

III. Kinetic Theory of Gases

III.A General Definitions

- **Kinetic theory** studies the macroscopic properties of large numbers of particles, starting from their (classical) equations of motion.

Thermodynamics describes the equilibrium behavior of *macroscopic objects* in terms of concepts such as work, heat, and entropy. The phenomenological laws of thermodynamics tell us how these quantities are constrained as a system approaches its equilibrium. At the *microscopic level*, we know that these systems are composed of particles (atoms, molecules), whose interactions and dynamics are reasonably well understood in terms of more fundamental theories. If these microscopic descriptions are complete, we should be able to account for the macroscopic behavior, i.e. derive the laws governing the macroscopic state functions in equilibrium. Kinetic theory attempts to achieve this objective. In particular, we shall try to answer the following questions:

- (1) How can we define “equilibrium” for a system of moving particles?
- (2) Do all systems naturally evolve towards an equilibrium state?
- (3) What is the time evolution of a system that is not quite in equilibrium?

The simplest system to study, the veritable work-horse of thermodynamics, is the dilute (nearly ideal) gas. A typical volume of gas contains of the order of 10^{23} particles. Kinetic theory attempts to deduce the macroscopic properties of the gas from the time evolution of the individual atomic coordinates. At any time t , the *microstate* of a system of N particles is described by specifying the positions $\vec{q}_i(t)$, and momenta $\vec{p}_i(t)$, of all particles. The microstate thus corresponds to a point $\mu(t)$, in the $6N$ dimensional *phase space* $\Gamma = \prod_{i=1}^N \{\vec{q}_i, \vec{p}_i\}$. The time evolution of this point is governed by the canonical equations

$$\begin{cases} \frac{\partial \vec{q}_i}{\partial t} = \frac{\partial \mathcal{H}}{\partial \vec{p}_i} \\ \frac{\partial \vec{p}_i}{\partial t} = -\frac{\partial \mathcal{H}}{\partial \vec{q}_i} \end{cases}, \quad (\text{III.1})$$

where the *Hamiltonian* $\mathcal{H}(\mathbf{p}, \mathbf{q})$, describes the total energy in terms of the set of coordinates $\mathbf{q} \equiv \{\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N\}$, and momenta $\mathbf{p} \equiv \{\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N\}$. The microscopic equations of motion have *time reversal symmetry*, i.e. if all the momenta are suddenly reversed, $\mathbf{p} \rightarrow -\mathbf{p}$, at $t = 0$, the particles retrace their previous trajectory, $\mathbf{q}(t) = \mathbf{q}(-t)$. This follows from the invariance of \mathcal{H} under the transformation $T(\mathbf{p}, \mathbf{q}) \rightarrow (-\mathbf{p}, \mathbf{q})$.

As formulated within thermodynamics, the *macrostate* M , of an ideal gas in equilibrium is described by a small number of state functions such as E , T , P , and N . The space of macrostates is considerably smaller than the phase space spanned by microstates. Therefore, there must be a very large number of microstates μ corresponding to the same macrostate M .

This many to one correspondence suggests the introduction of a statistical *ensemble* of microstates. Consider \mathcal{N} copies of a particular macrostate, each described by a different *representative point* $\mu_n(t)$, in the phase space Γ . Let $d\mathcal{N}(\mathbf{p}, \mathbf{q}, t)$ equal the number of representative points in an infinitesimal volume $d\Gamma = \prod_{i=1}^N d^3\vec{p}_i d^3\vec{q}_i$ around the point (\mathbf{p}, \mathbf{q}) . A phase space density $\rho(\mathbf{p}, \mathbf{q}, t)$ is then defined from

$$\rho(\mathbf{p}, \mathbf{q}, t)d\Gamma = \lim_{\mathcal{N} \rightarrow \infty} \frac{d\mathcal{N}(\mathbf{p}, \mathbf{q}, t)}{\mathcal{N}}. \quad (\text{III.2})$$

This quantity can be compared with the *objective* probability introduced in the previous section. Clearly $\int d\Gamma \rho = 1$, and ρ is a properly normalized *probability density function* in phase space. To compute macroscopic values for various functions $\mathcal{O}(\mathbf{p}, \mathbf{q})$, we shall use the *ensemble averages*

$$\langle \mathcal{O} \rangle = \int d\Gamma \rho(\mathbf{p}, \mathbf{q}, t) \mathcal{O}(\mathbf{p}, \mathbf{q}). \quad (\text{III.3})$$

When the exact microstate μ is specified, the system is said to be in a *pure state*. On the other hand, when our knowledge of the system is probabilistic, in the sense of its being taken from an ensemble with density $\rho(\Gamma)$, it is said to belong to a *mixed state*. It is difficult to describe equilibrium in the context of a pure state, since $\mu(t)$ is constantly changing in time according to eqs.(III.1). Equilibrium is more conveniently described for mixed states by examining the time evolution of the phase space density $\rho(t)$, which is governed by the Liouville's equation introduced in the next section.

III.B Liouville's Theorem

- **Liouville's Theorem** states that the phase space density $\rho(\Gamma, t)$, behaves like an incompressible fluid.

Proof: Follow the evolution of $d\mathcal{N}$ pure states in an infinitesimal volume $d\Gamma = \prod_{i=1}^N d^3\vec{p}_i d^3\vec{q}_i$ around the point (\mathbf{p}, \mathbf{q}) . According to eqs.(III.1), after an interval δt these states have moved to the vicinity of another point $(\mathbf{p}', \mathbf{q}')$, where

$$q'_\alpha = q_\alpha + \dot{q}_\alpha \delta t + \mathcal{O}(\delta t^2) \quad , \quad p'_\alpha = p_\alpha + \dot{p}_\alpha \delta t + \mathcal{O}(\delta t^2). \quad (\text{III.4})$$

In the above expression, the q_α and p_α refer to any of the $6N$ coordinates and momenta, and \dot{q}_α and \dot{p}_α are the corresponding velocities. The original volume element $d\Gamma$, is in the shape of a hypercube of sides dp_α and dq_α . In the time interval δt it gets distorted, and the projected sides of the new volume element are given by

$$\begin{cases} dq'_\alpha = dq_\alpha + \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} dq_\alpha \delta t + \mathcal{O}(\delta t^2) \\ dp'_\alpha = dp_\alpha + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} dp_\alpha \delta t + \mathcal{O}(\delta t^2) \end{cases}. \quad (\text{III.5})$$

To order of δt^2 , the new volume element is $d\Gamma' = \prod_{i=1}^N d^3 \vec{p}_i' d^3 \vec{q}_i'$. From eqs.(III.5) it follows that for each pair of conjugate coordinates

$$dq'_\alpha \cdot dp'_\alpha = dq_\alpha \cdot dp_\alpha \left[1 + \left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right) \delta t + \mathcal{O}(\delta t^2) \right]. \quad (\text{III.6})$$

But since the time evolution of coordinates and momenta are governed by the canonical eqs.(III.1), we have

$$\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial}{\partial q_\alpha} \frac{\partial \mathcal{H}}{\partial p_\alpha} = \frac{\partial^2 \mathcal{H}}{\partial p_\alpha \partial q_\alpha}, \quad \text{and} \quad \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} = \frac{\partial}{\partial p_\alpha} \left(-\frac{\partial \mathcal{H}}{\partial q_\alpha} \right) = -\frac{\partial^2 \mathcal{H}}{\partial q_\alpha \partial p_\alpha}. \quad (\text{III.7})$$

Thus the projected area in eq.(III.6) is unchanged for any pair of coordinates, and hence the volume element is unaffected, $d\Gamma' = d\Gamma$. All the pure states $d\mathcal{N}$, originally in the vicinity of (\mathbf{p}, \mathbf{q}) are transported to the neighborhood of $(\mathbf{p}', \mathbf{q}')$, but occupy exactly the same volume. The ratio $d\mathcal{N}/d\Gamma$ is left unchanged, and ρ behaves like the density of an incompressible fluid.

The incompressibility condition $\rho(\mathbf{p}', \mathbf{q}', t + \delta t) = \rho(\mathbf{p}, \mathbf{q}, t)$, can be written in differential form as

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \cdot \frac{\partial p_\alpha}{\partial t} + \frac{\partial \rho}{\partial q_\alpha} \cdot \frac{\partial q_\alpha}{\partial t} \right) = 0. \quad (\text{III.8})$$

Note the distinction between $\partial \rho / \partial t$ and $d\rho / dt$: The former *partial* derivative refers to the changes in ρ at a particular location in phase space, while the latter *total* derivative follows the evolution of a volume of fluid as it moves in phase space. Substituting from eq.(III.1) into eq.(III.8) leads to

$$\frac{\partial \rho}{\partial t} = \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \cdot \frac{\partial \mathcal{H}}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha} \cdot \frac{\partial \mathcal{H}}{\partial p_\alpha} \right) = \{\rho, \mathcal{H}\}, \quad (\text{III.9})$$

where we have introduced the *Poisson bracket* of two functions in phase space as

$$\{A, B\} \equiv \sum_{\alpha=1}^{3N} \left(\frac{\partial A}{\partial p_{\alpha}} \cdot \frac{\partial B}{\partial q_{\alpha}} - \frac{\partial A}{\partial q_{\alpha}} \cdot \frac{\partial B}{\partial p_{\alpha}} \right) = -\{B, A\}. \quad (\text{III.10})$$

Consequences of Liouville's Theorem:

(1) Under the operation of time reversal symmetry, $T(\mathbf{p}, \mathbf{q}, t) \rightarrow (-\mathbf{p}, \mathbf{q}, -t)$, the Poisson bracket changes sign, and eq.(III.9) implies that the density reverses its evolution, i.e. $\rho(\mathbf{p}, \mathbf{q}, t) = \rho(-\mathbf{p}, \mathbf{q}, -t)$.

(2) The time evolution of the ensemble average in eq.(III.3) is given by (using eq.(III.9))

$$\frac{d\langle \mathcal{O} \rangle}{dt} = \int d\Gamma \frac{\partial \rho(\mathbf{p}, \mathbf{q}, t)}{\partial t} \mathcal{O}(\mathbf{p}, \mathbf{q}) = \sum_{\alpha=1}^{3N} \int d\Gamma \mathcal{O}(\mathbf{p}, \mathbf{q}) \left(\frac{\partial \rho}{\partial p_{\alpha}} \cdot \frac{\partial \mathcal{H}}{\partial q_{\alpha}} - \frac{\partial \rho}{\partial q_{\alpha}} \cdot \frac{\partial \mathcal{H}}{\partial p_{\alpha}} \right). \quad (\text{III.11})$$

The partial derivatives of ρ in the above equation can be removed by using the method of integration by parts, i.e. $\int f \rho' = -\int \rho f'$ since ρ vanishes on the boundaries of the integrations. Therefore

$$\begin{aligned} \frac{d\langle \mathcal{O} \rangle}{dt} &= - \sum_{\alpha=1}^{3N} \int d\Gamma \rho \left[\left(\frac{\partial \mathcal{O}}{\partial p_{\alpha}} \cdot \frac{\partial \mathcal{H}}{\partial q_{\alpha}} - \frac{\partial \mathcal{O}}{\partial q_{\alpha}} \cdot \frac{\partial \mathcal{H}}{\partial p_{\alpha}} \right) + \mathcal{O} \left(\frac{\partial^2 \mathcal{H}}{\partial p_{\alpha} \partial q_{\alpha}} - \frac{\partial^2 \mathcal{H}}{\partial q_{\alpha} \partial p_{\alpha}} \right) \right] \\ &= - \int d\Gamma \rho \{ \mathcal{O}, \mathcal{H} \} = \langle \{ \mathcal{H}, \mathcal{O} \} \rangle. \end{aligned} \quad (\text{III.12})$$

(3) If the members of the ensemble correspond to an equilibrium macroscopic state, the ensemble averages must be independent of time. This can be achieved by a stationary density, $\partial \rho_{\text{eq}} / \partial t = 0$, i.e. by requiring

$$\{ \rho_{\text{eq}}, \mathcal{H} \} = 0. \quad (\text{III.13})$$

A possible solution to the above equation is $\rho_{\text{eq}}(\mathbf{p}, \mathbf{q}) = \rho(\mathcal{H}(\mathbf{p}, \mathbf{q}))$, since $\{ \rho(\mathcal{H}), \mathcal{H} \} = \rho'(\mathcal{H}) \{ \mathcal{H}, \mathcal{H} \} = 0$. This solution implies that the value of ρ is constant on surfaces of constant energy \mathcal{H} , in phase space. This is indeed the *basic assumption of statistical mechanics*. For example, in the microcanonical ensemble, the total energy E , of an isolated system is specified. All members of the ensemble are then located on the surface $\mathcal{H}(\mathbf{p}, \mathbf{q}) = E$ in phase space. Eq.(III.9) implies that a uniform density of points on this surface is stationary in time. The assumption of statistical mechanics is that the macrostate is indeed represented by such a uniform density of microstates. This is equivalent to replacing the objective measure of probability in eq.(III.2) with a subjective one.

There may be additional *conserved quantities* associated with the Hamiltonian which satisfy $\{L_n, \mathcal{H}\} = 0$. In the presence of such quantities, a stationary density exists for any function of the form $\rho_{\text{eq}}(\mathbf{p}, \mathbf{q}) = \rho(\mathcal{H}(\mathbf{p}, \mathbf{q}), L_1(\mathbf{p}, \mathbf{q}), L_2(\mathbf{p}, \mathbf{q}), \dots)$. Clearly, the value of L_n is not changed during the evolution of the system, since

$$\begin{aligned} \frac{dL_n(\mathbf{p}, \mathbf{q})}{dt} &\equiv \frac{L_n(\mathbf{p}(t+dt), \mathbf{q}(t+dt)) - L_n(\mathbf{p}(t), \mathbf{q}(t))}{dt} \\ &= \sum_{\alpha=1}^{3N} \left(\frac{\partial L_n}{\partial p_\alpha} \cdot \frac{\partial p_\alpha}{\partial t} + \frac{\partial L_n}{\partial q_\alpha} \cdot \frac{\partial q_\alpha}{\partial t} \right) \\ &= - \sum_{\alpha=1}^{3N} \left(\frac{\partial L_n}{\partial p_\alpha} \cdot \frac{\partial \mathcal{H}}{\partial q_\alpha} - \frac{\partial L_n}{\partial q_\alpha} \cdot \frac{\partial \mathcal{H}}{\partial p_\alpha} \right) = -\{L_n, \mathcal{H}\} = 0. \end{aligned} \quad (\text{III.14})$$

Hence, the functional dependence of ρ_{eq} on these quantities merely indicates that all accessible states, i.e. those that can be connected without violating any conservation law, are equally likely.

(4) The above postulate for ρ_{eq} answers the first question posed at the beginning of this chapter. However, in order to answer the second question, and to justify the basic assumption of statistical mechanics, we need to show that non-stationary densities converge onto the stationary solution ρ_{eq} . This contradicts the time reversal symmetry noted in (1) above: For any solution $\rho(t)$ converging to ρ_{eq} , there is a time reversed solution that diverges from it. The best that can be hoped for, is to show that the solutions $\rho(t)$ are in the neighborhood of ρ_{eq} the majority of the time, so that *time averages* are dominated by the stationary solution. This brings us to the problem of *ergodicity*, which is whether it is justified to replace time averages with ensemble averages. In measuring the properties of any system, we deal with only one representative of the equilibrium ensemble. However, most macroscopic properties do not have instantaneous values and require some form of averaging. For example, the pressure P exerted by a gas results from the impact of particles on the walls of the container. The number and momenta of these particles varies at different times and different locations. The measured pressure reflects an average over many characteristic microscopic times. If over this time scale the representative point of the system moves around and uniformly samples the accessible points in phase space, we may replace the time average with the ensemble average. For a few systems it is possible to prove an *ergodic theorem*, which states that the representative point comes arbitrarily close to all accessible points in phase space after a sufficiently long time. However, the proof usually works for time intervals that grow exponentially with the number of particles N , and thus exceeds by far any reasonable time scale over which the pressure of a gas is typically measured. Thus the proofs of the ergodic theorem have so far little to do with the reality of macroscopic equilibrium.