Work in Mechanical Systems

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Abstract

Traditionally in thermodynamics mechanical work is defined in terms of PdV. Although it is empirically correct to consider all mechanical work in terms of PdV, we shall show that it is theoretically incorrect to do so. More specifically, from a theoretical perspective, mechanical work should often be expressed in terms of VdP and not PdV.

Key words: mechanics, work, pressure, volume, energy, thermodynamics, first law

1. INTRODUCTION

The basis of thermodynamics was formulated in the 19th century, and the 20th-century use of statistical physics just served as a continuation of its proof. Accordingly, to many, thermodynamics is void of any doubt. However, such an assertion puts statistical ensembles over and above simple differential calculus and possibly common sense.

The first law of thermodynamics is often written in the form[1–4]

$$du = dq - dw, \qquad (1)$$

where du represents the infinitesimal change to a system's internal energy, while dq and dw, respectively, represent any heat absorbed and any work done by that system. We traditionally limit dw to the isobaric, isothermal case, writing

$$dw = Tds = du + Pdv, \qquad (2)$$

where ds and dv, respectively, represent any infinitesimal change to the system's entropy and volume, while T and P, respectively, signify some constant temperature and pressure. Combining (1) and (2) gives "the *fundamental equation* of equilibrium thermodynamics for homogeneous fluids":[1]

$$ds = (du + Pdv)/T. \qquad (3)$$

Another fundamental traditional thermodynamic principle is the second law:

$$dS \geq 0. \qquad (4)$$

A statistical physics representation of entropy is given by

$$S = k \ln \Omega, \qquad (5)$$

where k is Boltzmann's constant and Ω represents the number of permissible states.

Entropy's indoctrination, via statistical physics, has become essential to all scientific disciplines.[5–8] Volchan[1] points out that "thermodynamics is an incredibly successful theory, in spite of being marred by a long history of conceptual problems ... Still it is a phenomenological theory in the sense that there is no hint about underlying mechanism that could explain the thermodynamic laws in terms of more basic constituents."

This paper will demonstrate that a simpler thermodynamic perspective does exist for mechanical systems. Its feasibility does not necessitate statistical mechanics, quantum theory, or any other elaborate device. Rather, it is based upon simple differentials of the enthalpy relation! The problem of acceptance may be more enshrined in human nature than logic, as those well versed in thermodynamics may distance themselves from any prospect of statistical mechanics becoming a valid mathematical device, which provides results rather than reasons.

Before we continue, it should be stated that there are those who question certain fundamental principles of traditional thermodynamics, that is, the small but growing group who are questioning the validity of the second law of thermodynamics.[9–13]

2. SIMPLE DIFFERENTIATION

Consider the fundamental parameters that define any system: entropy (S), absolute temperature (T), pressure (P), volume (V), and energy (E). S and T are the thermal parameters, while P and V are the mechanical parameters. E is taken to represent all other forms of energy, including the internal energy (U) associated with interactions between the system's molecules and energies associated with any tensile surfaces. The parameters are related by

$$TS = E + PV, \qquad (6)$$

with the right-hand side of (6) being the enthalpy relation. The simplest approach to thermodynamic change should be attainable by differentiating (6):

$$d(ST) = dE + d(PV). \qquad (7)$$

Some would argue that thermodynamics is more than the above simple differentiation! Accordingly, we utilize the inherent physical principles held within (1) through (5) and employ differentiation when it suits those physical principles. Should we be satisfied with believing that the physical principles are more valid than differential calculus? Perhaps. But what if this is not the case?

If the change is both isobaric and isothermal, then (7) becomes the traditional equation for work (W):[1–3]

$$W = TdS = dE + PdV. \qquad (8)$$

By limiting mechanical work to volume change, from a purely mathematical perspective, we have failed to equally treat pressure and volume as parameters of relevance. Must we believe that work cannot be associated with pressure change? This seems contrary to Gibbs,[14] who considered the work required to nucleate a globule in terms of pressure change.[1]

Furthermore, when we consider the nucleation of droplets or bubbles, the energy required for the nucleation process is often defined in terms of work. The work required is the energy needed to form any tensile layer plus any energy changes associated with PV space (enthalpy). Interestingly, traditional thermodynamics, when applied to nucleation theory, has led to numerous complicated theories,[15–22] none of which seem to properly explain the energy requirements for either bubble or droplet nucleation.

Based upon the very premise that we should treat pressure and volume equally in terms of the work

required for nucleation, a correlation between theory and laser-induced bubble nucleation has been found by Mayhew.[23] The correlation was obtained by examining the data from Wolfrum et al.,[24] wherein it was stated that current theory cannot properly explain their findings for the energy required to nucleate water vapor bubbles. The fit between data and Mayhew's bubble equation[2] has been confirmed by one of Wolfrum's associates (W. Lauterborn[3]).

Mayhew[23] has hypothesized that a general equation for the work done by, or on, any system, be written as follows:

$$W = dE + d(PV). \qquad (9)$$

Of course the problem for most scholars in accepting (9) is that it does not necessitate the convoluted path of limiting work to the isobaric isothermal case, nor does it define thermodynamics in terms of an ensemble of molecules with certain energy states. It simply treats pressure and volume equally as parameters of relevance! Its simple differentiation is no longer biased against by questionable physical principles!

3. IDEAL GAS

Consider an ideal gas in terms of PV space. Both its internal energy and total energy remain constant during adiabatic compression or expansion, within an insulated container. In this case we can write

$$PdV = -VdP. \qquad (10)$$

In (10) we considered pressure and volume as being equals. Interestingly, the following conundrum arises. If volume change multiplied by pressure (PdV) signifies mechanical work, then why isn't the energy associated with the pressure change (VdP) considered work? We accept that one counters the other in (10). One may argue that (10) can be explained in terms of (1) with $dw = pdv$ and $dq = vdp$. But is that a simpler explanation than saying that the total work done on the gas is zero because the work associated with pressure change (VdP) counters that associated with volume change (PdV)?

4. WALLS

Traditional thermodynamics in part dodges the previous conundrum by considering that the work is done on the system's walls (Reif,[4] p. 77): "consider an arbitrary slow expansion of the system from the volume enclosed by the solid boundary to that en-

closed by dotted boundary in" Fig. 1. "If the mean pressure is $\overline{P}$, the mean force on an element of area dA is $\overline{P}\,dA$ in the direction of the normal **n**. If the displacement of this element of area is by an amount ds in the direction making an angle θ with the normal, then the work done by the pressure on this area $(\overline{P}\,dA)ds\cos\theta = \overline{P}\,dv$, where $dv \equiv (dAds\cos\theta)$ is the volume of the parallelepiped swept out by area element dA in its motion through ds. Summing over all the elements of area of the boundary surface gives for the total work" $dW = \overline{P}\,dV$.

If traditional thermodynamics is correct in its assertion that the work is done on the container's walls in an expanding volume, then it must be the container's walls that perform the work when the system is contracting. Certainly, the above has some validity when applied to walls that are elastic in nature (i.e., a balloon), but we can readily disprove the generalization of such a thought process by considering the expansion and/or compression of a sealed cylinder of ideal gas.

5. WORK IN THE EXPANSION AND COMPRESSION OF A SEALED CYLINDER

Consider a hermetically sealed cylinder filled with an ideal gas, at 1-atm pressure, as is shown in Fig. 2. Next we pull the piston outward a distance, dx, with a force of magnitude F, as is shown in Fig. 3. The work (W) required for the piston to move dx is

$$W = Fdx. \tag{11}$$

Dividing the force (F) by the piston's surface area (A) gives the pressure ($P = F/A$). Also, multiplying the distance, dx, by the piston's surface area (A) gives the volume ($V = Adx$). Accordingly,

$$W = (F/A)Adx = PdV. \tag{12}$$

Up to now we have considered that work simply depends upon the endpoints. In order to solve (12) traditional thermodynamics realized that the force we need to apply to the piston increases the farther away from the neutral position we are. Since the force varies depending upon position, we must use the concept of the integration of increments of work: $W = \int dw$. Also, we substitute in for $P = NkT/V$, which is based upon the ideal gas law, where k is Boltzmann's constant and N represents the number of gas molecules. We also let subscripts 1 and 2, respectively, represent the initial and final states and obtain

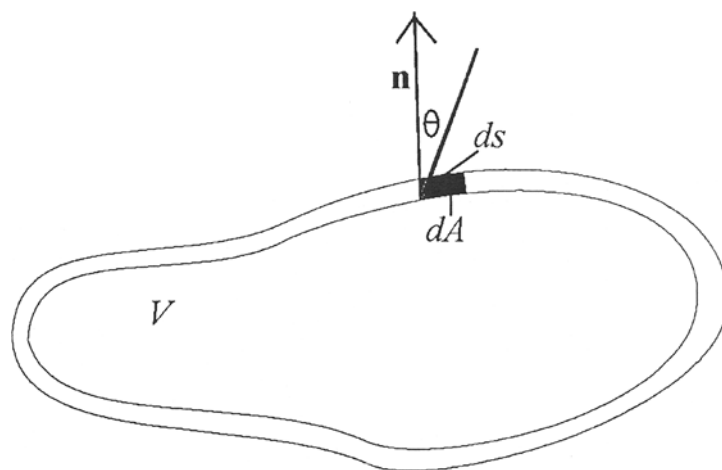$$W = \int_{V_1}^{V_2} Pdv = NkT \int_{V_1}^{V_2} dv/v. \tag{13}$$

Figure 1. The arbitrary expansion of a system of volume V. Sketched from Reif (Ref. 4, p. 77).

Integrating, we arrive at the traditional answer

$$W = (NkT)\ln(V_2/V_1). \tag{14}$$

When the gas inside the cylinder is considered ideal, the energy change of that gas is zero, as defined by (10). So on what is the work, as is defined by (14), done? The traditional argument is that the work goes into the walls of the piston-cylinder apparatus itself. To this author it lacks logic that energy is stored anywhere within the piston-cylinder apparatus!

The reality is this: When we release the plunger, the higher-pressure atmosphere pushes the piston back to its neutral position. Since the atmosphere drives the piston back, the atmosphere is doing the work. Therefore, during expansion, work must have been done on the surrounding atmosphere and not on the system's walls.

Consider it this way. If we were to raise the expanded cylinder up into the atmosphere, eventually we would reach an altitude where the pressure outside the cylinder equals the pressure inside the cylinder. The act of bringing both the cylinder and its gaseous contents to this higher elevation requires energy. The work required to elevate only the cylinder's gaseous contents should equal the work that was required to expand the cylinder in the first place.

Let us consider that the work is being done on the system's surroundings, i.e., Earth's atmosphere. The correlation between the height above Earth's surface and atmospheric pressure is obtained from the law of atmospheres:
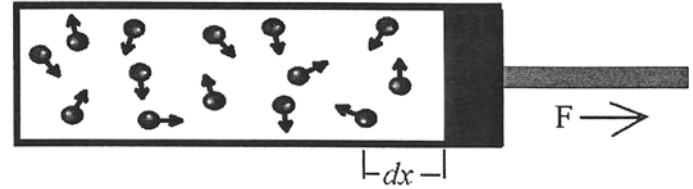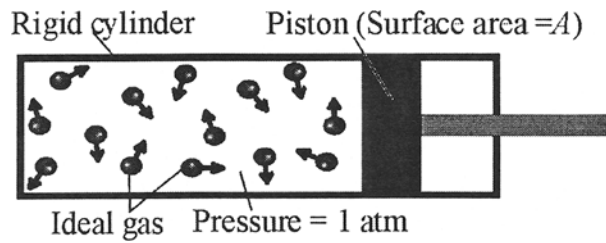
Figure 2. A gas-filled expandable cylinder.

Figure 3. The expansion of the cylinder in Fig. 2.

$$P(h) = P_0 e^{-m'gh/(kT)}, \qquad (15)$$

where $P(h)$ is the function of how the pressure changes with height, while P_0 is a constant taken as the pressure at height $h = 0$ and m' is the molecular mass.

Dividing both sides by the constant P_0 and then taking the natural logarithm, we obtain

$$\ln[P(h)/P_0] = -m'gh/kT. \qquad (16)$$

Then, expressing the relation in terms of height (h), we obtain

$$h = (kT/(m'g))\ln[P_0/P(h)]. \qquad (17)$$

Let h represent the elevation above Earth's surface and M be the total mass of the ideal gas inside the cylinder. Then the work required to raise M to h is

$$W = Mgh, \qquad (18)$$

where g is the gravitational constant. By substituting (17) into (18) and canceling the gravitational constant (g), we obtain for work

$$W = (MkT/m')\ln[P_0/P(h)]. \qquad (19)$$

Mass divided by the molecular mass gives the number of molecules (N). Therefore we can rewrite (19) as

$$W = (NkT)\ln[P_0/P(h)]. \qquad (20)$$

Interestingly, we could rewrite (20) in terms of volume. We realize that $P(h)$ is nothing more than the pressure within our piston-cylinder apparatus when the apparatus is in the expanded position and that P_0 was the original pressure inside our apparatus. For the

compression/expansion of an ideal gas, $P_1/P_2 = V_2 = V_1$. Obviously, we can rewrite (20) in terms of volume change, and the result becomes (14), which is the traditionally accepted result. Which equation is correct depends upon your choice: (1) Work was mysteriously done on the walls of the piston-cylinder apparatus, or (2) work was done on the surrounding atmosphere.

The traditional thought that work is solely defined in terms of volume change may be based upon a series of misconceptions. Certainly, defining work in terms of (14) may be empirically valid but it is conceptually weak because it requires energy to be stored in all walls. In many applications logic may be better served if we express the work done in terms of pressure change, as (20) does.

6. WORK IN PRESSURE INCREASE

To emphasize the last point consider a common mass-transfer mechanical device involving the addition of gaseous molecules to a rigid vessel, thus increasing the vessel's pressure. Consider a rigid vessel containing X gaseous molecules whose internal pressure is 1 atm. Based upon the ideal gas law, the energy within our system can be expressed as

$$PV = XkT. \qquad (21)$$

Consider a mechanical device that now isothermally increases the pressure in our rigid vessel by pushing Y more molecules into the vessel, so the vessel now contains $X + Y$ molecules. The energy is now defined by $PV = (X + Y)kT$.

Since V is constant, the pressure increase (dP) due to the addition of Y molecules into the vessel is

$$dP = YkT/V. \qquad (22)$$

From the perspective of the system, that being the vessel and all the molecules within, the work done

(W) is the pressure increase multiplied by the volume (V) over which the pressure increase occurs:

$$W = VdP = YkT. \qquad (23)$$

Once more, traditional thermodynamics only considers the work done in terms of volume change in some isobaric processes. Equation (23) tells us that, from the perspective of the higher-pressure vessel, the work should be expressed in terms of VdP, where dP represents the pressure change in the vessel's volume V. From the perspective of the mechanical device, at constant 1-atm pressure, the work it performed on the high-pressure system could be expressed in terms of PdV, where dV is the volume of ideal gas driven into the vessel when that volume is measured at pressure P.

It is understood that the above is overly simplified. Certainly, a more general case considers the realistic rather than the ideal, meaning that changes to bonding and other energies must be considered. Then again we could change our perspective and view the problem from the perspective of viewing Earth's atmosphere, and we should get an equally persuasive answer. No matter, the simple drives home a point better than the complicated ever could. The point is that whether we choose to express the work done by a machine in terms of PdV or VdP all depends upon our perspective. The implication is that traditional thermodynamics chooses to define work only in terms of PdV, out of convenience. In so doing, traditional thermodynamics ignores the simplest explanation of them all, that being we should start by expressing work in terms of (9)!

7. CONCLUSIONS

The concept that traditional thermodynamics presents laws in terms of its most basic constituents[1] is being challenged. The origin of the problem is our traditional understanding of work and heat, namely we separate the two entities before we even begin to contemplate the question at hand. The traditional understanding of work is given by (8): $W = dE + PdV$. We all acknowledge that (8) represents the mechanical work in isothermal, isobaric processes. Bewildering is the fact that traditional thermodynamics has limited all forms of work, mechanical and otherwise, to being defined by (8), even though many mechanical processes are clearly not isobaric. When contemplating a problem we should begin by defining work in terms of (9): $W = dE + d(PV)$.

Most importantly, the way we decide to define work is often based upon our perspective. By using

(9) we can consider the work from the perspective of an isometric higher-pressure system. Then the theoretically correct way to express its energy advantage over its surroundings should be $W = dE + VdP$, while from the perspective of one standing on isobaric Earth the work that can be obtained from the isometric higher-pressure system may be defined in terms of (8).

Furthermore, traditional thermodynamics is hampered by the dogma that the work is magically done on the system's walls. However, such a concept seemingly lacks logic if the walls are not elastic. It is much more palatable to think in terms of the work being done on Earth's atmosphere! Moreover, (20), $W = (NkT)\ln[P_0/P(h)]$, proves that it is empirically correct to do so! Once more, whether we choose to define work in terms of volume change versus pressure change is somewhat arbitrary, even though logic dictates one over the other.

Accepting that work cannot be limited to volume change raises questions as to whether certain laws should be reexamined. Generalizations should be removed. That is, perhaps the first law should be simplified to the following statement: Energy is conserved.

Since work is best described by (9), we should also question the isobaric change to an ensemble of the molecular energy states (5): $S = k \ln \Omega$. Specifically, we use such statistical arguments to validate what is taught in thermodynamics, but has anyone ever asked what would happen if the number of molecular energy states were a simple consequence of a system of molecules, at a given pressure and volume, plus any energy considerations associated with the specific nature of the molecules? Is our traditional approach correct or do we use it because considering molecular energy state change for the isometric case is not as easily visualized? Whatever our reason may be, the net result of using differentials, if and only if they suit the isobaric changes to energy states, may be complicating the simple. It must be said that we have not proven anything at the statistical level. But we should start the questions.

Why has mechanical work not been previously questioned in this manner? Perhaps it has but those being quizzical dwelled upon statistical physics. Perhaps the answer resides in the fact that we live on/in an isobaric (1-atm) open system. No matter, the time has come to question some of the cornerstones of thermodynamics.

Résumé

Traditionnellement en thermodynamique, le travail mécanique est défini en termes de PdV. Bien que ce soit empiriquement correct de considérer tout travail mécanique en termes de PdV, nous démontrerons qu'il serait erroné de procéder ainsi d'un point de vue théorique. Plus spécifiquement, la théorie impose que le travail mécanique soit souvent exprimé en termes de VdP et non pas en termes de PdV.

Endnotes

[1] The work (W_{gl}) required to nucleate a Gibbs globule is $W_{gl} = A_{gl}\sigma + V_{gl}(P_{gl} - P_l)$, where A_{gl} is the globule's surface area, σ is the globule's surface tension, V_{gl} is the globule's volume, P_{gl} is the pressure inside the globule, and P_l is the pressure in the surrounding liquid.

[2] The work (W_b) required to nucleate a bubble is[23] $W_b = A_b\sigma + U_l - U_b + V_bP_b - V_lP_l$, where $A_b\sigma$ is the energy required to form the tensile layer; U_l and U_b, respectively, represent the bonding energy in the liquid and bubble states; V_b and V_l, respectively, represent the volume in the bubble and liquid states; and P_b and P_l, respectively, represent the pressure in the bubble and liquid states.

[3] Personal correspondence via e-mail. In an effort to confirm my work I mailed some notes to the Wolfrum et al.[24] group. The notes contained analysis of their data using Mayhew's equation for the work required in bubble nucleation. Via e-mail, W. Lauterborn stated: "I just had found time to only quickly look through your calculations. As there is a perfect fit to our measurements, everything looks fine. Thus no comments from my side and I look forward to the publication."

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