Notes on Thermodynamics

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ABSTRACT: This is the Notes of Thermodynamics. Released February 14, 2016.

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1 Introduction

This is the notes of classical Thermodynamics. It is found that some typical textbooks of thermodynamics will not satisfy the logic of a content rigid theory. Thus, this notes will largely focus on elaborating and axiomatizing the classical Thermodynamics theory.

This document will comply the following logic. First, we will illustrate the mathematical form of thermodynamic states as well as the basic thermodynamic parameter as a complete set of commutative observable. Next, we will introduce four classical thermodynamic state functions, followed by the three thermodynamic theorems. Finally, several applications of the laws will be elucidated.

In this document, Greek letters represent abstract indexes and Latin letters represent specific indexes.

2 Mathematical Formulation

2.1 Introduction

The description of Thermodynamics requires Functional Analysis as mathematical foundations. However, a complete introduction of the application of Functional Analysis can be much too exhausting. Thus, we only elucidate some necessary concepts and applications. More details can be found in arbitrary books about Functional Analysis.

2.2 Hilbert Space

First, we need the concept of inner product space

Definition. *A complex vector space V is a* ***inner product space*** *if it is defined a inner product map $i : V \times V \to \mathbb{C}$ satisfying*

(a) $i(f, g+h) = i(f, g) + i(f, h)$

(b) $i(f, cg) = ci(f, g)$
(c) $i(f, g) = \overline{i(g, f)}$
(d) $i(f, f) \geq 0$ *and* $i(f, f) = 0 \Leftrightarrow f = 0$

Next, define the Hilbert space

Definition. *The* ***Hilbert space*** *is a complete inner product space.*

The definition of *complete* can be found in Functional Analysis.

In Quantum Mechanics, we use a special case of Hilbert space — square-integrable function space $\mathrm{L}^2(\mathbb{R}^n)$ whose inner product is defined as

$$\langle f|g\rangle = \int \bar{f} g \, \mathrm{d}^n x \tag{2.1}$$

The integral here is Lebesgue integral, and we have used the Dirac notation to denote the inner product.

In our system of Thermodynamics theory, the thermodynamics state is represented by a ray in Hilbert space.

2.3 Operators on Hilbert Space

Definition. *An operator in Hilbert space is a map* $A : D \to \mathcal{H}$ *where* $D \subset \mathcal{H}$

Usually, the operator we use in Quantum Mechanics is linear.

Definition. *The* ***adjoint operator*** $A^\dagger$ *of an operator* A *is defined as*

$$i(A^\dagger f, g) = i(f, Ag) \tag{2.2}$$

A very important case of operator is the self-adjoint operator

Definition. *An operator* A *is* ***self-adjoint*** *if*

$$A = A^\dagger \tag{2.3}$$

In Quantum Mechanics, the observables are defined as a rigorous self-adjoint operator.

The average value or mathematical expectation of an operator at certain state is defined as

Definition. *The* ***expectation*** *or* ***average*** *of an operator* A *is defined as*

$$\bar{A} = \langle f|A|g\rangle \tag{2.4}$$

In our system of Thermodynamics theory, the thermodynamic parameters and observables of the system is represented by the operators in Hilbert space.

2.4 Generating Hilbert Space

The pure theoretical part of Quantum Mechanics does not value the generation of Hilbert space very much. However, in Quantum Field Theory and many aspects of the application of Quantum Mechanics, generating Hilbert space is a crucial procedure. To do this, we need the complete set of commutative observables

Definition. *The complete set of commutative observables is a set of commutative observables with their spectrum can determine a unique state.*

Thus, a system can be determined and labelled by the spectrum of complete set of commutative observables.

3 Thermodynamic States

3.1 Microscopic States

Classical Thermodynamics concerns the macroscopic state consisting of huge amount of microscopic states. Thus, it is beneficial to first analyse microscopic states. Since we deal with microscopic Physics, we need to invoke Quantum Mechanics. In Quantum Mechanics, states are represented by the rays of Hilbert space. In Dirac notation, this is represented by

$$|\omega\rangle$$

Hilbert space is a complete inner product space of square-integrable function. Thus, we are allowed to introduce the normalization condition

$$\langle\omega|\omega\rangle = 1 \tag{3.1}$$

If there is a representation $|x\rangle$, the state can be expanded as a wave function

$$\omega(x) = \langle x|\omega\rangle \tag{3.2}$$

Define the density operator as

$$\hat{\rho} = |\omega\rangle\langle\omega| \tag{3.3}$$

Under certain eigenstates of complete set of commutative observables $|n\rangle$ we have the density matrix

$$\rho_{mn} = \langle m|\hat{\rho}|n\rangle \tag{3.4}$$

In the density operator formulation, the expectation of an operator G can be calculated from

$$\langle \hat{G} \rangle = \mathrm{tr}(\hat{\rho}\hat{G}) \tag{3.5}$$

The density operator formulation has been widely used in statistical mechanics and is equivalent to the conventional representation of microscopic states. Thus, in the subsequent content, microscopic states and parameters will be written in the density operator formulation.

3.2 Macroscopic States

Orthodox Quantum Mechanics does not claim to step into macroscopic area. However, in Quantum Mechanics, there does exist the many-particle theory. Thus, the macroscopic states we now consider is actually many-particle states denoted by

$$|\psi\rangle$$

This state may contain a large number of microscopic degrees of freedom. However, if the system contains large enough microscopic degrees of freedom, we are able to use some mean value as macroscopic degrees of freedom. Thus, this macroscopic state is determined through only limited macroscopic parameters. Hence, we have the following definition

Definition. *The thermodynamic macroscopic state is a ray* $|\psi\rangle$ *in macroscopic Hilbert space generated by macroscopic parameter operators.*

The generation of macroscopic Hilbert space will be discussed in the next section. From now on, unless claimed, the state represents the macroscopic state.

Also, if we have a representation $|\varepsilon\rangle$, we can construct a wave function

$$\psi(\varepsilon) = \langle \varepsilon | \psi \rangle \tag{3.6}$$

For a microscopic state, the square of the wave function represents certain possibility distribution. However, a macroscopic state contains a huge number of microscopic states, and thus the square of the wave function represents the ratio of microscopic states with certain parameters (e.g. ε).

3.3 Hilbert Spaces of States

In Quantum Mechanics, we have a rigorous construction of Hilbert space. And thus, the construction of the Hilbert space seems just to construct a many-particle state. Nevertheless, things are not so easy. For instance, a microscopic state $\hat{\rho}$ usually have discrete energy spectrum, however, a macroscopic state can have a continuous energy spectrum due to the large amount of particles.

In this sense, the Hilbert space of macroscopic states can be different from the that of many-particle states. However, since any macroscopic system can be regarded in essence as a many-particle state, all physical macroscopic states can be identical to the corresponding many-particle states.

3.4 Equilibrium States

A macroscopic state can include a huge number of microscopic states, and thus different combination of microscopic states can form disparate macroscopic states. However, there exists a special case that some macroscopic parameters of the disparate states are the same, which means the system is uniform. This kind of uniformity corresponds to equilibrium in Thermodynamics.

To define the equilibrium states, decompose the state into

$$|\psi\rangle = |\psi_1\rangle|\psi_2\rangle \cdots |\psi_m\rangle \tag{3.7}$$

where all the states in the right hand side is not able to decompose. It is crucial to notice that the number m might not equal to the particle number in the state since there might be entanglement inside the state. The state $|\psi_i\rangle$ is called the minimum divisible state. Therefore, the equilibrium is defined by

Definition. *A state is* ***equilibrated with respect to parameter*** $\boldsymbol{x}$ *if all its minimum divisible states have the same spectrum of the parameter.*

The equilibrium plays an important role in first law of Thermodynamics when identifying the energy and the internal energy.

4 Thermodynamic Parameter

4.1 Interpretation

For macroscopic states, there are in total five independent parameters to describe — pressure, volume, temperature, entropy and particle number. In our system of Thermodynamics theory, the states are rays in Hilbert space. By analogy, the macroscopic parameter should be interpreted as operators.

The operators of microscopic and macroscopic states are not in fact mathematically equivalent, since the Hilbert spaces of them respectively are not equivalent although closely linked. Thus, the microscopic operator will be denoted by $\hat{G}$ with hat and macroscopic operator will be denoted by $\widehat{G}$ with wide hat. The only exception is the density operator as well as the operator generated by the density operator. They are able to exert on both Hilbert spaces.

4.2 Heat, Work and Energy

The energy conservation law is one of the most rigid law in Physics. So now we consider the formulation of energy conservation law in Thermodynamics. First of all, we need the definition of energy

Definition. *The* ***energy*** *of a Thermodynamics state is defined as*

$$\widehat{E}\,|\psi\rangle = \mathrm{tr}(\hat{\rho}\hat{\mathcal{H}})|\psi\rangle \tag{4.1}$$

where $|\psi\rangle$ is any state, $\hat{\rho}$ is the density operator and $\hat{\mathcal{H}}$ is the Hamiltonian operator.

We want to know the alteration of the energy after some time. So we define the thermodynamic process as

Definition. *A* ***thermodynamic process*** *is a smooth curve in phase space parametrized by proper time.*

Now, we define the work and heat as

Definition. *The* ***work*** *of a process is defined by*

$$\delta\widehat{W}\,|\psi\rangle = \mathrm{tr}(\hat{\rho}\,\delta\hat{\mathcal{H}})|\psi\rangle \tag{4.2}$$

where $|\psi\rangle$ is any state and δ is the variation operator.

Definition. *The* ***heat*** *of a process is defined by*

$$\delta\widehat{Q}\,|\psi\rangle = \mathrm{tr}(\hat{\mathcal{H}}\delta\hat{\rho})|\psi\rangle \tag{4.3}$$

where $|\psi\rangle$ is any state.

From the definition can we easily conclude the energy conservation law

Energy Conservation Law. *The variation of energy is the sum of the variation of work and heat, formulated by*

$$\delta\widehat{E} = \delta\widehat{W} + \delta\widehat{Q} \tag{4.4}$$

Here we write a wide operator equation. The meaning of the equivalence relation should be comprehended as that the result after the two sides of equation act on any state is equal.

4.3 Particle Number

Definition. *The* ***particle number operator*** *$\widehat{n}$ is defined by*

$$\widehat{n}|\psi\rangle = n|\psi\rangle \tag{4.5}$$

where $|\psi\rangle$ is any state and n is the total particle number in this state.

From the definition we can see that all states are the eigenstates of particle number operator. And the function of this operator is to measure the particle number of the state.

4.4 Entropy

Definition. *The* ***entropy operator*** *$\widehat{S}$ is defined as*

$$\widehat{S}\,|\psi\rangle = -\kappa\,\mathrm{tr}(\hat{\rho}\ln\hat{\rho})\,|\psi\rangle \tag{4.6}$$

where $|\psi\rangle$ is any state and $\hat{\rho}$ is the density operator corresponds to the state.

There is a special case that $\hat{\rho}$ is a diagonal operator and all the diagonal elements satisfy

$$\hat{\rho}_i = \hat{\Omega}^{-1} \tag{4.7}$$

where $\hat{\Omega}$ is the microscopic state number operator. We find that there are in total Ω diagonal elements and thus the trace operation becomes the summation of Ω equal quantities, which makes equation (4.6) become

$$\widehat{S}\,|\psi\rangle = \kappa\ln\hat{\Omega}\,|\psi\rangle \tag{4.8}$$

Thus, we see that the entropy correlates with the total microscopic state number.

4.5 Temperature

Definition. *The* ***temperature operator*** *$\widehat{T}$ is defined by*

$$\delta_{ij}\kappa\widehat{T}\,|\psi\rangle = \langle\chi_i\frac{\partial\hat{\mathcal{H}}}{\partial\chi_j}\rangle|\psi\rangle \tag{4.9}$$

where $|\psi\rangle$ is any state, κ is the Boltzmann constant, chi_i is the independent variable in phase space and $\hat{\mathcal{H}}$ is the Hamiltonian.

This definition infers that the temperature is proportional to the microscopic kinematic energy.

4.6 Pressure

Definition. *The* ***pressure operator*** $\widehat{p}$ *is defined as*

$$\widehat{p}|\psi\rangle = n\langle\hat{p}\hat{v}\rangle|\psi\rangle \tag{4.10}$$

where $|\psi$ *is any state,* n *is the particle number of the system,* p *is the momentum and* v *is the velocity of certain direction.*

If the spacetime background has a dimension of q, equation (4.10) can also be written as

$$\widehat{p}\,|\psi\rangle = \frac{n}{q}\langle\hat{p}_\mu\hat{v}^\mu\rangle|\psi\rangle \tag{4.11}$$

Considering that any state is the eigenstate of particle number operator, we have

$$\widehat{p}\,|\psi\rangle = \langle\hat{n}\hat{p}\hat{v}\rangle|\psi\rangle \tag{4.12}$$

from which we can conclude that the pressure operator is to generate the expectation of total momentum flow.

4.7 Volume

Definition. *The* ***volume operator*** $\widehat{V}$ *is defined as*

$$\widehat{V}\,|\psi\rangle = V|\psi\rangle \tag{4.13}$$

where $|\psi\rangle$ *is any state and* V *is the volume of the state.*

It can be seen that the volume operator is to generate the volume of a state.

The volume operator has a absolute distinction with the previous operators. The previous operators all have a clear microscopic significance which is the average of some quantities. However, the volume operator does not. This indicates that the volume is an absolute macroscopic parameter.

5 Thermodynamic Function

5.1 Internal Energy

Definition. *The* ***internal energy*** $\widehat{U}$ *is defined by*

$$\mathrm{d}\widehat{U} = \widehat{T}\,\mathrm{d}\widehat{S} - \widehat{p}\,\mathrm{d}\widehat{V} + \mu\,\mathrm{d}\widehat{n} \tag{5.1}$$

where d *is the exterior differential operator and* μ *is the chemical potential.*

5.2 Enthalpy

Definition. *The* ***Enthalpy*** $\widehat{H}$ *is defined by*

$$\mathrm{d}\widehat{H} = \widehat{T}\,\mathrm{d}\widehat{S} + \widehat{V}\,\mathrm{d}\widehat{p} + \mu\,\mathrm{d}\widehat{n} \tag{5.2}$$

Utilizing Legendre transformation, we can write an equivalent formulation of enthalpy by internal energy

$$\widehat{H} = \widehat{U} + \widehat{p}\,\widehat{V} \tag{5.3}$$

5.3 Helmholtz Free Energy

Definition. *The* ***Helmholtz free energy*** *or* ***free energy*** $\widehat{F}$ *is defined by*

$$\mathrm{d}\widehat{F} = -\,\widehat{S}\,\mathrm{d}\widehat{T} - \widehat{p}\,\mathrm{d}\widehat{V} + \mu\,\mathrm{d}\widehat{n} \tag{5.4}$$

Utilizing Legendre transformation, we can write an equivalent formulation of enthalpy by internal energy

$$\widehat{F} = \widehat{U} - \widehat{T}\widehat{S} \tag{5.5}$$

5.4 Gibbs Free Energy (Free Enthalpy)

Definition. *The* ***Gibbs free energy*** *or* ***free enthalpy*** $\widehat{G}$ *is defined by*

$$\mathrm{d}\widehat{G} = -\,\widehat{S}\,\mathrm{d}\widehat{T} + \widehat{V}\,\mathrm{d}\widehat{p} + \mu\,\mathrm{d}\widehat{n} \tag{5.6}$$

Utilizing Legendre transformation, we can write an equivalent formulation of enthalpy by internal energy

$$\widehat{G} = \widehat{U} + \widehat{p}\,\widehat{V} - \widehat{T}\widehat{S} \tag{5.7}$$

6 Thermodynamic Ensemble

6.1 Equilibrium State

Until now, we have not yet put forward any special requirements of any concepts in our system of Thermodynamics. However, such a general system can hardly move forward now. Thus, we need to add some constraints on the concepts we have introduced for further analysis. Here, we introduce the thermodynamic equilibrium

Definition. *The state is* ***thermodynamic equilibrated*** *if*

(a) it is equilibrated with respect to temperature
(b) it is equilibrated with respect to pressure
(c) it is equilibrated with respect to chemical potential

Our further deductions in thermodynamic ensemble are all based on the equilibrium state.

6.2 Energy Distribution Function

The distribution function we are going to illustrate needs the following hypothesis

Hypothesis. *The thermodynamic state has continuous energy spectrum.*

Hence, we are able to decompose the state $|\psi\rangle$ through energy spectrum

$$|\psi\rangle = \int \mathrm{d}\varepsilon\, |\varepsilon\rangle\langle\varepsilon|\psi\rangle \tag{6.1}$$

Thus, we are able to define a wave function with respect to the energy

$$\psi(\varepsilon) = \langle\varepsilon|\psi\rangle \tag{6.2}$$

Now we are going to determine the formulation of the wave function. Notice that we have two properties of the states

$$\begin{cases} \langle\psi|\psi\rangle = 1 \\ \langle\psi|\hat{\varepsilon}|\psi\rangle = \bar{\varepsilon} \end{cases} \tag{6.3}$$

Expand the above conditions with respect to the energy spectrum and we get the constraints for the distribution function as

$$\begin{cases} \displaystyle\int \mathrm{d}\varepsilon\langle\psi|\varepsilon\rangle\langle\varepsilon|\psi\rangle = \int \mathrm{d}\varepsilon\, \psi^2(\varepsilon) = 1 \\ \displaystyle\int \mathrm{d}\varepsilon\langle\psi|\varepsilon\rangle\langle\varepsilon|\hat{\varepsilon}|\varepsilon\rangle\langle\varepsilon|\psi\rangle = \int \mathrm{d}\varepsilon\, \varepsilon\psi^2(\varepsilon) = \bar{\varepsilon} \end{cases} \tag{6.4}$$

The orthodox idea suggest us construct the energy distribution function as

$$\psi^2(\varepsilon) = A\exp\{-B\varepsilon\} \tag{6.5}$$

where A and B are positive real numbers. With the help of the above constraints, we can conclude

$$A = B = \bar{\varepsilon}^{-1} \tag{6.6}$$

Thus, the energy distribution function can be written as

$$\psi^2(\varepsilon) = \frac{1}{\bar{\varepsilon}}\exp\{-\frac{\varepsilon}{\bar{\varepsilon}}\} \tag{6.7}$$

6.3 Maxwell Speed Distribution

From the hypothesis of continuous energy spectrum, we can infer that the thermodynamic state has continuous speed spectrum. Thus, we have the wave function

$$\psi(v) = \langle v|\psi\rangle \tag{6.8}$$

Now, condition (6.3) gives

$$\begin{cases} \displaystyle\int \mathrm{d}v\langle\psi|v\rangle\langle v|\psi\rangle = \int \mathrm{d}v\, \psi^2(v) = 1 \\ \displaystyle\int \mathrm{d}v\langle\psi|v\rangle\langle v|\hat{\varepsilon}_k^{\mathrm{nr}}|v\rangle\langle v|\psi\rangle = \int \mathrm{d}v\, \varepsilon_k^{\mathrm{nr}}\psi^2(v) = \bar{\varepsilon}_k^{\mathrm{nr}} \end{cases} \tag{6.9}$$

where

$$\varepsilon_k^{\mathrm{nr}} = \frac{1}{2}m\hat{v}^2 \tag{6.10}$$

From (4.9) we can conclude that if the energy has the form as (6.10), there is

$$\bar{\varepsilon}_k^{\mathrm{nr}} = \frac{i}{2}\kappa T \tag{6.11}$$

where i is the translation degrees of freedom and T is defined by

$$\widehat{T}\,|\psi\rangle \equiv T|\psi\rangle \tag{6.12}$$

The same as what we do in the energy distribution function, write the speed distribution function as

$$\psi^2(v) = A\exp\{-Bv^2\} \tag{6.13}$$

With similar calculation

$$\begin{cases} A = \left(\dfrac{m}{2\pi\kappa T}\right)^{\frac{i}{2}} \\ B = \dfrac{m}{2\kappa T} \end{cases} \tag{6.14}$$

6.4 Gibbs Ensemble

The **Gibbs ensemble** suggests constructing the density operator as

$$\hat{\rho} = \frac{1}{Z}\exp\{-\beta\hat{\mathcal{H}}\} \tag{6.15}$$

where β is a positive real number and Z is the **partition function** defined as

$$Z = \mathrm{tr}(\exp\{-\beta\hat{\mathcal{H}}\}) \tag{6.16}$$

Thus we can see that the partition function serves as the normalization factor in Gibbs ensemble.

Now we are going to determine the the positive real number β. Suppose the Hamiltonian of the state goes to infinity at the boundary of the state. The normalization condition requires

$$\int \hat{\rho}\,\mathrm{d}\mathit{\Gamma} = \hat{I} \tag{6.17}$$

where $\hat{I}$ is the identity operator and

$$\mathrm{d}\mathit{\Gamma} = \bigwedge_{i=1}^{q} \mathrm{d}x_i\,\mathrm{d}p_i \tag{6.18}$$

Integrate by parts for certain i and get

$$\int \hat{\rho}\chi_i \,\mathrm{d}\mathit{\Gamma}^i + \int \hat{\rho}\chi_i\beta\frac{\partial\hat{\mathcal{H}}}{\partial\chi_i}\,\mathrm{d}\mathit{\Gamma} = \hat{I} \tag{6.19}$$

where $\mathrm{d}\mathit{\Gamma}^i$ is the induced surface volume element. The first term vanishes according to our assumption. Thus we have

$$\int \hat{\rho}\chi_i\beta\frac{\partial\mathcal{H}}{\partial\chi_i}\,\mathrm{d}\mathit{\Gamma} = \beta\langle\chi_i\frac{\partial\hat{\mathcal{H}}}{\partial\chi_i}\rangle = \beta\kappa T\hat{I} = \hat{I} \tag{6.20}$$

Therefore, we have

$$\beta = \frac{1}{\kappa T} \tag{6.21}$$

which is the well-renowned thermodynamic beta.

7 Thermodynamic Theorem

7.1 First Law of Thermodynamics

In order to describe the first law of Thermodynamics, we need preliminarily several concepts

Definition. *A process is **quasi-static** if for any time τ the state $|\psi(\tau)\rangle$ is an equilibrium state.*

The quasi-static state plays an important role in the first law of Thermodynamics. The quasi-static condition indicates that we can regard every instant of the state in the process as an equilibrium state, which validates Gibbs ensemble in the whole process. Thus, we can introduce the first law of Thermodynamics

First Law of Thermodynamics. *For a quasi-static process with the state being a Gibbs ensemble and only acted by pressure-volume work, there is*

$$\mathrm{d}\widehat{U} = \delta\widehat{Q} + \text{đ}\widehat{W} \tag{7.1}$$

Proof. Let's first calculate the variation of entropy

$$\delta\widehat{S}\,|\psi\rangle = -\kappa\,\mathrm{tr}[(\ln\hat{\rho} + 1)\delta\hat{\rho}]|\psi\rangle \tag{7.2}$$

Utilizing Gibbs ensemble (6.15)

$$\delta\widehat{S}\,|\psi\rangle = \kappa\,\mathrm{tr}(\beta\hat{\mathcal{H}}\delta\hat{\rho})|\psi\rangle + (\ln Z - 1)\,\mathrm{tr}(\delta\hat{\rho})|\psi\rangle \tag{7.3}$$

The second term vanishes owing to

$$\mathrm{tr}(\hat{\rho} + \delta\hat{\rho}) = \mathrm{tr}(\hat{\rho}) + \mathrm{tr}(\delta\hat{\rho}) = \mathrm{tr}(\hat{\rho}) \tag{7.4}$$

since the density operator still needs to satisfy normalization condition even after the variation. Thus, we have

$$\delta\widehat{S}\,|\psi\rangle = \kappa\beta\,\mathrm{tr}(\hat{H}\delta\hat{\rho}) = \frac{\delta\widehat{Q}}{T} \tag{7.5}$$

Consequently

$$\delta\widehat{Q} = \widehat{T}\delta\widehat{S} = \widehat{T}\,\mathrm{d}\widehat{S} \tag{7.6}$$

The last equality is due to that entropy in macroscopic system is a coordinate and thus its variation will equal to its exterior differential form.

Next, the pressure-volume work is easily seen to become the variation of work

$$\text{đ}\widehat{W} = -\,\widehat{p}\,\mathrm{d}\widehat{V} \tag{7.7}$$

Also, for the Gibbs ensemble in quasi-static process, the particle number in each phase in the system will remain invariant. Hence

$$\mathrm{d}\widehat{n} = 0 \tag{7.8}$$

Therefore

$$\mathrm{d}\widehat{U} = \widehat{T}\mathrm{d}\widehat{S} - \widehat{p}\,\mathrm{d}\widehat{V} + \mu\,\mathrm{d}\widehat{n} = \delta\widehat{Q} + \text{đ}\widehat{W} \tag{7.9}$$

which finishes our proof. ☐

7.2 Second Law of Thermodynamics

The second law of Thermodynamics has become the most important but the most controversy law in Physics. It is important because the so-called "perpetual motion machine of the second kind" is banned as a result of the second law. It is controversy since it does not have a microscopic meaning. Also, it is considered to have potential to define a direction for time arrow but face great difficulties on account of the time reverse symmetry of microscopic theories.

Therefore, we now give a version of the second law of Thermodynamics. It is needed to first clarify that although classical Thermodynamics regards the second law as a universal law, we still consider it in a microscopic view that it is a law with strict conditions. Thus, we have the second law of Thermodynamics

Second Law of Thermodynamics. *The entropy of a state with large enough particles being uniformly perturbed for a long enough time in non-relativistic limit will not decrease*

$$\delta\widehat{S} \geqslant 0 \tag{7.10}$$

Proof. First let's calculate the change rate of entropy with respect to time

$$\frac{\mathrm{d}\widehat{S}}{\mathrm{d}t}|\psi\rangle = -\kappa\sum_{r}\mathrm{tr}(\frac{\mathrm{d}\hat{\rho}_r}{\mathrm{d}t}\ln\hat{\rho}_r)|\psi\rangle \tag{7.11}$$

where we have considered

$$\mathrm{tr}(\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t}) = \frac{\mathrm{d}}{\mathrm{d}t}\mathrm{tr}(\hat{\rho}) = 0 \tag{7.12}$$

If the system is perturbed by Hamiltonian $\hat{\mathcal{H}}_{pt}$ for large enough time, we have the Fermi's first order perturbation of the transition rate

$$\sigma_{rs} = \frac{2\pi}{\hbar}|\langle r|\hat{\mathcal{H}}_{pt}|s\rangle|^2 \tag{7.13}$$

Thus

$$\frac{\mathrm{d}\hat{\rho}_r}{\mathrm{d}t} = \sum_{s}\sigma_{rs}\hat{\rho}_s = \sum_{s\neq r}\sigma_{rs}\hat{\rho}_s + \sigma_{rr}\rho_r \tag{7.14}$$

Utilizing

$$\sum_{s}\sigma_{rs} = \sum_{s\neq r}\sigma_{rs} + \sigma_{rr} = 0 \tag{7.15}$$

We can write

$$\frac{\mathrm{d}\hat{\rho}_r}{\mathrm{d}t} = \sum_{s\neq r}\sigma_{rs}(\hat{\rho}_s - \hat{\rho}_r) \tag{7.16}$$

Take this into (7.11) and we have

$$\begin{aligned}\frac{\mathrm{d}\widehat{S}}{\mathrm{d}t}|\psi\rangle &= -\kappa\sum_{s\neq r}\mathrm{tr}(\sigma_{rs}\ln\hat{\rho}_r)(\hat{\rho}_s - \hat{\rho}_r)|\psi\rangle \\ &= \frac{1}{2}\kappa\sum_{s\neq r}\mathrm{tr}[\sigma_{rs}(\ln\hat{\rho}_r - \ln\hat{\rho}_s)(\hat{\rho}_r - \hat{\rho}_s)]|\psi\rangle\end{aligned} \tag{7.17}$$

The last equality is the result of the symmetry of matrix σ_{rs}. We see from the result that the right hand side will be equal or greater than zero. Thus

$$\frac{\mathrm{d}\widehat{S}}{\mathrm{d}t} \geqslant 0 \tag{7.18}$$

Regard the entropy as a quantity and rewrite in variation formulation

$$\delta\widehat{S} \geqslant 0 \tag{7.19}$$

which finishes our proof. ☐

Remarks. We can see here that there are at least four strict conditions needed to validate the second law

(a) particle number is large enough
(b) each energy spectrum is uniformly perturbed
(c) perturbation time is long enough
(d) non-relativistic

Taken a theoretical view, these conditions are so strict that it does not have any chance to become a universal law. Nonetheless, these conditions can in fact be easily satisfied in the scale of our application. Also, we need to mention that this is only one version of the second law. Thus, we can not eliminate the possibility for proofs of stronger theorems.

7.3 Third Law of Thermodynamics

Compared with the first and second law of Thermodynamics, the third law of Thermodynamics seems not so well-known, since largely speaking, it does not have very strong application significance. Besides, it is vital to notice that although one version of the law can be strictly proven, there is another wide-spread version is not able to. Before introducing the law, we need the following concept

Definition. *A* ***perfect crystal*** *is a system satisfying*

$$\mathcal{H}_i\delta^i_0 = 0 \;\; and \;\; \mathcal{H}_i\delta^i_j \neq 0 \;\; for \;\; j > 0 \tag{7.20}$$

where $\mathcal{H}_i$ is the Hamiltonian of the ith eigenstate.

Now we can introduce the third law of Thermodynamics. The proven version is formulated as

Third Law of Thermodynamics. *The entropy of a perfect crystal at* 0K *is zero.*

Proof. The condition $T = 0\mathrm{K}$ yields

$$\langle\chi_i\frac{\partial\hat{\mathcal{H}}}{\partial\chi_j}\rangle = \mathrm{tr}(\hat{\rho}\chi_i\frac{\partial\hat{\mathcal{H}}}{\partial\chi_j}) = 0 \tag{7.21}$$

because the only Hamiltonian element with zero value is the ground state Hamiltonian. Thus, the above condition is satisfied if and only if

$$\hat{\rho} = \hat{\rho}_0 \tag{7.22}$$

where $\hat{\rho}_0$ is the ground state of the system. This indicates that the temperature of a state being zero is equivalent to the state being ground state. However, ground state is a definite state with

$$\mathrm{tr}(\hat{\rho}\ln\hat{\rho}) = 1\cdot\ln 1 = 0 \tag{7.23}$$

Hence

$$\widehat{S}\,|\psi\rangle = -\kappa\,\mathrm{tr}(\hat{\rho}\ln\hat{\rho})\,|\psi\rangle = 0 \tag{7.24}$$

which finishes our proof. ☐

It is important to notice that this law cares only about the perfect crystal and thus may fail when this condition is not satisfied.

There is also another version of the third law

It is impossible to reach 0K in finite steps.

However, we have to say that this law has not yet been rigorously proven. More precisely, we need a condition that is too strict to make the above statement a law.

8 Application

8.1 Temperature Scale

The thermodynamic temperature is defined through the triple point of pure water. Specifically, define the temperature of triple point of pure water as

$$T_{tp} = 273.16\mathrm{K}$$

This definition of temperature is the thermodynamic temperature scale.

8.2 Condensation Statistics

8.2.1 Maxwell Distribution

The Maxwell Distribution function is formulated as

$$\psi^2(v) = \left(\frac{m}{2\pi\kappa T}\right)^{\frac{i}{2}} \exp\{-\frac{1}{2}\beta m v^2\} \tag{8.1}$$

We have the two characteristic average. First is the root-mean-square speed

$$v_{\mathrm{rms}} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{i\kappa T}{m}} \tag{8.2}$$

Second is the average speed with three degrees of freedom

$$\bar{v} = \langle v\rangle = \sqrt{\frac{8\kappa T}{\pi m}} \tag{8.3}$$

8.2.2 Boltzmann Distribution

The Boltzmann distribution function is formulated as

$$\psi^2(\varepsilon_p) = n_0 \exp\{-\beta\varepsilon\} \tag{8.4}$$

where ε_p is certain potential energy.

8.2.3 Fermi-Dirac Statistics

Fermi-Dirac statistics describes the condensation statistics of Fermions. Suppose we have in total q energy level and level i has degeneracy g_i. Also, suppose we have equal possibility for n_i Fermions to stay at each configuration. Due to the Pauli exclusion, the total number of configuration is the product of choosing n_i states in g_i total states, i.e.

$$\Omega(n, g) = \prod_{i=0}^{q} \frac{g_i!}{n_i!(g_i - n_i)!} \tag{8.5}$$

Besides, we have two constraints

$$\begin{cases} \sum_{i=1}^{q} n_i = n \\ \sum_{i=1}^{q} n_i\varepsilon_i = E \end{cases} \tag{8.6}$$

where ε_i is the energy of the level i. Thus, construct the Lagrange function as

$$\tilde{\mathcal{L}} = \ln\Omega + \alpha(N - \sum_{i=0}^{q} n_i) + \beta(E - \sum_{i=0}^{q} n_i\varepsilon_i) \tag{8.7}$$

where tilde means it is not a Lagrangian but a Lagrange function. Thus, we derive the equation of motion through Lagrange equation

$$\frac{\partial\tilde{\mathcal{L}}}{\partial n_i} = \ln\left(\frac{g_i - n_i}{n_i}\right) - \alpha - \beta\varepsilon_i = 0 \tag{8.8}$$

Thus, we calculate the distribution function of particles

$$n_i = \frac{g_i}{\exp\{\alpha + \beta\epsilon_i\} + 1} \tag{8.9}$$

Take this expression back to (8.5) and perform the exterior differential on $\ln\Omega$

$$\begin{aligned} \mathrm{d}\ln\Omega &= \sum_{i=0}^{q} \ln\left(\frac{g_i - n_i}{n_i}\right)\mathrm{d}n_i = \sum_{i=0}^{q}(\alpha_i + \beta\varepsilon_i)\,\mathrm{d}n_i \\ &= \alpha\,\mathrm{d}N + \beta\,\mathrm{d}E \end{aligned} \tag{8.10}$$

Notice that the conditions we now consider satisfy the conditions of first law of Thermodynamics. Thus, we identify the energy as internal energy and get

$$\mathrm{d}E = T\,\mathrm{d}S + \mu\,\mathrm{d}N \tag{8.11}$$

Hence we solve the constant α and β

$$\beta = \frac{1}{\kappa T}, \quad \alpha = -\frac{\mu}{\kappa T} \tag{8.12}$$

Substitute these into (8.9) and get

$$n_i = \frac{g_i}{\exp\{(\epsilon_i - \mu)/\kappa T\} + 1} \tag{8.13}$$

This is the Fermi-Dirac statistics.

8.2.4 Einstein-Bose Statistics

Apart from fermions, we have also bosons. So, the Einstein-Bose Statistics aims at describing the statistics of Bosons. Unlike fermions, bosons does not have any exclusion properties. Thus, there might be arbitrary number of particles in one eigenstate. This means the configuration is the product of choosing n_i places for particles and $g_i - 1$ places for the rest partitions from in total $n_i + g_i - 1$ places, i.e.

$$\Omega(n, g) = \prod_{i=0}^{q} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \tag{8.14}$$

Through similar procedure, we can solve the particle distribution function

$$n_i = \frac{g_i}{\exp\{(\epsilon_i - \mu)/\kappa T\} - 1} \tag{8.15}$$

This is the Einstein-Bose statistics.

8.3 Heat Capacity

Heat can in fact be influenced by several parameters. However, if we only care about the temperature and keep the other parameters at a static point, heat can be a function of temperature. Thus, we can define the heat capacity as

Definition. *The **heat capacity** is defined by*

$$C_\chi = \left.\frac{\partial Q}{\partial T}\right|_\chi \tag{8.16}$$

where χ consists of all parameters that can influence heat.

We have two special heat capacity

Definition. *The **isochoric heat capacity** is defined as*

$$C_u = \frac{\partial U}{\partial T} \tag{8.17}$$

Definition. *The **isobaric heat capacity** is defined as*

$$C_h = \frac{\partial H}{\partial T} \tag{8.18}$$

Also, we have the heat capacity in phase transition

Definition. *The **latent heat** Λ is the heat during the phase transition.*

8.4 Equation of State

Previously, we only consider the state to be in the condition of equilibrium state and quasi-static process. Now, for furthermore analysis, we need to specify the type of matter. For certain type of matter, we can have some equations which it will satisfy. This is the equation of state for that type of matter. We can see that the equation of state can have an injection with the type of matter. Thus, we use the equation of state to label the matter.

8.4.1 Ideal Gas

We first introduce the ideal gas as

Definition. *The **ideal gas** is the gas satisfying*

$$\widehat{p}\widehat{V} = \widehat{n}R\widehat{T} \tag{8.19}$$

where R is a positive constant defined by

$$R = \kappa N_A \tag{8.20}$$

Within N_A is the Avogadro constant.

The ideal gas has a number of good properties. For example, we are going to see that the internal energy of ideal gas is irrelevant to the volume. Also, it is a relatively good approximation of the real gas. These properties make it the most widely used gas model.

8.4.2 Van der Waals Gas

Another gas model closer to the real gas is the Van de Waals gas model as

Definition. *The **Van de Waals gas** is the gas satisfying*

$$\tilde{\widehat{p}}\tilde{\widehat{V}} = \widehat{n}R\widehat{T} \tag{8.21}$$

where $\tilde{\widehat{p}}$ is defined as

$$\tilde{\widehat{p}} = \widehat{p} + a\nu^2 \widehat{V}^{-2} \tag{8.22}$$

and $\tilde{\widehat{V}}$ is defined as

$$\tilde{\widehat{V}} = \widehat{V} - b\nu \tag{8.23}$$

Within, a and b are constants.

Although the ideal gas has many good properties, the simulation of some particular gases can fail. In fact, the ideal gas can become more accurate when $T \to 0$. However, this reduces it applicability. Thus, a modification of the ideal gas model was put forward, which is the Van de Waals model. This model can better describe gas at room temperature, and hence more applicable in some situations.

8.4.3 Maxwell Relation

Maxwell relation is a widely used relationship in Thermodynamics, especially when the matter is specified and thus equation of state can be inferred. However, in Mathematics, Maxwell relation is just a very simple interpretation of the commutation relation of the second partial derivative

Definition. ***Maxwell relation*** *is formulated as*

$$\mathrm{d}(\mathrm{d}\phi) = 0 \tag{8.24}$$

where d *is the exterior differential operator and* ϕ *is a scalar field.*

Now we apply this equation to the enthalpy

$$\begin{aligned} \mathrm{d}(\mathrm{d}\widehat{H}) &= \mathrm{d}\widehat{T}\,\mathrm{d}\widehat{S} + \mathrm{d}\widehat{V}\,\mathrm{d}\widehat{p} \\ &= \frac{\partial \widehat{T}}{\partial \widehat{p}}\,\mathrm{d}\widehat{p} \wedge \mathrm{d}\widehat{S} + \frac{\partial \widehat{V}}{\partial \widehat{S}}\,\mathrm{d}\widehat{S} \wedge \mathrm{d}\widehat{p} \\ &= \left(\frac{\partial \widehat{T}}{\partial \widehat{p}} - \frac{\partial \widehat{V}}{\partial \widehat{S}} \right) \mathrm{d}\widehat{p} \wedge \mathrm{d}\widehat{S} = 0 \end{aligned} \tag{8.25}$$

Thus we have

$$\frac{\partial \widehat{T}}{\partial \widehat{p}} - \frac{\partial \widehat{V}}{\partial \widehat{S}} = 0 \tag{8.26}$$

If we have the equation of state, we have the following result

$$\frac{\partial \widehat{U}}{\partial \widehat{V}} = \frac{1}{\widehat{T}} \frac{\partial \widehat{S}}{\partial \widehat{V}} - \widehat{p} = \frac{1}{\widehat{T}} \frac{\partial \widehat{T}}{\partial \widehat{p}} - \widehat{p} \tag{8.27}$$

With similar derivation, we have also

$$\frac{\partial \widehat{H}}{\partial \widehat{p}} = \frac{1}{\widehat{T}} \frac{\partial \widehat{V}}{\partial \widehat{T}} + \widehat{V} \tag{8.28}$$

And we can also have other relations from free energy and free enthalpy. These relations return normal if there is no equation of state and thus the first term vanishes. Now, if we have an equation of state, the first term will have a non-vanishing value. For example, the internal energy of Van de Waals gas is relative to the volume. But, the good properties of ideal gas make its internal energy free of volume since the equation of state annihilates the first term.

8.4.4 Clausius-Clapeyron Relation

The Clausius-Clapeyron relation describes the state during phase transition. The Clausius-Clapeyron relation states

Clausius-Clapeyron Relation. *The state under phase transition satisfies*

$$\delta \Lambda = \widehat{T}\, \frac{\partial \widehat{p}}{\partial \widehat{T}}\, \text{đ}\widehat{V} \tag{8.29}$$

Through this relation, we can calculate the pressure-temperature relation if the latent heat is known.

8.5 Thermodynamic Process of Gas

In this section, we care about some particular processes of gas. It is essential to state ahead that all the processes we consider here should satisfy the condition of first law of Thermodynamics.

8.5.1 Isochoric Process

Definition. *The* ***isochoric process*** *is defined as*

$$\delta \widehat{V}(\tau) = 0 \tag{8.30}$$

This leads to a basic relation as

$$\text{đ}\widehat{U} = \delta \widehat{Q} \tag{8.31}$$

This relation is important in defining the isochoric heat capacity and therefore important in calculating the internal energy.

8.5.2 Isobaric Process

Definition. *The* ***isobaric process*** *is defined as*

$$\delta \widehat{p}(\tau) = 0 \tag{8.32}$$

This leads to a basic relation as

$$\text{đ}\widehat{U} = \delta \widehat{W} \tag{8.33}$$

This relation is important in defining the isobaric heat capacity.

8.5.3 Isothermal Process

Definition. *The* ***isothermal process*** *is defined as*

$$\delta \widehat{T}(\tau) = 0 \tag{8.34}$$

We can not read a basic relation of isothermal process from the first law of Thermodynamics since it annihilates neither heat nor work. Thus, we need equation of state for further analysis. Suppose we now only consider the ideal gas. And then we have

$$\widehat{p}\widehat{V} = \text{constant} \tag{8.35}$$

This is the basic relation of ideal gas under isothermal process.

8.5.4 Adiabatic Process

Definition. *The **adiabatic process** is defined as*

$$\delta\widehat{Q}(\tau) = 0 \tag{8.36}$$

The first law of Thermodynamics infers

$$\text{đ}\widehat{U} = \delta\widehat{W} \tag{8.37}$$

Again, we need to invoke equation of state. And we also work on ideal gas this time. From the first law

$$-\,\widehat{p}\,\mathrm{d}\widehat{V} = C_u\,\mathrm{d}\widehat{T} \tag{8.38}$$

Also, from the equation of state

$$\widehat{p}\,\mathrm{d}\widehat{V} + \widehat{V}\,\mathrm{d}\widehat{p} = \nu R\,\mathrm{d}\widehat{T} \tag{8.39}$$

We solve

$$\widehat{p}\widehat{V}^{\gamma} = \text{constant} \tag{8.40}$$

where

$$\gamma = C_h/C_u \tag{8.41}$$

8.5.5 Polytropic Process

Except for the processes with certain parameters or quantities invariant, there is also a process who is the superposition of several process. This can be generalized as

Definition. *The **polytropic process** is defined as*

$$\widehat{p}\widehat{V}^{n} = constant \tag{8.42}$$

In this process, we have a special corresponding heat capacity as

$$C_n = C_u\left(\frac{\gamma - n}{1 - n}\right) \tag{8.43}$$

8.6 Carnot Cycle and Carnot Engine

Previously, the processes we discuss are all non-self-intersecting process. However, a real process can return to its initial state after some time, which is what is usually called cyclic process. To discuss this, first we need the definition of thermodynamic cyclic process

Definition. *The **thermodynamic cyclic process** is a thermodynamic process satisfying*

$$|\psi(\tau)\rangle = |\psi(\tau')\rangle \tag{8.44}$$

where τ and τ' represent certain proper time.

Using the thermodynamic cyclic process, we can build the heat machine

Definition. *A **heat machine** is a state in thermodynamic cyclic process.*

For chosen coordinates, the cycle can have directions. Usually, we will initially choose a direction as the standard direction of a cycle. And if the direction of a process is against the standard direction, this cycle is then the reverse cycle.

In order to define the direction of the cycle, we need some preliminary illustration. Assume that there are finite number of parameters served as coordinates to specify a state. Then we can set up a manifold. Thus, a cycle can be expressed as a *curve* in the manifold. We need to assume that the manifold is orientable, and assume we have already chosen an orientation.

Now, we give the definition of standard and reverse cycle

Definition. *A cycle is **standard** if*

$$\oint \text{đ}\widehat{W} \geqslant 0 \tag{8.45}$$

*A cycyle is **reverse** if*

$$\oint \text{đ}\widehat{W} < 0 \tag{8.46}$$

Thus, the heat machine is furthermore divided into

Definition. *A **heat engine** is a state in standard thermodynamic cyclic process.*

*A **refrigerator** is a state in reverse thermodynamic cyclic process.*

After a period of cyclic process, the energy of the state remains invariant. Thus, we have an equation

$$\delta\widehat{Q} = -\text{đ}\widehat{W} \tag{8.47}$$

Thus, a cyclic process can be divided into a heat absorption process and a heat release process. In this sense, we can calculate the heat absorbed and released in the cycle, defined by

Definition. *The absorbed heat in a cycle is defined as*

$$\widehat{Q}_{\text{ab}} = \max \int \delta\widehat{Q} \tag{8.48}$$

The released heat in a cycle is defined as

$$\widehat{Q}_{\text{rs}} = \min \int \delta\widehat{Q} \tag{8.49}$$

It can be easily proven that the sum of the absorbed and released heat is the total work of a cycle. For a heat machine, we can define the efficiency through this two concepts

Definition. *The efficiency of a heat engine is defined as*

$$\eta_e = \frac{\widehat{W}}{\widehat{Q}_{\mathrm{ab}}} \tag{8.50}$$

The efficiency of a refrigerator is defined as

$$\eta_r = \frac{\widehat{Q}_{\mathrm{rs}}}{\widehat{W}} \tag{8.51}$$

In our application, the cyclic process usually satisfies some macroscopic conditions. Thus, we have the constrained thermodynamic cyclic process

Definition. *A* ***constrained thermodynamics cyclic process*** *is a thermodynamic cyclic process constrained by conditions of first and second law of Thermodynamics*

This constrained cyclic process can be used to build a special kind of heat machine

Definition. *A* ***reversible heat machine*** *is a state in constrained thermodynamic cyclic process.*

We can see that a reversible heat machine have the capacity to be both a heat engine and a refrigerator. This property plays an important role in proving the Carnot theorem.

From now on, unless stated, all the cyclic process we mention refers to the constrained thermodynamic cyclic process.

Now, we introduce a special kind of cyclic process — Carnot cycle

Definition. *The* ***Carnot cycle*** *is a cyclic process consists of two isothermal processes and two adiabatic processes.*

Suppose the temperature of the two isothermal process is T_h and T_l, where $T_h > T_l$. Then the Carnot cycle can be used as a heat machine touched by heat reservoir with temperature T_h and T_l.

Definition. *A Carnot heat machine is a heat machine working in Carnot cycle.*

Theorem. *The efficiency of Carnot heat engine is*

$$\eta_c e = 1 - \frac{T_l}{T_h} \tag{8.52}$$

The efficiency of Carnot refrigerator is

$$\eta_c e = \frac{T_l}{T_h - T_l} \tag{8.53}$$

This theorem is obvious if we write the entropy as

$$\Delta \widehat{S} = \oint \frac{\delta \widehat{Q}}{\widehat{T}} \tag{8.54}$$

and notice the entropy is invariant under cyclic process, which lead to

$$\widehat{Q} \propto \widehat{T} \tag{8.55}$$

Last but not least, we introduce a significant theorem — Carnot theorem

Carnot Theorem. *Any reversible heat machine working under the same source has the same efficiency, and the efficiency of reversible heat machine is higher than that of irreversible heat machine.*

Proof. Suppose we have two heat machine x and y working under the same source with efficiency η_x and η_y respectively. Machine x is any heat machine and machine y is the reversible heat engine.

(1) If machine x is reversible, there is reasoning like follows: first let x be heat engine and drive y to be refrigerator. Engine x will release work

$$\widehat{W} = \eta_x \, \widehat{Q}_{\mathrm{ab}} \tag{8.56}$$

And the high temperature reservoir will lose heat Q_{ab} but gain from y

$$\widehat{Q}_{\mathrm{rs}} = \eta_y^{-1} \, \widehat{W} = \frac{\eta_x}{\eta_y} \, \widehat{Q}_{\mathrm{ab}} \tag{8.57}$$

According to the second law of Thermodynamics, the entropy of the combination should not decrease, which leads to

$$\widehat{Q}_{\mathrm{rs}} \leqslant \widehat{Q}_{\mathrm{ab}} \tag{8.58}$$

which leads to

$$\eta_x \leqslant \eta_y \tag{8.59}$$

Reverse the two machine, i.e, let x be refrigerator driven by y as heat engine. Similar reasoning will provide

$$\eta_y \leqslant \eta_x \tag{8.60}$$

Thus

$$\eta_y = \eta_x \tag{8.61}$$

Consequently we prove the first part of the theorem.

(2) If machine x is an irreversible heat engine, similar reasoning will produce

$$\eta_x \leqslant \eta_y \tag{8.62}$$

Consequently, the second part of the theorem is proved.

Synthesizing the above deduction can the theorem be proved. □

8.7 Entropy Measurement

The entropy is defined through the density operator. However, for a macroscopic system, it can be too hard to determine the density operator, which causes difficulties in measuring the entropy. Nonetheless, if some macroscopic properties are known for certain situations, we can calculate the entropy through the other thermodynamic parameters.

To do this, first formulate the entropy as

$$\mathrm{d}\widehat{S} = \frac{\delta\widehat{Q}}{\widehat{T}} \tag{8.63}$$

Notice that if the system is constrained by conditions of first and second law of Thermodynamics

$$\delta\widehat{Q} = \mathrm{d}\widehat{U} + \widehat{p}\,\mathrm{d}\widehat{V} = \mathrm{d}\widehat{H} - \widehat{V}\,\mathrm{d}\widehat{p} \tag{8.64}$$

Now if we have the heat capacity C_u, C_h and suppose we have some equation of state, we can write

$$\begin{aligned}\mathrm{d}\widehat{S} &= \frac{C_u}{\widehat{T}}\,\mathrm{d}\widehat{T} + \frac{1}{\widehat{T}}\left(\frac{\partial\widehat{U}}{\partial\widehat{V}} + \widehat{p}\right)\mathrm{d}\widehat{V} \\ &= \frac{C_h}{\widehat{T}}\,\mathrm{d}\widehat{T} + \frac{1}{\widehat{T}}\left(\frac{\partial\widehat{H}}{\partial\widehat{p}} - \widehat{V}\right)\mathrm{d}\widehat{p}\end{aligned} \tag{8.65}$$

Next, we use this to calculate entropy in three specific situations.

8.7.1 Entropy of Ideal Gas

For ideal gas, there is

$$\frac{\partial\widehat{U}}{\partial\widehat{V}} = 0 \qquad \frac{\partial\widehat{H}}{\partial\widehat{p}} = 0 \tag{8.66}$$

Thus

$$\mathrm{d}\widehat{S} = \frac{C_u}{\widehat{T}}\,\mathrm{d}\widehat{T} + \nu R\,\mathrm{d}\ln\widehat{V} = \frac{C_h}{\widehat{T}}\,\mathrm{d}\widehat{T} + \nu R\,\mathrm{d}\ln\widehat{p} \tag{8.67}$$

8.7.2 Entropy of Mixing Process of Ideal Gas

Suppose the total amount of substance is ν and each sort of gas takes up c_i and there is not temperature change during the mixing. Then the process can be regarded as the diffusion of each sort of gas with parameter χ_i to χ. Therefore

$$\Delta\widehat{S} = -\nu R\sum_{i=1}^{q} c_i \ln\frac{\chi_i}{\chi} = -\nu R\sum_{i=1}^{q} c_i \ln c_i \tag{8.68}$$

8.7.3 Entropy of Phase Transition

The entropy of phase transition is quite simple. Since the temperature is invariant during the phase transition, there is

$$\Delta\widehat{S} = \frac{\mathit{\Lambda}}{\widehat{T}} \tag{8.69}$$

where $\mathit{\Lambda}$ is the latent heat and $\widehat{T}$ is the temperature during the phase transition.