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# STATISTICAL MECHANICS: A COMPLETE GUIDE

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PHYS 449

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*Solo Pursuit of Learning*



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# **Part I**

## **Thermodynamics**

# Chapter 1

## Energy in Thermal Physics

### 1.1.0 Basic Notation and Work

**Definition 1.1.1.** *Thermodynamics is a phenomenological description of properties of macroscopic systems in thermal equilibrium.*

By a phenomenological description we mean a description based on observations and direct experience of the experimenter with the system, considered as a “black box” (a system whose internal structure is unknown, or is just not considered).

**Definition 1.1.2 (Systems).** *There are a number of different thermodynamic systems. We summarize them as follows:*

- **Thermodynamic or Macroscopic System:** *A system consisting of a large number of constituents. For example, a mole of gas (approximately  $10^{23}$  particles) can be considered as a macroscopic system.*
- **Isolated Thermodynamic System:** *A system which exhibits no exchange of any type with the surroundings; no exchange of work, heat, matter, etc.*
- **Closed Thermodynamic System:** *A system which exhibits no exchange of matter with its surroundings.*
- **Open Thermodynamic System:** *A system for which it is possible for exchange of any type with the surroundings (work, heat, matter, etc.)*

**Definition 1.1.3 (Equilibrium).** *Two thermodynamic systems are in equilibrium if and only if they are in contact such that they can exchange a given conserved quantity (for example particles) and they are relaxed to a state in which there is no average net transfer of that quantity between them anymore. A thermodynamic system  $S$  is in equilibrium with itself, if and only if, all its subsystems are in equilibrium with each other. In this case,  $S$  is called an equilibrium system.*

From this definition we find that different types of exchanged quantities can lead to different types of equilibria:

Exchanged Quantity	Type of Equilibrium
Particles/Matter	Diffusive Equilibrium
Work	Mechanical Equilibrium
Heat	Thermal Equilibrium

**Definition 1.1.4. Complete Thermodynamic Equilibrium** corresponds to a state where all the conserved fluxes between two coupled thermodynamic systems vanish.

A way of testing if a given system is in a complete thermodynamic equilibrium is if the properties of the system do not change appreciably over the observation time, which is to say the properties reflect the true asymptotic long-term properties after any initial relaxation time is over.

The state of thermodynamic systems in complete thermodynamic equilibrium can be described by a set of independent thermodynamic coordinates or state variables; this fact is based on empirical observations.

## Boyle-Mariotte's Experiment

**Law.** For a given mass of gas at a constant temperature  $T$ , the volume  $V$  is inverseley proportional to the pressure  $P$ :  $V \propto P^{-1}$ .

We consider Robert Boyle's (1627-1691) experiment, conducted at room temperature, which should remain constant during the time of the experiment. We use a vertical tube with markings to indicate the volume of gas, and oil at the bottom. By applying pressure on the oil, we also exert a pressure on the air in the tube above the oil, causing the volume to decrease. Drawing the graph of volume versus  $P^{-1}$  we obtain a straight line, so  $V \cdot P = C$  for some constant  $C$ , given a fixed temperature. As further measurements show, the constant is proportional to the temperature  $T$ , so  $V \cdot P \propto T$ . More precisely, the full equation of a state of simple low-density gase is given by

$$PV = Nk_B T \quad (1.1.1)$$

where  $N$  is the number of gas particles and  $k_B \approx 1.381 \times 10^{-23} \text{ J/K}$  is a natural constant called the **Boltzmann's constant**. The above equation is called the ideal gas law or the equation of state for an ideal gas since it relates the three state variables, or thermodynamic coordinates,  $P$ ,  $V$ , and  $T$  at equilibrium.

## Work

**Definition 1.1.5.** Given a vector force field  $\vec{F}$  defined along a path  $\gamma$ , the work  $W$  is of  $\vec{F}$  along  $\gamma$  is defined to be:

$$W = \int_{\gamma} \vec{F} \cdot d\vec{r} \quad (1.1.2)$$

**Recall 1.1.1.** Recall that pressure is force per unit area, so we have that

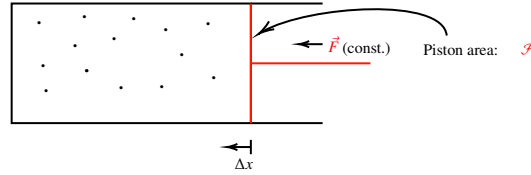
$$P = \frac{F}{A}$$

where  $F$  is the normal component of the force to the area  $A$ . More precisely, pressure is the proportionality constant that relates the force and normal vectors:

$$d\vec{F}_n = -pd\vec{A}$$

where  $\vec{F}_n$  denotes the normal component of the force vector  $\vec{F}$ .

**Example 1.1.1.** Consider the compression of a gas by a piston with a constant force of magnitude  $F$ .



so the work is

$$W = \int_{\gamma} \vec{F} \cdot d\vec{r} = F \int_{\gamma} dr = F\Delta x = PA\Delta x = -P\Delta V$$

where  $P$  is the pressure and  $\Delta V$  is the change in volume. Since the change in volume is negative, the work  $W$  done on the system (here the gas) is positive: Energy is added to the system by a force (macroscopic) process (here the piston).  $W < 0$  if energy is removed from the system.

**Definition 1.1.6.** The generalized differential form for work is given by

$$\delta W = \sum_{i=1}^m J_i dq_i \quad (1.1.3)$$

where  $q_i$  are the generalized coordinates and the  $J_i$  are the conjugate generalized forces such that  $J_i dq_i$  has units of energy.

Here are a few examples of generalized coordinates and their corresponding generalized conjugate forces:

	Generalized Force $J_i$	Generalized Coordinate $dq_i$
Pressure	$-P$	$dV$ (change in volume)
Surface tension	$\sigma$	$dS$ (change in surface area)
Magnetic field	$\vec{B}_0$	$d\vec{m}$ (change in magnetic moment)
Electric field	$\vec{E}$	$d\vec{P}$ (change in electric dipole moment)

**Definition 1.1.7.** *Differential changes in a systems property are said to be **quasi-static** if the changes occur on time scales much longer than the relaxation time such that the system remains in equilibrium at all times.*

To ensure thermodynamics is a self-consistent description of macroscopic systems in thermal equilibrium we must assume that the differential changes  $\delta W$  are quasi-static. This also ensures that we can describe the state of such a thermodynamic system by a set of thermodynamic coordinates at all times.

Depending on the macroscopic generalized force, the work necessary to transfer a thermodynamic system in complete thermodynamic equilibrium from state  $A$  to state  $B$  might or might not depend on the path taken. For example, if  $\gamma_1$  and  $\gamma_2$  are two paths from state  $A$  to state  $B$ , it is possible that  $\int_{\gamma_1} \delta W \neq \int_{\gamma_2} \delta W$ . (Note that this justifies the use of the notation  $\delta W$  over  $dW$ , which would denote an exact differential)

## Conservative Forces

**Recall 1.1.2.** Recall that a conservative force is a force  $\vec{F}$  with an associated potential energy function  $E$  such that  $\vec{F} = \nabla E$ .

**Proposition 1.1.1.** *If the macroscopic generalized force  $\vec{J}$ , depending on  $m$  generalized coordinates  $q_i$ , is conservative with potential energy  $E_{pot}$  which is twice continuously differentiable and the domain of integration is simply connected, then the following are equivalent:*

- $\vec{J}(\vec{q}) = -\nabla E_{pot}(\vec{q})$
- $dW$  is an exact differential form, so

$$\int_{\gamma} dW = \int_{\gamma} \vec{J} \cdot d\vec{r}$$

*depends only on the endpoints of  $\gamma$ .*

- For any simple closed path  $\gamma$ ,

$$\oint_{\gamma} dW = \oint_{\gamma} \vec{J} \cdot d\vec{r} = 0$$

- The curl of  $\vec{J}$  is trivial over the domain of integration

$$\nabla \times \vec{J} = 0$$

*provided that  $m = 3$*

- For all  $i, j \in \{1, 2, \dots, m\}$ , we have that

$$\frac{\partial J_i}{\partial q_j} - \frac{\partial J_j}{\partial q_i} = 0$$



- The differential  $dW$  is exact, and we have that

$$dW = -\nabla E_{pot} \cdot d\vec{r} = -\sum_{i=1}^m \frac{\partial E_{pot}}{\partial q_i} dq_i = -dE_{pot}$$

**Definition 1.1.8.** For a function  $A(q_1, q_2, \dots, q_m)$  the total differential or exact differential of  $A$  is given by

$$dA = \sum_{i=1}^m \frac{\partial A}{\partial q_i} dq_i$$

This corresponds to a generalized chain rule:

$$\frac{dA}{dt} = \nabla A \cdot \frac{d}{dt} \vec{q} = \sum_{i=1}^m \frac{\partial A}{\partial q_i} \frac{dq_i}{dt}$$

called the total derivative of  $A$  with respect to  $t$ . An exact differential corresponds to an integrable differential form:

$$\int_{\gamma} \sum_{i=1}^m \frac{\partial A}{\partial q_i} dq_i = \int_{\gamma} dA = A(\vec{q}_f) - A(\vec{q}_i)$$

where  $\vec{q}_i$  and  $\vec{q}_f$  are the initial and final point of the path  $\gamma$ , respectively.

Consequently, an integrable, or exact, differential form does not depend on the path taken and in physics we would consider  $A$  to be a potential function.

**Note 1.1.3.** For non-conservative forces,  $\delta W$  is an inexact differential form.

**Theorem 1.1.2.** A differential form

$$\delta A \equiv \sum_{i=1}^m a_i(q_1, q_2, \dots, q_m) dq_i$$

for functions  $a_i : D \subseteq \mathbb{R}^m \rightarrow \mathbb{R}$  is exact if and only if

$$\frac{\partial a_i}{\partial q_j} = \frac{\partial a_j}{\partial q_i}$$

for all  $i, j \in \{1, 2, \dots, m\}$ .

**Definition 1.1.9.** An integrating factor  $\mu$  is a factor that makes an inexact differential form exact upon multiplication.

**Theorem 1.1.3.** For  $m = 2$ , an integrating factor always exists. Specifically, for  $\delta A = a_1 dx_1 + a_2 dx_2$ , we can define  $df := \mu \delta A = (\mu a_1) dx_1 + (\mu a_2) dx_2$ , with  $\mu$  determined non-uniquely by the equation

$$\frac{\partial(\mu a_1)}{\partial x_2} = \frac{\partial(\mu a_2)}{\partial x_1}$$

## 1.2.0 Heat and the 1st Law of Thermodynamics

**Definition 1.2.1.** Recall that work corresponds to the change in energy of a thermodynamic system by a **macroscopically forced process**. On the other hand the **heat**  $Q$  is the energy added to or removed from a thermodynamic system by a **spontaneous process**.

For example, consider the energy transfer between a cooking plate and a pot of water. The origin of this type of process lies in the underlying microscopic dynamics, which we will explore using Statistical Mechanics.

**Law (First Law of Thermodynamics).** For an isolated thermodynamic system, the total **internal energy**  $U$  is a constant and  $dU = 0$ . By the definition of internal energy,  $dU$  is an exact differential; consequently,  $U$  should be unique for a given state. For various systems we have the following:

- For a closed system,  $dU = \delta Q + \delta W$ .
- For an open system,  $dU = \delta Q + \delta W + \delta E_c$ , with

$$\delta E_c := \sum_{i=1}^{\alpha} \mu_i dN_i$$

where  $N_i$  is the number of particles of type  $i$  and  $\mu_i$  is the **chemical potential** associated with particles of type  $i$  for all  $1 \leq i \leq \alpha$  with  $\alpha$  being the number of different particle types. The chemical potential corresponds to the energy needed to add a particle of type  $i$  to a given thermodynamic system while no other type of energy is exchanged, which is to say  $\delta W = 0$  and  $\delta Q = 0$ .

In summary, the empirical first law is a reformulation of the conservation of energy and requires the inclusion of heat.

## **Chapter 2**

# **Thermodynamical Systems**

## **Chapter 3**

# **Thermodynamical Potentials and Equilibrium**

# **Part II**

## **Statistical Mechanics**

## **Chapter 4**

# **Microstates and Entropy**

## **Chapter 5**

# **Ensemble Theory and Free Energy**

## **Chapter 6**

# **Boltzmann Statistics and the Canonical Ensemble**



## **Chapter 7**

# **Breakdown of Classical Statistical Mechanics**

# **Part III**

## **Probability Theory**

## **Chapter 8**

# **Characteristics of Probability Theory**

## **Chapter 9**

# **Continuous Random Variables and the Gaussian Distribution**

## **Chapter 10**

# **Information and Entropy**

## **Part IV**

# **Real Gases and Phase Transitions**

## **Chapter 11**

# **Kinetic Theory of Gases**

## **Chapter 12**

### **Classification of Phase Transitions**



## **Part V**

# **Quantum Statistics**

# **Chapter 13**

## **Quantum States**

## **Chapter 14**

### **Ideal Quantum Gases**

# **Appendices**