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Article 12. Essay: Materials and Thermodynamics

Author: Liu Huan (1983-), Master of Science (First Class Honours, 2009), The University of Auckland.

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Abstract

The classical theory of thermodynamics have been comprehensively summarized in this article firstly, including definition of internal energy, the first, second and third Law of thermodynamics, the equation of state, the exergy and efficiency of energy, and the specific heat capacity, with several case studies illustrating the above theme. Finally, the original viewpoints have been proposed, mainly from the prospective of electromagnetic wave demonstrating the classical theories of thermodynamics.

Key Words: The First Law of Thermodynamics, The Second Law of Thermodynamics, Energy Exergy and Efficiency, Equation of State, Specific Heat Capacity.

Introduction

Understanding the thermodynamics plays the essential role in the energy recycling and saving strategy, which have been paid more attention today under the global social pressure of net carbon zero. Consequently, this article attempts to more accurately discuss and quantify the relevant theories on thermodynamics for future improvement.

1.Internal Energy Definition

1.1.Electromagnetic Theory

The inner energy discussed from the viewpoint of electromagnetic theory is presented below: any physical object is consisted of electrons, protons and neutrons. Among them, electrons are negatively charged, while protons are positively charged. When an object moves, every electron, proton in its structure moves with it, which leads to the magnetic field and induced electric field generated by the charged electrons and protons inside the object. In the process of moving an object, the energy related to the moving speed is the kinetic energy of the object, while the energy related to the internal magnetic field and induced electric field is the internal energy of the object [4].

1.2.Molecular Motion

In comparison, the inner energy discussed from the angle of molecular motions includes: internal energy is the total energy of all microscopic particles in the motion form of a physical object or a system composed of several objects, which is represented by the symbol U and the international unit is joule (j). Internal energy is an inherent property of an object or system, that is all objects or systems possess internal energy. It is the sum of kinetic energy of molecules and molecular potential energy when all molecules in an object are in thermal motion [5].

2.Wave Interference

2.1. Definition of Wave Interference

When two waves propagate in the space filled with the same medium, leading to the overlapping, the particles in the medium within the overlapping spaces are determined by two waves at the same time. If the amplitude of the wave is not big, the vibration displacement between two wave particles in the overlapping range is equal to the sum of the vector displacement caused by each wave, which is called the superposition of the waves. If the peaks (or bottoms) of the two waves reach the same spatial point at the same time, it is defined that the two waves are in the same phase at this point, and the interference wave will produce the maximum amplitude, which is called constructive interference; If the peak of one of the two waves meets the bottom of the other wave at the same spatial point at the same time, then the interference waves will produce the minimum amplitude, which is called destructive interference[1].

2.2. Conditions of Wave Coherence

There are several conditions of coherence between two beams of waves: when the length of optical path difference is the even times of half wavelength, the amplitude of synthetic wave is the largest; when the length of optical path difference is the odd times of half wavelength, the synthetic amplitude is zero; the electromagnetic wave frequency between two interfering waves is the same; the vibration direction between two interfering waves is the same; the interference points of the two beams of waves is in the same phase [2]. However, the waves excited by each wave source can propagate independently in the same medium, and when they are separated after meeting, their propagation conditions (frequency, wavelength, propagation direction, period, etc.) are the same as those when they are not met, and they do not interfere with each other again, as if they have not met other waves [3].

3.The First Law of Thermodynamics

3.1.Energy Conservation and The First Law

The first Law of thermodynamics is defined as below: heat can be transferred between different physical objects, or converted between different forms of energy, but the total value of energy remains conservative and constant in the conversion process. The universal law of energy conversion and conservation is applicable on all the

macro processes involving thermal phenomena [6].

3.2. Engineering Thermodynamics and The First Law

In the scope of engineering thermodynamics, the first law of thermodynamics can be defined as: when thermal energy and mechanical energy are transferred or converted between each others, the total amount of energy must be constant. There are several explanations in this definition: heat can be transformed into work, and work can also be transformed into heat; Consuming a defined quantity of work will generate the according amount of heat, and when a defined quantity of heat disappears, it will also produce the corresponding amount of work [6].

The mathematical formula expressed as the first thermodynamics Law is:

$$\Delta U=Q+W$$

In thermodynamics, when the system changes, if the heat exchanged with the environment is Q (positive heat absorption and negative heat release), and the work exchanged with the environment is W (negative external work and positive external work on the object), the change of thermodynamic energy (also known as internal energy) is ΔU [6].

3.3. The P - V System and The First Law

Further more, the application of the first law of thermodynamics on the P-V system is defined as: heat capacity and enthalpy. For gases, liquids and isotropic solids, without considering surface tension and external force field, their state can be described by any two of the three quantities including P, V and T as state parameters, which is defined as a P-V system [6].

For P-V system, in the infinitesimal quasi-static process, the micro work done by the outside environment to the system $dW = - p dv$. Therefore, the differential form of the first law of thermodynamics can be expressed as $dQ = dU + p dv$ [6].

4. The Second Law of Thermodynamics

The second law of thermodynamics describes the irreversible thermodynamic processes: the spontaneous evolution of isolated systems undergoes towards thermodynamic equilibrium - the maximum entropy state. Similarly, the second kind of perpetual motion machine can never be realized. There are three representative arguments in the second law of thermodynamics[7]:

4.1. Clausius Definition: it is impossible to transfer heat from a low-temperature object to a high-temperature object without causing other changes[7];

4.2. Kelvin Definition: it is impossible to make a cycle heat engine that taking heat

from a single heat source and turn it into work without causing other changes[7];

4.3. Entropy Increase Principle: the entropy of an isolated system never decreases automatically. The entropy remains unchanged in the reversible process and increases in the irreversible process. In a virtual reversible process, the entropy (DS) in the infinitesimal process of the system is defined as the increment of heat (δQ) transferred to a closed system (allowing energy to enter or exit, but not allowing mass to transfer in this closed system), which is divided by the common temperature (T) of the balance system and the environment providing heat[7]:

$$DS = \frac{\delta Q}{T}$$

However, for the practical infinitesimal process in which there is no mass exchange with the surrounding environment, the second law requires the increment of system entropy to meet the following inequality[7]:

$$DS > \frac{\delta Q}{T}$$

This is because the general process in this case may include the work done by the environment to the system, which produces friction or viscous effect in the system. For example, the chemical reaction may be in progress, or heat transfer actually occurs only irreversibly, so more entropy is required for the practical heating process, which is driven by a finite difference between system temperature and ambient temperature[7].

4.4. Carnot Definition: Carnot cycle is a simple cycle with only two heat sources (two heat sources varies in temperature). Because the working material can only exchange heat between two heat sources, the reversible Carnot cycle consists of two isothermal processes and two adiabatic processes. Carnot cycle was proposed to analyze the working process of heat engine, which includes four steps: reversible constant temperature heating absorption, reversible adiabatic expansion, reversible constant temperature heating release and reversible adiabatic compression. Under the ideal conditions, gas absorbs heat at constant temperature from state 1 (P_1, V_1, T_1) to state 2 (P_2, V_2, T_2), then expands adiabatically from state 2 to state 3 (P_3, V_3, T_3), then releases heat at constant temperature from state 3 to state 4 (P_4, V_4, T_4), and finally compresses adiabatically from state 4 back to state 1 [8].

5. Case Studies on the First and Second Law of Thermodynamics

5.1. Ma et al.,(2002) examined the gas engine heat pump according to the the first law of thermodynamics.The results showed that the gas engine heat pump performed as high thermodynamic efficiency and the energy utilization process was reasonable. The energy utilization formula are designed as below [10]:

The energy index of heat pump system is usually measured by heating coefficient

COP and primary energy utilization (PER). COP of gas engine heat pump during heating can be expressed by the below formula[10]:

$$\text{COP}_{\text{GEHP}} = \frac{Q_c + Q_r}{N} \quad \text{equation 1}$$

Where Q_c is the condensation heat release, kW; Q_r is the heat energy obtained by the heated fluid from the waste heat of the gas engine, kW; N is the mechanical energy supplied to the heat pump system, kW[10].

Although COP can indicate the heating performance of heat pump, it can not reflect the conversion efficiency of heat pump prime mover, so it can not fully reflect the energy utilization efficiency of heat pump system. Therefore, it is often to use the index of primary energy utilization ratio PER to compare the performance of different equipment[10].

The primary energy utilization rate PER_{GEHP} of gas engine heat pump can be expressed by the following formula[10]:

$$\text{PER}_{\text{GEHP}} = \frac{Q_c + Q_r}{Q_1} \quad \text{equation 2}$$

Where, Q_1 is the thermal energy input to the gas engine, kJ/S. The waste heat recovery rate of the gas engine α is introduced in this formula, that is defined as the ratio of the recovered waste heat of the gas engine to the total waste heat of the gas engine. So equation (2) can be modified as[10]:

$$Q_r = \alpha \times (1 - \eta_b) \times Q_1 \quad \text{equation 3}$$

$$\text{PER}_{\text{GEHP}} = \eta_b \times \text{COP}_{\text{HP}} + \alpha \times (1 - \eta_b) \quad \text{equation 4}$$

Where η_b is the engine efficiency of gas engine; COP_{HP} is the performance coefficient of heat pump system without considering waste heat recovery. In practice, α is estimated as 0.6; and the η_b is estimated to be 0.30[10].

5.2. The expansion of solid skeleton caused by adsorption is determined by complex energy conversion or transfer between solid and fluid. Based on this understanding, Bai & Li (2007) applied the first law of thermodynamics on the general method of establishing constitutive equation, proposing that humidity (adsorption capacity) was regarded as the state variable of the system, and the humidity stress field theory presented by Miao Xiexing was strictly proved, with detailed analysis of the applicable conditions on the mechanical significance of this theoretical model [11].

5.3. A quantum thermal engine cycle model of irreversible harmonic oscillator

system is established by Wang et al., (2006). Based on the Heisenberg representation operator equation of motion and semi group analysis method, the first law of thermodynamics and the temporal evolution formula of the cycle in the harmonic oscillator system are obtained. The important engine performance parameters such as output work, efficiency, output power and entropy yield of the quantum heat engine cycle are derived, with the estimation of optimal values and intervals of the main performance parameters in the heat engine cycle under the condition of maximum output power[14].

5.4. Koslff (1984) has established the cycle model of quantum heat engine, and the general expression of the first law of thermodynamics of quantum system is below[14]:

$$\begin{aligned}dU &= \sum_i (E_i \times dP_i + P_i \times dE_i) \\dQ &= \sum_i E_i \times dP_i \\dW &= \sum_i P_i \times dE_i\end{aligned}$$

E_i and P_i are the occupation probabilities of the energy level and the corresponding energy level of the system, respectively. In addition, the cycle efficiency of the two-level quantum heat engine is expressed as below[14]:

$$\eta = 1 - \Delta c / \Delta h$$

Δc and Δh is the difference of the quantum system at low and high energy level respectively. This equation points out that the efficiency of the quantum heat engine is independent of the heating source temperature and is similar to the efficiency expression of the classical reversible Carnot heat engine, except that the two energy level difference of the system is used to replace the temperature in the classical reversible thermodynamic cycle[14].

The main difference between quantum thermodynamic cycle and classical thermodynamic cycle includes: (I) for the quantum cycle, the working substance involves spin system, harmonic oscillator system, quantum gas, micro particles and photon gas in potential well, etc; (II) the working state of quantum thermodynamic cycle is expressed by density operator, and the observable quantity of working state is the average value of operator. In the process of quantum cycle, the state of the working medium changes with it, which is described by the operator equation of motion; (III) the evolution behavior of observable quantity with time in the process of quantum thermodynamic cycle is also defined by the operator equation of motion, so as to avoid the use of phenomenological heat transfer law in classical thermodynamic cycle[14].

5.5. Based on the first law of thermodynamics, Pei et al., (2008) examined the energy efficiency from the perspective of energy quantity, and the comprehensive efficiency performance analysis of the first law of thermodynamics was the main method in the early PV/T system, which was defined as follows[15]:

$$\eta_{pvt} = \frac{A_c E_i + A_{pv} E_{pv}}{A_c H} = \eta_1 + \xi \eta_{pv}$$

Where, E_i , E_{pv} and H were photothermal output, photoelectric output and irradiation input per unit area respectively, W/m^2 ; A_c and A_{pv} were collector area and photovoltaic cell area respectively, m^2 ; η_1 , η_{pv} , ξ were battery efficiency, photothermal efficiency and coverage, respectively, defined as below[15]:

$$\eta_{pv} = E_{pv}/H$$

$$\eta_1 = E_i/H$$

$$\xi = A_{pv}/A_c$$

From the perspective of the second law of thermodynamics, the energetic efficiency or available energy efficiency in PV/T system was defined as[15]:

$$\varepsilon_{pvt} = \frac{A_{pv} EX_{pv} + A_c EX_i}{A_c EX_{sun}} = \varepsilon_i + \xi \varepsilon_{pv}$$

EX_{pv} , EX_i , EX_{sun} were the photoelectric energetic output, photothermal energetic output, and energetic irradiation per unit area respectively, W/m^2 [15].

The results concluded that from the perspective of the first law of thermodynamics, using the energy efficiency as the criterion in the change process of various parameters examined in this paper, the comprehensive efficiency of the working condition with cover plate was always better than that without cover plate; in comparison, based on the second law of thermodynamics by using energetic efficiency as the criterion, the working condition with cover plate was higher than that without cover plate in some cases, whereas the working condition without cover plate was higher than that with cover plate in other cases. However, if PV/T system tended to put more weights on the quality of output energy, or more emphasis on the supply of electric energy, it was recommended to use the energetic efficiency as the assessment criterion[15].

5.6. There are many thermodynamic evaluation indexes for new compact heat exchangers. With the increasing development of ‘enhanced heat transfer’ technology,

the flow resistance of thermal conversion is becoming more and more prominent. The second law of thermodynamics and the entropy increase are the important methods to analyze the conservation of energy, heat transfer and flow resistance. A new method based on the second law of thermodynamics was designed by Ni (1985) to evaluate the heat exchanger as[16]:

The entropy increase (ds) is defined as the formula based on the independent T , P parameters:

$$ds = (\partial s / \partial T)_p dT + (\partial s / \partial p)_T dP$$

$$T(\partial s / \partial T)_p = C_p$$

According to the Maxwell fourth formula, $(\partial s / \partial p)_T = - (\partial v / \partial T)_T$, and $(\partial v / \partial T)_T \approx V/T$, which is approximately considered as linear relationship.

$$ds = C_p dT/T - (V/T) dP$$

The formula was used to evaluate the waste heat heating project of a plant in Beijing as case study, it was concluded that [16]:

1. The comprehensive evaluation of heat exchanger performance was difficult, complex but very important, which was not only related to performance, but also related to geometry and size, so it was the key problem in design, research and selection [16];
2. The two major factors of heat transfer and resistance were assessed by the increase in entropy $\Delta S_{\Delta T}$ and $\Delta S_{\Delta P}$, which were incorporated into pump power:

$W \approx T_0 \Delta S_{\Delta P}$, with obversion parameter N . These indexes consequently became the comparable energy values, based on in-depth analysis of the working process of the heat exchanger [16].

5.7. A low temperature power cycle system for efficient recovery of cold energy from Liquefied Natural Gas (LNG) was designed by Cheng et al., (1999) [17]. This cycle was analyzed in detail by the second law of thermodynamics, with the optimal design scheme of its parameters. The calculation results showed that this method could recover about 50% of the cold energy of LNG. In this improved combined cycle, LNG was extracted from the liquid storage tank and the pressure increases through the liquid pump; The high-pressure liquefied natural gas passed through the condenser and re-generator of the secondary refrigerant cycle respectively, and part of the cold energy of the liquefied natural gas was absorbed by the secondary refrigerant, so as to vaporize into gas natural gas; The natural gas continued to be heated to normal

temperature by seawater through a heat exchanger, and the temperature decreased due to external work through turbine expansion. At this time, although the pressure was also reduced, it was still higher than the pressure supplied to the user; Reheating it with seawater, raising its temperature to normal temperature, and working externally through turbine expansion again, and the pressure was reduced to the pressure required by the user. At this time, the temperature of natural gas was low, so it must be heated by seawater again, and finally supplied to the user [17].

Based on the second law of thermodynamics, the maximum recoverable cooling capacity of LNG is as following[17]:

$$W_{\max} = (h_0 - T_0S)_{\text{tank}} - (h - T_0S)_{\text{consumer}}$$

where T_0 is the ambient temperature, and the subscript 'tank' and 'consumer' represent the initial (storage tank) and final (delivery to users) states of natural gas respectively. The efficiency of this power cycle is defined as[17]:

$$\varepsilon = \frac{W_{\text{Total}}}{W_{\text{Max}}}$$

where W_{total} represents the total net output work of the power cycle, it includes the output work of secondary refrigerant steam power cycle and the output work of direct expansion of natural gas. Of course, the work consumed by various pumps should be deducted from the total work[17].

Based on the above formula, the calculation results showed that the recovery efficiency of LNG cold energy by this method could reach about 50%, which was much higher than other methods[17].

6.The Third Law of Thermodynamics

The definition of third law of thermodynamics: at absolute zero temperature, the entropy of any idealized crystal is zero; the third law of thermodynamics holds that when the system approaches absolute temperature zero, the entropy change of the isothermal reversible process of the system approaches zero. The third law can only be applicable on the stable equilibrium, but any substances can not be regarded as an ideal gas. Hence the absolute zero entropy cannot be reached, which is just the idealized assumption [9].

7.The equation of state

Thermodynamics test is usually incorporated by the equations of state as sub-models. The most remarkable function of equation of state is that it predicts the various states of gas and liquid through defined conditions. The simple equation of state with this

purpose is the ideal equation of state of gas, which can roughly estimate the state of gas under the condition of low pressure and moderate temperature. However, when the pressure rises and the temperature decreases, the accuracy of this equation will decrease, and it cannot be predicted because gas will liquefy into liquid. Therefore, scientists have developed a series of more accurate equations of state between gas and liquid. However, so far there is no single equation that can accurately predict the state of substances under all circumstances [21].

In addition, there are also other ways to predict the volume of solid, and even the transformation of solid from one crystalline state to another. For stars and neutron stars, there are also special models to describe their state changes with the equation of state of ideal fluid [21]. There are three representative state equations below:

7.1. Classical state equation of ideal gas

$$PV = nRT$$

In this state equation, P is the air pressure; V is the air volume; n is the amount of gas particles; R is the thermodynamic temperature scale; T is the gas constant [21].

$$P = \rho(\gamma - 1)e$$

$$\gamma = \frac{C_p}{C_v}$$

$$e = C_v T$$

In this state equation, ρ is the density; γ is the adiabatic index; e is the internal energy per unit mass; C_p is the heat capacity at constant volume; C_v is the heat capacity at constant pressure [21].

7.2. Van der Waals state equation

$$\left(P + \frac{a}{v_m^2}\right)(V_m - b) = RT$$

V_m^2 is the molar volume, a and b are the two constants that characterize the nature of the substance itself [21].

7.3. Redlich-Kwong state equation

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)}$$

This state equation is modified by Soavi as:

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)}$$

$$\alpha = (T, \omega)$$

In this modified equation, ω is the deviation coefficient of this substance. This α function equation is introduced to suit for the evaporation pressure of hydrocarbons, which has been proved that this equation is more accurate in the related calculation of these substances [21].

7.4. Peng–Robinson State Equation

Zhang et al., (2007) utilized the first law of thermodynamics to calculate the P-R equation for the properties of ammonia water mixture, with the thermodynamic analysis of Kalina Cycle of first-order distillation. The calculation program of Kalina Cycle thermodynamic in the properties of ammonia water with mixed working medium was compiled. The main thermodynamic properties of Kalina Cycle thermal power conversion were theoretically calculated, analyzing the effects of key parameters including turbine inlet pressure, turbine inlet temperature, turbine back pressure, working solution concentration, basic solution concentration and cycle multiplication rate on cycle performance [12].

The main formula of this P-R state is defined as[12]:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v - b) + b(v - b)}$$

However, in comparison, the original formula of this P-R (Peng-Robinson, 1976) formula is expressed as [13]:

$$P = \frac{RT}{v - b} - \frac{a\alpha}{V_m^2 + 2bVm - b^2}$$

Obviously, the formula used by Zhang et al., (2007) is modified from the original P-R state formula according to the specific devices examined. The application conditions of P-R formula is summarized below:

1. The parameters should be expressed by the critical parameters and deviation coefficients;
2. The model can show high accuracy near the critical state, especially for the calculation of compression factor and fluid density;

3. The hybrid specification should not refer to parameters that are more complex than binary interaction parameters, but should be independent of temperature, pressure and material composition;

4. The equation should be applicable to the properties of all fluids, such as natural gas [13].

8. Exergy and Efficiency

8.1. Definition of Exergy and Efficiency

When the system changes reversibly from any state to a state in equilibrium under certain environment conditions, the part of energy that can be infinitely converted into any other forms of energy in theory is defined as exergy. Because only the reversible process is capable of carrying out the complete conversion, it can be considered that exergy is the maximum active work that can be made or the minimum active work consumed theoretically in the reversible process under given environmental conditions [20].

Correspondingly, all energy (E) that cannot be converted into exergy (Ex) is called energy (An), so any energy consists of Ex and An [20]:

$$E = E_x + A_n$$

Exergy is only the available energy part of the energy, but its revenue and expenditure is generally unbalanced in practice. In the actual conversion process, part of the available energy is transformed into unavailable energy, and exergy is reduced, which is called exergy loss. The input exergy passing through the system boundary can be defined as $E_{x_{in}}$, and the output exergy is defined as $E_{x_{out}}$, with the internal exergy loss of the system (I_i) and the external work (W), then their balanced relationship is [20]:

$$E_{x_{in}} + W = E_{x_{out}} + I_i$$

Efficiency of exergy is the ratio of revenue exergy to expenditure exergy [20]:

$$\text{Exergy efficiency} = E_x (\text{revenue}) / E_x (\text{expenditure})$$

With the concept of exergy efficiency, it is to establish the equilibrium relationship for a thermal system for analysis, so as to achieve the following purposes [20]:

(1) To quantitatively calculate the revenue, expenditure, utilization and loss of energy on the basis of balance between revenue and expenditure. The direction of energy flow includes incoming items and various loss items, and its major and minor sources can be distinguished according to the distribution proportion of each item.

(2) By calculating the efficiency, the effectiveness of utilization in energy conversion is determined.

(3) By analyzing the rationality of energy utilization, various losses and accordingly influencing factors, it is to design the ways of improvement, and predict the energy-saving effect after improvement.

Exergy is the part of energy that has the ability to do work. Therefore, the value of energy is not only determined by the quantity, but also the quality, so it is to measure the proportion of exergy contained in unit energy, defined as energy level coefficient (ϵ) [20]:

$$\text{Energy level coefficient } (\epsilon) = \frac{Ex}{E}$$

8.2. Case Studies of Exergy and Efficiency

1. According to the unit consumption analysis theory, Zhou et al., (2012) analyzed the heat absorption of the working medium on each heating surface of the boiler regarded as different thermal products, and three irreversible thermodynamic processes were included, establishing the unit consumption analysis model of power plant boiler [19].

According to the second law of thermodynamics, the balance of any energy utilization process can be generally described as [19]:

$$\text{Fuel exergy} = \text{Product exergy} + \text{Consumption exergy}$$

As known, any actual thermodynamic process is irreversible and will lead to entropy production, and the irreversible loss (I) is directly proportional to entropy production (ΔS). In the formula, T_o is the absolute temperature of the environmental reference state. It is assumed that the amount of fuel consumed to produce a certain product yield P is B kg. If e_t is the fuel ratio of exergy and e_p is the product ratio of exergy, formula can be written as [19]:

$$E_t = E_p + \sum I_{t,p}$$

$$I_t = T_o \Delta S_{et}$$

$$B_{et} = P_{ep} + \sum I_{t,p}$$

Finally, the second law of efficiency (%) for the production process of any energy consuming product is [19]:

$$\eta_{\text{ex}} = \frac{Pe_p}{B e_t} = \frac{b_{\text{min}}}{b}$$

$b_{\text{min}} = e_p / e_t$, which represents the theoretical minimum unit fuel consumption of the unit product, that is the unit fuel consumption (b) of the product without any loss.

According to the second law of thermodynamics efficiency, it was concluded that the heat flow obtained by the working medium in the economizer was the smallest with the lowest efficiency, consequently becoming a restrictive factor for the further improvement of power generation efficiency of coal-fired thermal power units [19].

2. Liu & Yu (2006) improved the working efficiency of pneumatic engine by optimizing the intake pressure, intake temperature and process parameters of pneumatic engine. The thermodynamics performance have been examined by both first and second law of thermodynamics. The first law of thermodynamics considers the effective utilization of the energy entering the system, which is defined as the ratio of the useful work done by the system to the input system energy. The energy entering the pneumatic engine system consists of two parts: one part is the pressure energy of high-pressure gas; and the other part exists in the form of gas internal energy. Taken together, it is the enthalpy of the gas entering the cylinder. Therefore, the expression of the first law of thermodynamics of pneumatic engine is [18]:

$$\eta_r = \frac{W_{\text{out}}}{m_i h_i} - \frac{m_e h_e - M_e H_e}{m_i h_i} = 1 - \frac{T_e}{T_i}$$

In the formula, W_{out} is the system output work; m_i, h_i is the input mass and energy respectively; M_e, H_e is the output mass and energy respectively; T_i and T_e is the input and output temperature respectively. This formula shows the same form as Carnot efficiency, indicating that the pneumatic engine possesses Carnot efficiency, and its size is determined by the ratio of cylinder outlet temperature to intake temperature. The increasing isentropic process can reduce T_e to improve the first law efficiency. Simply increasing intake temperature, the efficiency of the first law of thermodynamics remains basically unchanged, and the efficiency of the first law of thermodynamics of pneumatic engine can not reach 100% [18].

The second law of thermodynamics efficiency represents the ratio between the active work done by the system and the work potential of the energy entering the system. It reflects the total potential where the real system can improve the output work. In engineering, entropy is used to represent the work potential of unit energy. Then the efficiency (η_n) expression of the second law of thermodynamics of pneumatic engine is [18]:

$$\eta_n = \frac{W_{out}}{m_i(X_i - X_e)}$$

X_i, X_e represents the input and output exergy. The loss of pneumatic engine system includes two parts: one part of the loss is directly related to the irreversible process of the system. The main reason for this part of loss is that some pressure energy can be transformed into heat energy, but heat energy can not be completely transformed into mechanical energy; The other part is the waste of work capacity due to the discharge of some gas higher than the ambient pressure out of the cylinder [18].

In this paper, the working efficiency of pneumatic engine is improved by optimizing the intake pressure, intake temperature and process parameters of pneumatic engine. The problem of parameter integration of pneumatic engine with massive variables and complex relationships is solved by optimization design [18].

9. Specific Heat Capacity

9.1. Definition of Specific Heat Capacity

Specific heat capacity (symbol C) refers to a physical quantity commonly used in thermodynamics, indicating the heat absorption or heat dissipation capacity of an object. The larger the specific heat capacity, the stronger the heat absorption or heat dissipation capacity of the object. It is defined as the heat absorbed or released by a substance per unit mass when it rises or falls per unit temperature[22].

$$C = \frac{Q}{M\Delta T}$$

Where, C is the specific heat capacity; q is the required heat energy; M is the mass and ΔT refers to the temperature difference[22].

Constant pressure specific heat capacity (C_p) refers to the energy absorbed or released by a unit mass of materials when the temperature increases or decreases by 1 °C or 1 K under the condition of constant pressure[22].

Constant volume specific heat capacity (C_v) refers to the internal energy absorbed or released by a unit mass of material when the temperature increases or decreases by 1 °C or 1 K under the condition of constant volume[22].

Specific heat capacity (C_s) in saturated state refers to the heat absorbed or released by a unit mass of material when the temperature increases or decreases by 1 °C or 1 K under the condition of saturation[22].

9.2. Case Studies of Specific Heat Capacity

In addition to the chemical composition of materials itself, the physical influence factors determining the specific heat capacity on the materials include:

1. Wang et al.,(2007) prepared for the disturbed loess samples with different density and water content for test, which selected the thermal conductivity and specific heat capacity of the loess as criteria. The experimental results showed that when the water content was constant, the thermal conductivity and specific heat capacity increased with the increase of density; Under the same density, the thermal conductivity and specific heat capacity also increased with the increase of water content. Compared with the influence factor of density, the thermal conductivity and specific heat capacity of loess were more sensitive to water content change of prepared samples[23].
2. Mu et al., (2021) reported that even if the geological composition were the same carbonate formation, the thermophysical parameters were still different under different geological structures. The initial temperature of the rock mass in the hanging wall of the fault was higher than that in the footwall, but other thermal parameters including the comprehensive thermal conductivity, volume specific heat capacity, thermal diffusivity and linear meter heat exchange under the same working conditions were lower than that in the footwall [24].

10.Original Viewpoints on Thermodynamics

There are original viewpoints proposed by me in my previous articles[25][26]:

This article distinguishes the difference between thermal energy and inner energy. The range of energy forms defined in inner energy is broader than thermal energy, because not all the energy forms defined in inner energy generate the thermal effects, for example, the kinetic energy of molecule motion, defined in inner energy, can not completely be converted into thermal effects. In my article, it is defined that the electromagnetic waves emitted by molecule motion is the transmission pathways/forms of thermal energy, excluding the kinetic energy transmission, the static magnetic field transmission, and the static electric field transmission. The collisions among molecules or atoms lead to energy lose. This energy lose is caused by the aging of dark matter energy binder, so the nature of materials perishing is the aging of dark matter binding micro-particles, which is further discussed in another article [27]. Nevertheless, the lower density among molecules usually leads to less collisions so that less energy lose is caused correspondingly.

When the molecules of materials is heated by other sources of thermal energy, the frequency of molecule revolution is risen so that higher intensity of electromagnetic waves is emitted by molecule motion and higher frequency of collisions among molecules is caused as well. More specifically and exactly, when the transmission pathway/form of thermal energy is defined as the electromagnetic waves emitted by

molecule motion, the molecule or atom motion forms are distinguished in my thermal energy definition: the molecule or atom itself revolution/rotation is the main source of thermal effects, whereas the relative motions among different molecules or atoms, which is irregular in comparison, becomes the minor thermal sources and leads to energy losses by the collisions among them. The dark matter plays the role in the resilience function like mechanical spring here: when the molecule or atom approaches another molecule or atom, the dark matter reduces the relative velocity between them; subsequently when the molecule or atom moves away from it, the dark matter accelerates the relative velocity between them. If there is no aging of dark matter binding micro-particles, the average relative speed between them is constant without energy loss. Once the external thermal sources stop heating the receptor materials, this process is reversible.

When the object materials is heated by external work (rather than thermal sources), such as squeezing force imposed, the accelerated relative motions among different molecules or atoms becomes the main sources of heating transmission (rather than the molecule or atom itself revolution/rotation). Consequently, compared with the external thermal sources, the work imposed by external physical movement usually leads to less efficiency due to the lower frequency of electromagnetic waves emitted by molecule motion and more energy loss caused by the collisions among molecules and atoms.

My article further discusses the 'heating' scenario: when the receptor materials is heated by external thermal sources, the thermal energy increases in the receptor materials [25]. Inside the space of receptor molecules (or atoms), the effects of stable constructive interference between the external thermal source of electromagnetic waves and the electromagnetic waves emitted from the receptor molecules (or atoms) becomes the major forces of accelerating the revolution/rotation motion of receptor molecules (or atoms) (Please go to Figure 1). Consequently, the most efficient 'heating' process is the electromagnetic waves from external thermal sources, which have the same frequency as the electromagnetic waves emitted by the molecule motion of receptor objects and show similar amplitude of vibration to the electromagnetic waves emitted by the molecule motion of receptor objects (the amplitude of vibration between these two waves should not show large variation), is able to accelerate the revolution/rotation motion of receptor molecules (or atoms) most effectively. In this definition, the acceleration rate of molecular angular velocity becomes the first indicator of specific heat capacity of the receptor objects. According to the spectrum line experiment, 'the frequency of light emitted by each element corresponds to the same frequency of light absorbed.' Consequently, this experimental conclusion further supports my thermal theory proposed [28].

However, the thermal energy, in terms of temperature ascending or descending capacity, varies among different frequencies of electromagnetic waves. Consequently, if the frequencies of electromagnetic waves emitted by the molecule motion of

receptor objects is the frequencies leading to higher thermal energy, in terms of higher thermal energy caused by temperature change per unit, then the specific heat capacity of this receptor object is higher! In this case, the efficiency of specific heat capacity is the not linear relationship with the increased frequency of electromagnetic waves emitted by materials (not received by materials), due to the buffering effects of dark matter [27]. Similarly, the increasing intensity of received electromagnetic waves is not the linear relationship with the specific heat capacity of the receptor objects as well due to different destructive phases in dark matters. This means that the specific heat capacity can show the 'jumped' and non-continuous relationship with the received intensity of electromagnetic waves in statistics when it reaches the critical values differentiating each destructive phases in dark matter, so that the past numerical modeling based on the linear regression analysis would be the inexact ones for the chemical engineering of new materials, especially under extreme conditions.

Consequently, both the exergy and anergy of energy would be re-defined as: in my article, any forms of energy are capable of converting into other forms of energy without exceptions. The available and measurable energy that is converted between different forms or states of energy is re-defined as exergy, whereas the energy lose caused by the aging of dark matter in this paper is re-defined as anergy. However, among all the available energy converted between different forms or states, the energy that is non-measurable (inaccuracy) is defined as exergy lose. Hence the equation is as below:

$$\text{The energy} = \text{exergy} + \text{anergy} + \text{exergy lose}$$

In this definition, the total energy lose includes both the anergy and exergy lose. The energy conservation Law does not stand in the micro-scale again: with the aging of the dark matter, the energy goes towards retrogradation. Once energy is converted into the storage in aging materials, the according anergy makes part of energy non-available. So far the energy conservation law is demonstrated on the basis of ideal physical simulation only, without accurate data to prove. In my energy efficiency definition, two comparable materials, that one is the fresh material and the other is the aging one, are selected to conduct physical simulation under the same conditions in situ, and the difference in energy conversion efficiency between fresh and aging materials reveals the energy conservation law no longer exist in micro-scale. In this article [27], the aging of materials is caused by the aging of dark matter, which reduces the adhesion force of dark matter, so the toughness and elasticity of materials is reduced with the aging of materials. It is further deduced that not only thermal energy, but also other forms of energy conversion results in anergy increasing with the aging of materials.

In the section 5.4 of this paper, a quantum heat engine cycle is proposed, which incorporates the different energy levels into the thermodynamics modeling. However, this theoretical modeling has not been validated by practical data so far. In my article,

the different energy levels proposed in the above quantum thermodynamics (in the section 5.4) is re-defined as the representative aging stages of materials, and the energy differentiation between energy levels refers to the anergy defined in my article, so the energy efficiency between energy levels calculated in quantum thermodynamics model indicates the efficiency of materials at quantum level correspondingly. Within each energy level, the first and second Law of thermodynamics is still effective and accurate as approximation. Once the current energy level switches to another energy level due to aging of materials, all the parameters will be re-estimated accordingly. Further more, the anergy between different energy levels are not linear relationship but jumping ones, when the energy conversion efficiency between different energy levels is calculated at quantum level. Consequently, the Koslff (1984) quantum system that is based on the calculus equation (continuous function is required) will be revised into:

$$\Delta U = \sum_i (E_i \times \Delta P_i + P_i \times \Delta E_i)$$

$$\Delta Q = \sum_i E_i \times \Delta P_i$$

$$\Delta W = \sum_i P_i \times \Delta E_i$$

There are two major reasons to analyze the energy loss at quantum level: firstly, the aging of dark matter in materials leads to the energy lose, which is the most common reason in materials; secondly, energy lose is due to the decay of radioactive materials. However, this is usually less applicable on the stable materials without apparent radioactive characteristics. Further more, the relationship between the events detected by the particle collider and the particle mass/energy should be linked with the aging characters for the design of new materials synthesizing (To be further discussed in the coming essay: Quantum and Materials).

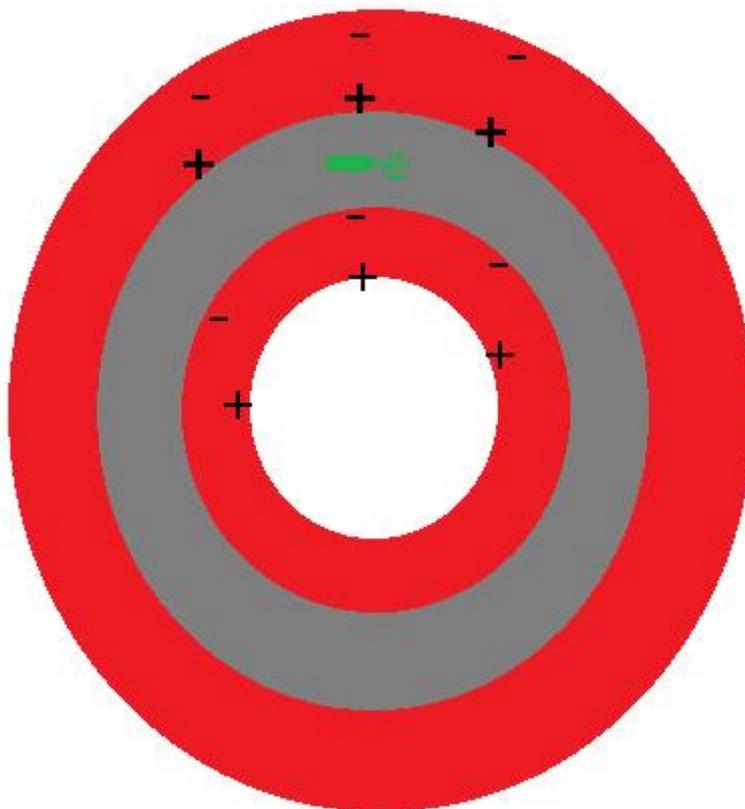


Fig 1. The red zone represents the constructive interference zones of two electromagnetic waves; The grey zone represents the destructive interference zones of two electromagnetic waves; The green 'e' represents the electrons inside the atom or molecule. This simple graph indicates the electron accelerating process inside the atom or molecule spaces due to the effects of stable constructive interference between the external thermal source of electromagnetic waves and the electromagnetic waves emitted from the receptor molecules (or atoms).

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