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Classical thermodynamics of particles in harmonic traps

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I develop simple thermodynamic relations for a system of noninteracting classical particles confined in an isotropic harmonic trap. The volume occupied by the particles in such a trap is not well defined, and the 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 the particles from the center of the trap. Thermodynamic relations are derived in terms of these variables, including the pressure and thermal equations of state, the entropy, and the heat capacities. I also consider cyclic thermodynamic processes in a harmonically confined gas. © 2010 American Association of Physics Teachers.
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I. INTRODUCTION

The pressure equation of state for a gas of N noninteracting particles in a rigid volume V is derived in almost every text on thermodynamics and statistical mechanics, yielding the familiar ideal gas law

$$PV = NkT, \quad (1)$$

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 the 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 traps, and the volume of the gas is not well defined. It is instructive to see how standard textbook statements of the first law of thermodynamics and the ideal gas law must be modified for this example of a gas in an inhomogeneous potential. Although much of the recent work on trapped atoms has been motivated by interest in the ultracold regime in which quantum statistics plays an important role, the focus of this paper is in the realm of classical thermodynamics.

There are many examples of thermodynamics applied to systems with inhomogeneous potentials, such as the atmosphere. In the standard treatment of such systems,¹⁻³ thermodynamic variables such as temperature and pressure become functions of position, and thermodynamic relations are converted into differential equations. In this paper I show that the atoms in a harmonic trap can be characterized by parameters that are not functions of position and therefore can be treated analogously to the ideal gas in a rigid volume without recourse to differential equations. The switch from the familiar pressure and volume to new variables provides an interesting exercise in which the meaning of familiar thermodynamic relations must be reconsidered in a new context.

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

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

where \mathbf{r} is the displacement of a particle from the minimum of the trap and b is an effective spring constant. The state of the familiar ideal gas can be specified by two of the three variables P , V , and T . Similarly, the state of the trapped gas can be specified by two variables, but they are chosen from a set including the temperature, a variable characterizing the strength of the confinement, and a variable characterizing the spatial extent of the trapped gas. 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 and develop simple thermodynamic relations in terms of these variables. These relations include expressions for the first law of thermodynamics, the pressure equation of state, and the internal energy, entropy, and heat capacities. I also consider cyclic thermodynamic processes for harmonically confined gases. The main results are collected in Table I.

II. FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is an expression of the work-energy theorem. For conventionally confined particles, work is done on the system when external forces act on the walls of the container to change its volume. If the forces act reversibly, the first law can be expressed as

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

For a system of harmonically trapped particles, there is no surface on which to apply external forces, and thus the term $-P\Delta V$ expressing the reversible work done on the system must be replaced. Reversible work can be done on the system of atoms plus trap only by changing the effective spring constant. Hence, I use b as a thermodynamic variable characterizing the confinement of the particles, and the expression for the mechanical work on the gas must have the form $\mathcal{A}db$, where \mathcal{A} is a quantity with dimensions of area that characterizes the physical size of the trapped gas. (The expression for \mathcal{A} will be determined in the following.) With this change the first law becomes

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

The sign of the second term in Eq. (4) is positive, reflecting that an increase in the spring constant corresponds to a stron-

Table I. Comparison of thermodynamic relations for noninteracting gases confined in rigid volumes and confined in harmonic traps with effective spring constant b .

	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	$S = Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3N\hbar^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$	$S = Nk \left\{ \ln \left[\frac{e}{N} \left(\frac{U}{3\hbar\omega} \right)^3 \right] + 3 \right\}$
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	$PV^\gamma = \text{constant}$ $\gamma = \frac{C_P}{C_V} \rightarrow \frac{5}{3}$	$\mathcal{A}b^{\gamma'} = \text{constant}$ or $\langle r^2 \rangle b^{\gamma'} = \text{constant}$ $\gamma' = \frac{C_{\mathcal{A}}}{C_b} \rightarrow \frac{1}{2}$

ger confinement of the gas, increased density, and positive work on the gas.

The form of the first law in Eq. (4) runs counter to the intuition that we develop in studying ideal gases in rigid containers. It might seem more natural to express the term describing mechanical work as $-b\Delta\mathcal{A}$ instead of $\mathcal{A}\Delta b$. The former would make the coefficient of the differential element an intensive variable (analogous to pressure in the familiar first law), and the differential element would represent the change in the variable characterizing the spatial extent of the system (analogous to volume). This reasoning is insufficient in this case. To see why, consider the familiar case of a gas in a rigid volume. There are processes, such as stirring, that can increase the pressure from P to $P + \Delta P$ (and increase the internal energy) while keeping the volume fixed, but none of these processes involve reversible work; reversible work can be effected only by external forces acting on the walls to change the volume. For a harmonically confined gas, processes such as stirring can increase the spatial extent of the gas without a change in the spring constant, but reversible work can only be affected if energy is expended by an external agent to change the spring constant and thus the state of the confined gas.

The fact that the role of intensive and extensive variables is reversed between Eqs. (3) and (4) is not really relevant. In most expressions of the first law, the differential element is expressed in terms of an extensive variable, but there is no *a priori* reason for this form to be the case.⁴ Additional support for the form of the first law in Eq. (4) will be seen in its consequences. As I discuss in Sec. V, the expressions for the heat capacities depend on the form of the first law, and the use of $-b\Delta\mathcal{A}$ as the work term leads to unphysical results.

As a first step in the determination of \mathcal{A} , I consider a single one-dimensional oscillator with constant mass m and slowly varying spring constant b with the displacement of the mass from its equilibrium position given by the real part

of the complex quantity $\tilde{x}(t)$. The form of the complex equation of motion for the oscillator is identical to the time-independent Schrödinger equation for a particle in a potential that varies slowly in space. The application of the WKB approximation gives (see, for example, Ref. 5)

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

Equation (5) represents an oscillation with a slowly varying amplitude that decreases as $1/\sqrt{\omega}$ or equivalently $1/b^{1/4}$. The energy of the oscillator is

$$E(t) \approx \frac{1}{2} mA_0^2 \omega(0) \omega(t), \quad (6)$$

which gives the differential relation

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

The term in parentheses is the square of the slowly varying amplitude, which I rewrite for convenience in terms of \bar{x}_{rms}^2 , the average over one cycle of the square of the real displacement,

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

For a three-dimensional oscillator, Eq. (8) becomes

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

For N particles in a trap we have

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

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 the work that is done to change the spring constant. Therefore the factor \mathcal{A} in the mechanical 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 $\langle r^2 \rangle$ to the spatial extent of the gas. For example, the first law of thermodynamics for N noninteracting particles in a trap can be written as

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

Note that knowledge of $\langle r^2 \rangle$ for a gas of particles in thermodynamic equilibrium in a harmonic trap is sufficient to determine the entire 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 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.⁶⁻⁹ In this treatment 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 $F=U-TS$ are not affected by the change from confinement in a rigid volume to confinement in a trap. If we combine the modified first law with the definition of free energy, we obtain the relation

$$dF = -SdT + \mathcal{A}db, \quad (13)$$

which implies

$$\mathcal{A} = + \left(\frac{\partial F}{\partial b} \right)_{T,N} \quad (14)$$

and

$$S = - \left(\frac{\partial F}{\partial T} \right)_{b,N}. \quad (15)$$

The relation between F and the partition function Z is based on general arguments regarding the entropy, and hence for particles in a trap it still holds that

$$F(T, b, N) = -kT \ln Z(T, b, N). \quad (16)$$

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, that is, $\beta \equiv 1/kT \ll \hbar\omega$, the sum can be approximated by an integral, yielding

$$Z_1 = \sum_s e^{-\beta\epsilon_s} \rightarrow \int_0^\infty f(\epsilon) e^{-\beta\epsilon} d\epsilon, \quad (17)$$

where $f(\epsilon)$ is the density of states. I substitute the density of states for a three-dimensional harmonic potential¹⁰ and find

$$Z_1 = \int_0^\infty \frac{\epsilon^2}{2(\hbar\omega)^3} e^{-\beta\epsilon} d\epsilon = \left(\frac{kT}{\hbar\omega} \right)^3. \quad (18)$$

The partition function for N noninteracting particles in a dilute gas is

$$Z = \frac{1}{N!} [Z_1(T, \omega)]^N \approx \left(\frac{e}{N} \right)^N \left(\frac{kT}{\hbar\omega} \right)^{3N}, \quad (19)$$

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

$$F = -kT \ln Z = -NkT \ln \left[\frac{e}{N} \left(\frac{kT}{\hbar\omega} \right)^3 \right]. \quad (20)$$

The expression for F in Eq. (20) can be used to derive thermodynamic expressions for \mathcal{A} and S using Eqs. (14) and (15). We have

$$\mathcal{A} = \left(\frac{\partial F}{\partial b} \right)_{T,N} = \left(\frac{\partial F}{\partial \omega} \right)_{T,N} \frac{d\omega}{db} = \frac{3NkT}{2b}. \quad (21)$$

If I combine Eq. (21) for \mathcal{A} in terms of thermodynamic variables with Eq. (11) derived by considering the work done on the particles, I find the analog to the ideal gas law for the trapped particles

$$\mathcal{A}b = \frac{3}{2} NkT \quad (22)$$

or equivalently

$$\langle r^2 \rangle b = 3kT. \quad (23)$$

The entropy S is given by

$$S = - \left(\frac{\partial F}{\partial T} \right)_{b,N} = Nk \left\{ \ln \left[\frac{e}{N} \left(\frac{U}{3\hbar\omega} \right)^3 \right] + 3 \right\}. \quad (24)$$

Equation (24) is an analog of the Sackur-Tetrode equation⁶ for the entropy of an ideal gas in a rigid volume.

The internal energy can also be derived from the partition function

$$U = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{N,\omega} = 3NkT. \quad (25)$$

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.

IV. CYCLIC THERMODYNAMIC PROCESSES

Although harmonically trapped gases do not provide a practical means for converting heat into work,¹¹ it is an instructive exercise to consider cyclic processes. In Fig. 1 I illustrate a reversible cycle that is analogous to the familiar Carnot cycle. The chosen state variables result in a change in interpretation from conventional P - V diagrams. That is, the work done by the gas is positive when paths in $\langle r^2 \rangle$ - b space are traversed in the direction of decreasing b . The equation

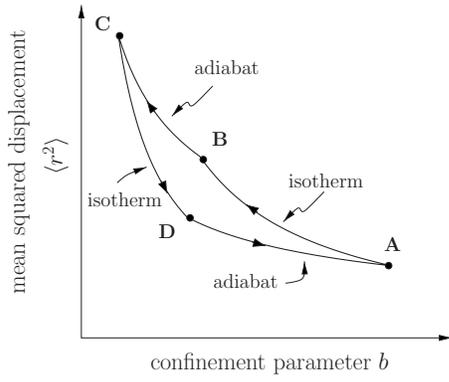


Fig. 1. A cyclic reversible process for a harmonically trapped gas. The gas begins at point A and undergoes the following sequence: Isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression. The cycle must be traversed in a counterclockwise direction if the work done by the gas is to be positive.

of state given in Eq. (22) or Eq. (23) shows that the isotherms for harmonically trapped gases are still hyperbolas. For adiabatic processes the combination of the equation of state with the first law given by Eq. (4) yields

$$\langle r^2 \rangle b^{\gamma'} = \text{constant}, \quad (26)$$

where

$$\gamma' = \frac{C_A}{C_b} \rightarrow \frac{1}{2}. \quad (27)$$

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, which raises the question of whether the gas approaches the conditions necessary for Bose–Einstein condensation during this cooling. (Approaching the critical temperature too closely would require a treatment that goes beyond the classical thermodynamics discussed in this paper.) During an adiabatic reduction of b , the product $\langle r^2 \rangle b^{1/2}$ is constant. I use the equation of state to eliminate $\langle r^2 \rangle$ and find that

$$T \propto b^{1/2} \quad (28)$$

during expansion and cooling. The critical temperature for the onset of Bose–Einstein condensation in an isotropic harmonic potential is^{10,12}

$$kT_c = \left(\frac{2N}{2.404} \right)^{1/3} \hbar\omega. \quad (29)$$

Because the critical temperature depends on ω and both ω and T scale as $b^{1/2}$, adiabatic cooling does not bring the gas closer to the critical temperature. This result can also be understood from simple scaling arguments. Even though the density n in the trap is not homogeneous and the de Broglie wavelength is not constant in the trapping potential, it is still

reasonable to consider an approximate phase space density. The number density scales as $1/\langle r^2 \rangle^{3/2}$, and the wavelength scales as $\lambda_{\text{dB}} \sim 1/\sqrt{T}$. The relation between temperature and spring constant given by Eq. (28) shows that the phase space density $n\lambda_{\text{dB}}^3$ is unaffected by adiabatic changes in the spring constant b .

V. HEAT CAPACITIES

The derivation of the appropriate heat capacities is straightforward but instructive. In particular, it highlights how the results for the heat capacity depend on the form of the first law. If T and b are chosen as the independent variables characterizing the trapped gas, then

$$dU = \left(\frac{\partial U}{\partial T} \right)_b dT + \left(\frac{\partial U}{\partial b} \right)_T db. \quad (30)$$

If we use Eq. (30) in the first law, Eq. (4), we obtain

$$dQ = \left(\frac{\partial U}{\partial T} \right)_b dT + \left[\left(\frac{\partial U}{\partial b} \right)_T - \mathcal{A} \right] db, \quad (31)$$

from which the heat capacity at fixed spring constant follows,

$$C_b = \left(\frac{\partial U}{\partial T} \right)_b = 3Nk. \quad (32)$$

Alternatively, if T and \mathcal{A} are chosen as the independent variables, then

$$dU = \left(\frac{\partial U}{\partial T} \right)_\mathcal{A} dT + \left(\frac{\partial U}{\partial \mathcal{A}} \right)_T d\mathcal{A} \quad (33)$$

and

$$db = \left(\frac{db}{dT} \right)_\mathcal{A} dT + \left(\frac{db}{d\mathcal{A}} \right)_T d\mathcal{A}. \quad (34)$$

Using these expressions in the first law gives

$$dQ = \left[\left(\frac{\partial U}{\partial T} \right)_\mathcal{A} - \mathcal{A} \left(\frac{db}{dT} \right)_\mathcal{A} \right] dT + \left[\left(\frac{\partial U}{\partial \mathcal{A}} \right)_T - \left(\frac{db}{d\mathcal{A}} \right)_T \right] d\mathcal{A}, \quad (35)$$

from which the heat capacity at constant \mathcal{A} , or equivalently constant density profile, follows,

$$C_\mathcal{A} = \left(\frac{\partial U}{\partial T} \right)_\mathcal{A} - \mathcal{A} \left(\frac{db}{dT} \right)_\mathcal{A} = C_b - \frac{3}{2}Nk. \quad (36)$$

The fact that $C_\mathcal{A}$ is less than C_b reflects the fact that to maintain the constant spatial extent of the gas as energy is added to the system, the spring constant b must increase, implying that work is being done on the system as the energy is added. For comparison, the familiar results for heat capacities of a conventionally confined gas at constant pressure and volume are given in Table I.

The results for the heat capacities given in Eqs. (32) and (36) depend critically on the form of the first law of thermodynamics. The alternative form of the first law discussed in the paragraph following Eq. (4) would give different results for the heat capacities. In particular, it would reverse the relative sizes of the two heat capacities C_b and $C_\mathcal{A}$, which is an unphysical result for a trapped gas.

VI. DISCUSSION

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 used the spring constant b and the mean squared displacement $\langle r^2 \rangle$ as state variables characterizing the confinement and the spatial extent respectively. (Other choices of variables have been made; see, for example, Refs. 13 and 14.) For isotropic harmonic traps the derivation of thermodynamics relations in terms of b and $\langle r^2 \rangle$ is straightforward and closely parallels the standard derivations of the more familiar relations appropriate for gases in rigid volumes. Some parts of the derivation are actually simpler for harmonically confined gases because of the ease of deriving an analytical expression for the partition function in this case. The relations summarized in Table I can be used to solve many textbook-style thermodynamic problems for harmonically trapped particles. Generalizations to anisotropic traps¹⁵ and more complicated potentials would make good student projects.

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¹¹In doing an experiment on a trapped gas, it is easy to conceive of ways in which to change the confinement parameter reversibly, such as slowly changing the current to the coils providing a magnetic field. Work is done by (or on) the electrical apparatus supplying the current. If the trapped gas is in a vacuum, adiabatic processes will result, and if the trapped gas interacts with a background gas that does not feel the trap and is maintained at a constant temperature, the processes will be isothermal. The experimental challenges of achieving these regimes and switching between them on the necessary time scale suggest that cyclic processes in trapped gases will remain as thought experiments.

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Physics and Engineering

Conceive of a sinner who is a Catholic and devout. What complexity in his feeling for the Church, what pieties of observance live between his sins. He has to make such intricate shows of concealment to his damned habits. Yet how simple is the Church's relation to him. Extreme Unction will deliver his soul from a journey through hell.

So it is with physics and engineering. Physics is the church, and engineering the most devout sinner. Physics is the domain of beauty, law, order, awe, and mystery of the purest sort; engineering is partial observance of the laws, and pattering with machines which never work quite as they should work: engineering, like acts of sin, is the process of proceeding boldly into complex and often forbidden matters about which one does not know enough – the laws remain to be elucidated – but the experience of the past and hunger for the taste of the new experience attract one forward. So bridges were built long before men could perform the mathematics of the bending moment.

Norman Mailer, *Of a Fire on the Moon* (Little, Brown & Co., Boston, 1970) p. 229–230. Quote suggested by Bartley L. Cardon.