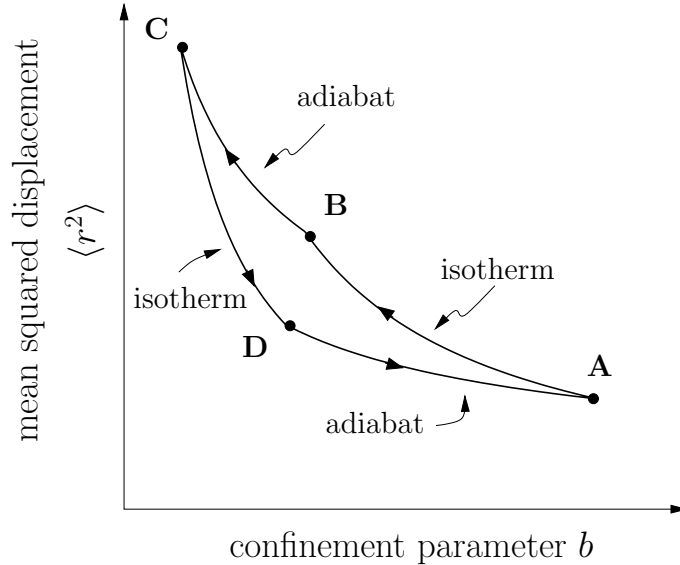


FIG. 1: A cyclic reversible process for a harmonically trapped gas. The gas begins at point **A** and undergoes the following sequence: i) isothermal expansion, ii) adiabatic expansion, iii) isothermal compression, and iv) adiabatic compression. Note that the cycle must be traversed in a *counter-clockwise* direction if the work done by the gas is to be positive.

Eq. (4) yields

$$\langle r^2 \rangle b^{\gamma'} = \text{constant}, \quad (27)$$

where

$$\gamma' = \frac{C_A}{C_b} \rightarrow \frac{1}{2}. \quad (28)$$

At the intersection of isotherms and adiabats the isotherms are “steeper,” which is the reverse of the situation in the usual Carnot cycle. Therefore the adiabats form the “top” and “bottom” of the closed cycle, and the isotherms are on the “sides.” It is straightforward to calculate the net work done by the trapped gas during the cycle, as well as the heat absorbed from the hot reservoir, and to show that the efficiency of the heat engine is  $1 - T_C/T_H$ , as it must be for any reversible cycle operating between two thermal reservoirs.

During the adiabatic reduction of the spring constant, the gas cools, and this raises the question of whether the gas approaches the conditions necessary for Bose-Einstein condensation during this cooling. During an adiabatic reduction of  $b$  the product  $\langle r^2 \rangle b^{1/2}$  is constant,

and using the equation of state to eliminate  $\langle r^2 \rangle$  we find that

$$T \propto b^{1/2} \quad (29)$$

during expansion and cooling. The critical temperature for the onset of Bose-Einstein condensation in an isotropic harmonic potential is<sup>6,7</sup>

$$kT_c = \left( \frac{2N}{2.404} \right)^{1/3} \hbar\omega. \quad (30)$$

Because the critical temperature depends on  $\omega$ , and both  $\omega$  and  $T$  scale as  $b^{1/2}$ , this adiabatic cooling process does not bring the gas closer to the critical temperature. Similar reasoning indicates that a gas of fermions does not approach the degeneracy limit.

## V. HEAT CAPACITIES

For conventionally confined ideal gases the heat capacity at constant volume is

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2}Nk, \quad (31)$$

and the heat capacity at constant pressure is

$$\begin{aligned} C_p &= \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p \\ &= C_V + Nk \end{aligned} \quad (32)$$

For trapped particles the heat capacity at constant spring constant  $b$  is

$$C_b = \left( \frac{\partial U}{\partial T} \right)_b = 3Nk, \quad (33)$$

and the heat capacity at constant  $\mathcal{A}$ , or equivalently constant density profile, is

$$\begin{aligned} C_{\mathcal{A}} &= \left( \frac{\partial U}{\partial T} \right)_{\mathcal{A}} - \mathcal{A} \left( \frac{\partial b}{\partial T} \right)_{\mathcal{A}} \\ &= C_b - \frac{3}{2}Nk. \end{aligned} \quad (34)$$

The fact that  $C_{\mathcal{A}}$  is less than  $C_b$  reflects the fact that in order to maintain the constant size of the gas as thermal energy is added to the system the spring constant  $b$  must increase, implying that work is being done on the system as the heat is added.

## VI. CONCLUSION

Thermodynamic variables and relations for gases confined in particle traps with smoothly varying long-range potentials are not the same as their counterparts for gases confined in rigid volumes. In this paper I have used the spring constant  $b$  and the mean squared displacement  $\langle r^2 \rangle$  as state variables characterizing the confinement and the size respectively. (I note that other authors have made chosen different variables.<sup>8,9</sup>) For isotropic harmonic traps the derivation of new thermodynamic relationships in terms of  $b$  and  $\langle r^2 \rangle$  is straightforward and closely parallels the standard textbook derivations of the more familiar relationships appropriate for gases in rigid volumes, and some parts of the derivation are actually simpler for harmonically confined gases because of the ease of the derivation of an analytical expression for the partition function in this case. (Fermi took advantage of this simplification in his early papers on the quantization of ideal gases<sup>10,11</sup> which are reprinted in his collected works.<sup>12</sup> In contrast to this work, Fermi considered position-dependent pressures and densities in harmonic potentials.) The relationships summarized in Table 1 can be used to solve many textbook-style thermodynamic problems for harmonically trapped particles. Generalizations to anisotropic traps<sup>13</sup> and more complicated potentials are certainly possible, and would make good student projects.

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