



Exact Calculation of the Internal Energy of the Ideal Gas in Statistical Mechanics

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Article Information

DOI: 10.9734/PSIJ/2017/32822

Editor(s):

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Complete Peer review History: <http://www.sciencedomain.org/review-history/18839>

Short Communication

Received 17th March 2017
Accepted 25th April 2017
Published 28th April 2017

ABSTRACT

Previously, in the calculation of the internal energy of the ideal gas in statistical mechanics, it has been supposed that the volume is a constant, which does not depend on any arguments. However, the volume depends on pressure and temperature and its partial derivative is not equal to zero. In this paper, the dependence of the volume on pressure and temperature is taken into account, and the internal energy is calculated exactly. It differs from the traditional internal energy by the product of the pressure and volume. This explains three paradoxes in thermodynamics. It follows that the isochoric heat capacity equals the isobaric one. It is shown that the derivation of the Mayer's relation which connects the isochoric and isobaric heat capacities, is wrong.

Keywords: Ideal gas; internal energy; enthalpy; heat capacity; partition function.

1. INTRODUCTION

The canonical partition function of a classical and discrete system in statistical mechanics is [1–4]:

$$Z = \sum_i \exp\left(-\frac{U_i}{kT}\right). \quad (1)$$

Here, k is the Boltzmann constant, T is temperature and U_i is the energy of the system in

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the respective microstate. The internal energy of a system can be obtained through the partition function:

$$U = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{U_i} \quad (2)$$

It is important to note that the derivative in the above equation must be taken at constant energies, but not at a constant volume. In [2,3] it was taken at a constant volume. This is a mistake, one can check that by simple calculation. The internal energy of the ideal gas was obtained from equation 2 for a continuous case:

$$U = \frac{3}{2} NkT \quad (3)$$

where N is the number of atoms.

However, the partition function of the ideal gas depends on the volume. In the previous calculation of the internal energy of the ideal gas, the derivative of the volume with respect to temperature was supposed to be zero, which is wrong. In the present paper, the exact calculation of the internal energy of the ideal gas has been performed taking this derivative into account.

2. THEORY

For a continuous system of N particles, the partition function is [1,5]:

This integral equals:

$$Z = \left[\int \exp \left(-\frac{p_1^2}{2mkT} \right) d\Gamma_1 \right]^N = \left[\int \exp \left(-\frac{p_1^2}{2mkT} \right) d\mathbf{p}_1 \right]^N \left[\int d\mathbf{r}_1 \right]^N = (2\pi mkT)^{3N/2} V^N \quad (8)$$

Here, $d\mathbf{p}_1$ and $d\mathbf{r}_1$ are the elements of the momentum space and position space respectively of the first particle.

Introducing equation 8 into equation 2, one obtains:

$$U = \frac{3}{2} NkT + \frac{kT^2 N}{V} \left(\frac{\partial V}{\partial T} \right)_U \quad (9)$$

In the previous calculations, it was supposed that V is a constant which does not depend on any arguments and the derivative in the right hand part of equation 9 equals zero. As is mentioned above, it is physically wrong to assume that the volume is a constant, which does not depend on any arguments. Even when the volume is constant, it depends on temperature and pressure, and the derivative $\partial V/\partial T$ is, in general, not zero. Let us take the partial derivative in equation 9 at a constant energy using the equation of state:

$$Z = \frac{1}{h^{3N}} \int \exp \left(-\frac{U(\Gamma)}{kT} \right) d\Gamma \quad (4)$$

where h is the Planck constant, and Γ is the phase space. The average energy of such a system is:

$$U = \frac{1}{h^{3N}} \frac{\int U(\Gamma) \exp \left(-\frac{U(\Gamma)}{kT} \right) d\Gamma}{Z} \quad (5)$$

This expression is equivalent to equation 2. It is important to note that both for discrete and continuous systems the only value being kept constant in the partial derivative in equation 2 is the energy U .

Let us perform a simplified derivation of the partition function for a monatomic ideal gas [1] (we omit h^{3N} for simplicity). The energy, $U(\Gamma)$, equals the sum of the kinetic energies of the atoms:

$$U(\Gamma) = \sum_{i=1}^N \frac{p_i^2}{2m} \quad (6)$$

Here, p_i is the momentum of the i -th atom, and m is its mass. Introducing equation 6 into equation 4, one obtains a $6N$ -dimensional integral:

$$Z = \int \dots \int \exp \left(-\sum_{i=1}^N \frac{p_{i=1}^2}{2mkT} \right) d\Gamma_1 \dots d\Gamma_N \quad (7)$$

$$PV = NkT. \quad (10)$$

One can show that, in this case, equation 9 turns to:

$$U = \frac{3}{2} NkT + PV. \quad (11)$$

If this result is correct, then the internal energy of the ideal gas (and may be that of all physical systems) has an intrinsic integral term PV . So, the internal energy of the ideal gas (or of a physical system) must be written like this:

$$U^* = U + PV = H \quad (12)$$

where U is the traditional internal energy, and H is enthalpy.

One can immediately explain the following contradiction in thermodynamics. For the heating of a substance by compression without the heat losses, the first law of thermodynamics is:

$$PdV = -dU. \quad (13)$$

From this equation, the following derivatives follow:

$$\left(\frac{\partial U}{\partial V}\right)_P = -P \quad (14)$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -P. \quad (15)$$

However, P and S cannot be constant simultaneously, and a contradiction occurs. It can be resolved using the result obtained. The first law of thermodynamics for the heating of a system by compression must look like:

$$PdV = -dU - VdP. \quad (16)$$

From this, equation 14 follows, but equation 15 is not true.

3. DISCUSSION AND CONCLUSIONS

If the derivations performed in this paper are correct, then the first law of thermodynamics for heat exchange has the following form:

$$\delta Q = dU^* = dH = dU + PdV + VdP \quad (17)$$

where δQ is the heat introduced into the system. For a constant volume, equation 17 turns to:

$$TdS = dU^* = dU + VdP \quad (18)$$

where dS is the change in entropy. Previously, it has been supposed that the last term in this equation is absent. For a constant pressure, equation 17 turns to:

$$TdS = dU^* = dU + PdV. \quad (19)$$

Previously, it has been supposed that this equation is valid also for varying pressure [4,6]. Let us prove that equation 19 is valid only for a constant pressure. Let us assume that the pressure is not constant in it. One can notice that $\delta Q = TdS = dH_P$ in equation 19 is a full differential, where dH_P is the enthalpy change at a constant pressure. Therefore, the derivatives $\left(\frac{\partial H}{\partial V}\right)_U$ and $\left(\frac{\partial H}{\partial U}\right)_V$ must be equal.

However, for the ideal gas, they equal 0 and $\frac{2}{3V}$, respectively. In reality, these derivatives must also be taken at a constant pressure, thus both are equal to zero.

From equations 18 and 19 it follows that the isochoric heat capacity, C_V , equals the isobaric heat capacity, C_P . In [7], the heat capacities of argon and nitrogen were measured experimentally, and it was found that $C_V = C_P$. Let us cite A. Guy [7]: "In a standard experiment in physical chemistry, students determine $C_P/C_V = 1.4$ for a diatomic gas such as nitrogen, but nowhere in the scientific literature is there a report on the direct experimental determination of both C_P and C_V for any gas."

There is a relation between the isobaric heat capacity and the isochoric heat capacity (Mayer's relation) [6]:

$$C_P - C_V = \frac{T\alpha^2}{\rho\beta}, \quad (20)$$

where α is the coefficient of thermal expansion, ρ is density, and β is the isothermal compressibility. One can show that the derivation of Mayer's relation is not correct. Let us consider

the key part of this derivation and expand S as a function of T and V :

$$dS(T, V) = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad (21)$$

whence

$$\left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad (22)$$

and

$$C_p - C_v = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad (23)$$

One can see that this consideration is equivalent to the following one. Let us take the following expansion:

$$dS(T, V, P = \text{const}) = \left(\frac{\partial S}{\partial T} \right)_{V, P} dT + \left(\frac{\partial S}{\partial V} \right)_{T, P} dV \quad (24)$$

and divide it by dT . The derivatives on the right hand side are equal to zero, and at a constant P the arguments V and T are not independent.

It is necessary to note that, from equation 19, the following derivative was obtained and given in the tables of thermodynamic derivatives, for example [8]:

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T} \quad (25)$$

Nevertheless, from equation 17, it follows that the partial derivative in equation 25 is taken also at a constant pressure, $\left(\frac{\partial S}{\partial U} \right)_{V, P}$, and should equal zero. From equation 18, it follows that equation 25 for heat exchange should be written like this:

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T} + \frac{V}{T} \left(\frac{\partial P}{\partial U} \right)_V = \frac{1}{T} + \frac{V}{T} \frac{\alpha}{\beta C_v} \quad (26)$$

The derivative of the pressure in equation 26 is given in [8]. For the ideal gas this equation turns to:

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{5}{3T} \quad (27)$$

The results of the present paper can explain a paradox in the ideal gas [9–12]. Two variables are necessary to determine the properties of a gas, such as its internal energy. In the kinetic theory, the internal energy of the ideal gas is given by equation 3. The paradox is that this energy depends only on one variable, T , but must depend on two. From equations 3 and 10 it follows that:

$$U(P, V) = \frac{3}{2} PV \quad (28)$$

Here, the energy depends on two variables.

This paradox is valid also for real gases because, in a wide range of temperatures and pressures, they only minimally deflect from the ideal gas. For example, the molar volumes of argon, helium, hydrogen, nitrogen, oxygen and methane deviate at about 0.1 percent of 22.414 litres at standard temperature and pressure and deviate even less for higher temperatures and lower pressures. For argon, the difference between the theoretical and experimental heat capacity is less than 0.1 percent [9–11,13]. For real gases, there will be a weak dependence of thermodynamic properties on volume in equation 3 and a strong dependence on volume in equation 10.

It is interesting to note that the obtained result explains the enthalpy paradox found in [10,11,14]. Thermodynamic potentials internal energy, U , and enthalpy, $U + PV$, are qualitatively different, but, for the ideal gas, they are identical thermodynamically and differ only in the multiplying factor in that U equals $1.5PV$, and H equals $2.5PV$. If everything were correct in traditional thermodynamics, then U would not be thermodynamically identical to H even for the ideal gas.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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