

Chapter 1

Basic Concepts

1.1 Introduction

Macroscopic bodies consist of a large number of constituent atoms and molecules. The exact mechanical description of such bodies is almost impossible to obtain as the initial positions and momenta of the constituents are not known. Apart from the lack of knowledge of the initial conditions there is a weightier objection to obtaining a dynamical solution. If Δt is the time required for a measurement to be done then the *uncertainty in the measurement of energy* $\Delta E \sim \frac{\hbar}{\Delta t}$. Again if N is the number of particles in the system then the *separation between 2 energy levels of the system* is $\delta E \sim e^{-aN}$ where a is a constant, and with the N for any macroscopic system $N \sim 6.022 \times 10^{23} = \text{Avogadro Constant}$, we have $\Delta E \gg \delta E$. Thus we cannot talk about a definite energy of the system and the very concept of *Hamiltonian dynamics* is meaningless for such macroscopic bodies.

Thermodynamics gives the description of a macrosystem in terms of a finite number of parameters like pressure, volume, temperature and obtains relationship between them without taking into account the dynamics of the system. In Kinetic Theory of gases, however, we try to explain thermodynamic concepts like pressure, temperature *etc.* in terms of the dynamics of the gas molecules. Statistical Physics is the generalization of thermodynamics and kinetic theory, applicable to all systems and not only to gases. It obtains the thermodynamic quantities taking into account the interactions between the large number of atoms and molecules. This is done under the **thermodynamic limit** $\lim N \rightarrow \infty$ for the number of particles N of the system and $\lim V \rightarrow \infty$ for the volume V of the system so that number density $\frac{N}{V} = \text{finite}$. Generally the value of a double limit depends on the order in which the limits are taken as is shown in the following example.

$$\lim_{N \rightarrow \infty} \lim_{V \rightarrow \infty} \frac{NV}{N + V^2} = 0, \quad \text{while} \quad (1.1.1)$$

$$\lim_{V \rightarrow \infty} \lim_{N \rightarrow \infty} \frac{NV}{N + V^2} = \infty. \quad (1.1.2)$$

The restriction that $\frac{N}{V} = \text{finite}$ makes the limit finite and unique,

$$\begin{aligned} \lim_{\substack{N \rightarrow \infty, \\ V \rightarrow \infty, \\ \frac{N}{V} = \text{finite}}} \frac{NV}{N + V^2} &= \frac{N}{V}, \end{aligned} \quad (1.1.3)$$

as any physical quantity should be.

We shall mention here that modern investigations have extended the domain of Statistical Physics also to **mesoscopic systems** where this limit breaks down.

The *largeness of the number* of constituents and the *complexities of their motion* give rise to some new laws, the statistical laws, on which the whole of equilibrium statistical physics is built. These laws can be enunciated as *two basic postulates*.

Postulate 1.1.1 Hypothesis of Equal á-priori probability: All microstates for an isolated system in equilibrium has equal probability of occupation.

Postulate 1.1.2 Ergodic hypothesis: The time average of a physical quantity which is the observed value of the quantity, is equal to the **ensemble average** of the quantity, which we derive from the theories of statistical physics.

A number of terms like **microstate** and **ensemble average** have been used in these postulates, which we shall define later.

Like building up any theory, in Statistical Physics also we start with the postulates, which are *intuitively obvious assumptions* that cannot be proved but may sometimes be justified. However, we must realize that the statistical mechanical description of macrosystems is probabilistic. This is due to the lack of knowledge of the initial coordinates and momenta and *not* due to any quantum mechanical uncertainties associated with measurements.

1.2 Master Equation and Hypothesis of Equal \hat{a} -priori Probability

The hypothesis of **equal \hat{a} -priori probability** can be justified from the following consideration. We consider a nearly isolated system approaching equilibrium by interacting with its surrounding to attain a final state of higher probability. The rate of change of population in each microstate of the system is governed by assuming the intuitively acceptable **Master Equation** connecting time rate of change of population, p_m , in the state m with the transition rates, $W_{k \rightarrow l}$, from the state k to the state l .

$$\frac{dp_m}{dt} = - \sum_{n \neq m} W_{m \rightarrow n} p_m + \sum_{n \neq m} W_{n \rightarrow m} p_n, \quad \text{separately for every } m. \quad (1.2.1)$$

The first term on the right hand side of Equation 1.2.1 denotes the rate of change of p_m due to transition to the state n , while the second term corresponds to transition from the state n to the state m . These transitions

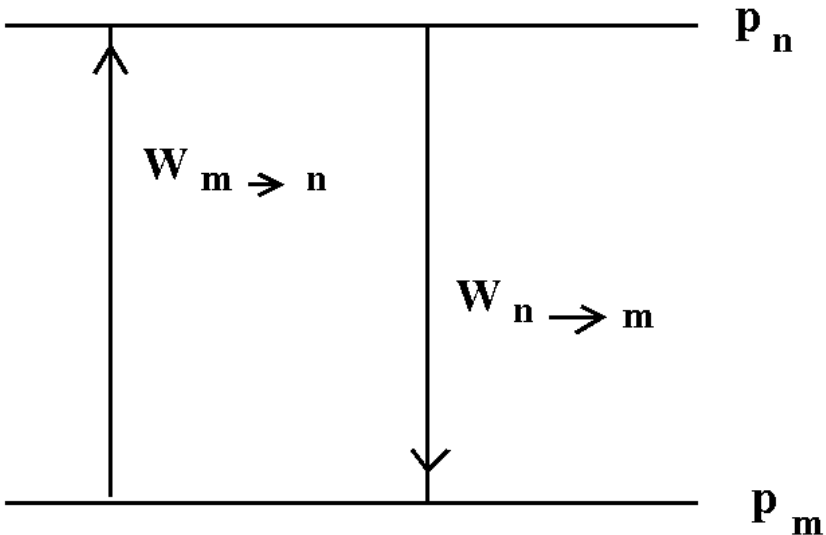


Fig. 1.2.1 Schematic diagram showing transitions between the states m and n .

are shown in Figure 1.2.1: Remembering that $W_{m \rightarrow m} = 0$ we can write

$$\frac{dp_m}{dt} = - \sum_n W_{m \rightarrow n} p_m + \sum_n W_{n \rightarrow m} p_n, \quad \text{separately for every } m. \quad (1.2.2)$$

Since in both Classical Mechanics as well as Quantum Mechanics $W_{n \rightarrow m} = W_{m \rightarrow n} = W_{(n,m)}$, depending only on the pair (n, m) , we can write the **Master Equation** as

$$\frac{dp_m}{dt} = \sum_n W_{(n,m)} (p_n - p_m), \text{ separately for every } m. \quad (1.2.3)$$

Since at statistical equilibrium $\frac{dp_m}{dt} = 0$ for every m , we immediately arrive at $p_m = p_n$ for all pairs of (n,m) as the **sufficient condition** of statistical equilibrium. Since the probabilities are proportional to the populations, we conclude that the **hypothesis of equal á-priori probability** is a **sufficient condition** for statistical equilibrium. It is also a **necessary condition** if the transition rates $W_{(n,m)}$ satisfy certain conditions. We shall have an idea of these conditions as we consider the example of the 3-level system in § 1.2.1.

1.2.1 Example of 3 Level Systems

In this subsection we consider a 3-level system, depicted in Figure 1.2.2. The explicit forms of the Master Equation for this system at equilibrium are;

$$\frac{dp_1}{dt} \equiv W_{(1,2)} (p_2 - p_1) + W_{(1,3)} (p_3 - p_1) = 0, \quad (1.2.4)$$

$$\frac{dp_2}{dt} \equiv W_{(1,2)} (p_1 - p_2) + W_{(2,3)} (p_3 - p_2) = 0, \quad (1.2.5)$$

$$\frac{dp_3}{dt} \equiv W_{(1,3)} (p_1 - p_3) + W_{(2,3)} (p_2 - p_3) = 0. \quad (1.2.6)$$

If the transition rates are all arbitrary, then $p_1 = p_2 = p_3$ i.e. **equal á-priori probability** will be the **necessary condition** for statistical equilibrium. If, however, one of the levels (say, level # 3) is completely disconnected (i.e. $W_{(1,3)} = W_{(2,3)} = 0$) from all the other levels (i.e. level # 1 and level # 2) then the only conclusion we can draw from statistical equilibrium is that $p_1 = p_2$. **Hypothesis of equal á-priori probability** is thus a **necessary condition** for statistical equilibrium only for connected states. This is actually true for any statistical system.

1.3 Phase Space, Phase Point, Phase Trajectory

To describe classically the states of a dynamical system one introduces the concept of **Phase Space**, which is a mathematical space consisting

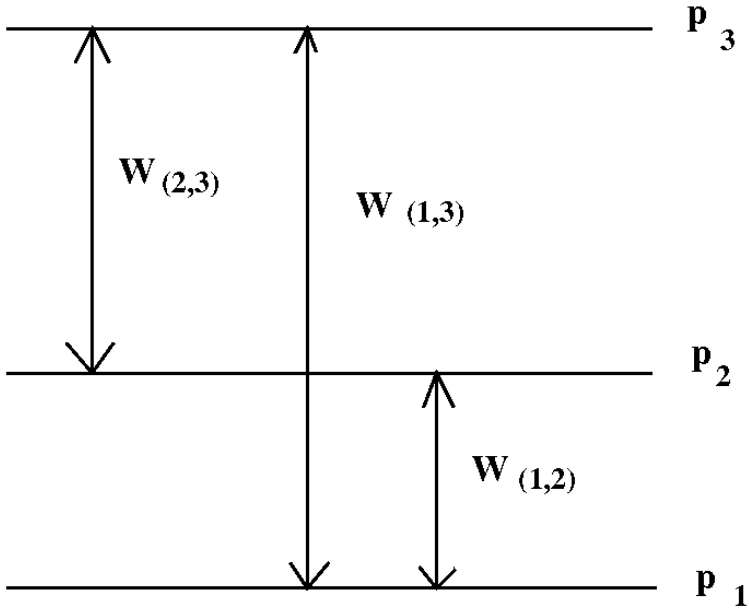


Fig. 1.2.2 Schematic diagram of the 3-level system.

of the *generalized coordinates* q_1, q_2, \dots, q_f and the *generalized momenta* p_1, p_2, \dots, p_f , f being the *degree of freedom* of the system under study. The phase space will be denoted by the symbol Γ . It is evident that this $2f$ -dimensional phase space has the *physical dimension* of f -dimensional action of Hamiltonian mechanics. Any point in the phase space will have fixed values of the f coordinates and the f momenta. This is called a **Phase Point**. At any point of time the state of the dynamical system is represented by a phase point in the phase space. As the system evolves in time the phase point traces out a curve in the phase space, called the **Phase Trajectory**. In Figure 1.3.1 we plot a schematic diagram of a phase trajectory in a phase space. The phase trajectories are *not self-intersecting*, because time evolution of a system has to be *unique*.

1.4 Statistical Distribution Function and Ergodic Hypothesis

We consider an elementary phase space volume $\Delta\Gamma = \prod_{i=1}^f (\Delta q_i \Delta p_i)$ so that the i -th component of generalized coordinate lies between q_i and $q_i + \Delta q_i$ and

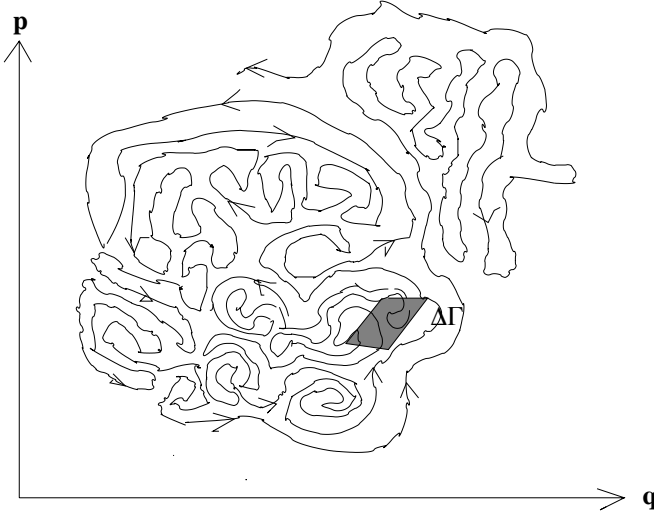


Fig. 1.3.1 Schematic representation of Phase Trajectory and infinitesimal Phase volume.

the i -th component of generalized momentum lies between p_i and $p_i + \Delta p_i$. Then the probability $\Delta\omega$ that the state of the system stays within $\Delta\Gamma$ can be defined in terms of time Δt spent by the phase trajectory inside $\Delta\Gamma$ as follows

$$\Delta\omega = \lim_{T \rightarrow \infty} \frac{\Delta t}{T}. \quad (1.4.1)$$

Then the time average of any physical quantity $F(q, p, t)$ is given by

$$\bar{F} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{t_0}^{t_0+T} F(q, p, t) dt. \quad (1.4.2)$$

By q and p we denote the generalized coordinates and the generalized momenta in a generic sense. We also tacitly assume that the value of the integral is independent of the starting point t_0 .

We now define **statistical distribution function** as

$$d\omega = \rho(q, p, t) d\Gamma. \quad (1.4.3)$$

The **statistical distribution function** $\rho(q, p, t)$ then represents the probability density function of the states of the system lying in the phase space

region $d\Gamma$ and so satisfies the *normalization condition*

$$\int \rho(q, p, t) d\Gamma = 1. \quad (1.4.4)$$

The statistical average

$$\langle F \rangle = \int F(q, p, t) \rho(q, p, t) d\Gamma \quad (1.4.5)$$

can be looked upon as if there are many copies of the system having states distributed in the phase space at a particular instant of time according to the distribution function $\rho(q, p, t)$. This collection of identically prepared copies of the system is called a **Statistical Ensemble** and the statistical average is called **Ensemble Average**.

Having introduced time average and ensemble average of a physical quantity we arrive at the equality of the two averages

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T F(q, p, t) dt = \int F(q, p, t) \rho(q, p, t) d\Gamma. \quad (1.4.6)$$

The hypothesis can be proved for many special cases but a general *proof* is still lacking and in spite of many attempts of *proving* the Ergodic Hypothesis it remains a *Hypothesis*. However, it has been proved that if the phase space is *metrically connected* then the Ergodic Hypothesis is valid.

1.5 Statistical Fluctuation and Statistical Independence

We first note that though the experimentally measured quantities are equal to their ensemble averages, they are *not* absolutely constant; in smaller time intervals they fluctuate about these average values. We define **Statistical Fluctuation** as

$$\Delta F = F - \bar{F} \quad (1.5.1)$$

with

$$\overline{\Delta F} = 0, \quad (1.5.2)$$

Root Mean Square Fluctuation as

$$(\Delta F)_{\text{rms}} = \sqrt{\overline{(\Delta F)^2}} = \sqrt{\overline{(F - \bar{F})^2}}, \quad (1.5.3)$$

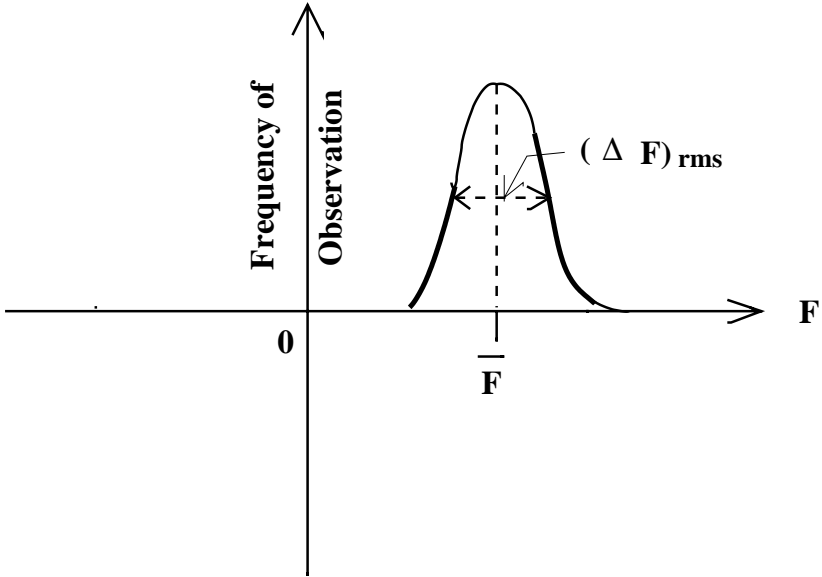


Fig. 1.5.1 Schematic plot of the frequency distribution of a physical quantity F , its average value \bar{F} and its root mean square fluctuation $(\Delta F)_{\text{rms}}$.

and **Relative Fluctuation** as

$$(\Delta F)_{\text{rel}} = \frac{(\Delta F)_{\text{rms}}}{\bar{F}}. \quad (1.5.4)$$

In Figure 1.5.1 we sketch a typical frequency distribution of a physical quantity F , its average value \bar{F} and its root mean square fluctuation $(\Delta F)_{\text{rms}}$.

The form of the statistical distribution function and fluctuation of a physical quantity takes particularly simple form for a special type of system. We consider a large isolated system which does *not* interact with its surrounding. We imagine the system to be made up of smaller parts called **subsystems** which also are *macroscopic*. These subsystems are *not* closed but interact with other subsystems surrounding them through their surfaces. Thus the interaction energy of a particular subsystem with others is much smaller (being $\propto R^2$ where R is its linear dimension) than the internal or volume energy $\propto R^3$. Thus the subsystems can be considered to be quasi-closed if they are observed for a time interval small compared to their relaxation time. It must, however, be noted that if observed for a long time these interaction energies cannot be neglected. As a matter

of fact it is these interactions that will lead to establishment of statistical equilibrium.

In this case the subsystems are called **Statistically Independent**. For statistically independent subsystems the state of one subsystem does *not* depend on the states of other subsystems. For systems consisting of N statistically independent subsystems the statistical distribution function of the total system is written in terms of those of the subsystems as

$$\rho(q, p, t) \stackrel{\text{def}}{=} \prod_{a=1}^N \rho_{(a)} \left(q^{(a)}, p^{(a)}, t \right). \quad (1.5.5)$$

If the subsystems are *not* statistically independent then such a factorization of the distribution function is *not* possible. Of course, for all systems the phase space volume can be factorized

$$d\Gamma = \prod_{a=1}^N d\Gamma_{(a)}. \quad (1.5.6)$$

Those physical quantities like number of particles, energy, entropy and other thermodynamic potentials which are sum of those of the constituent subsystems are called *additive*. For such additive physical quantities fluctuations of the total system can be written in terms of those of the constituent subsystems in particularly convenient form. If

$$F(q, p, t) = \sum_{a=1}^N F_{(a)} \left(q^{(a)}, p^{(a)}, t \right), \quad (1.5.7)$$

then, because of Equation 1.5.5

$$\overline{F} = \sum_{a=1}^N \overline{F_{(a)}} = Nm \quad (1.5.8)$$

$$\begin{aligned} \text{and} \\ \overline{(\Delta F)^2} &= \overline{(F - \overline{F})^2} \\ &= \overline{\left[\sum_{a=1}^N (F_{(a)} - \overline{F_{(a)}}) \right]^2} \\ &= \sum_{a=1}^N \sum_{b=1}^N \overline{(F_{(a)} - \overline{F_{(a)}}) (F_{(b)} - \overline{F_{(b)}})} \end{aligned}$$

$$\begin{aligned}
&= \sum_{a=1}^N \overline{(F_{(a)} - \overline{F_{(a)}})^2} + \sum_{a=1}^N \sum_{b=1, a \neq b}^N \overline{(F_{(a)} - \overline{F_{(a)}})(F_{(b)} - \overline{F_{(b)}})} \\
&= \sum_{a=1}^N \overline{(\Delta F_{(a)})^2} + \sum_{a=1}^N \sum_{b=1, a \neq b}^N \overline{(\Delta F_{(a)})(\Delta F_{(b)})} \\
&= \sum_{a=1}^N \overline{(\Delta F_{(a)})^2} + \sum_{a=1}^N \sum_{b=1, a \neq b}^N \overline{(\Delta F_{(a)}) \cdot (\Delta F_{(b)})} \\
&= \sum_{a=1}^N \overline{(\Delta F_{(a)})^2} = N\sigma^2. \tag{1.5.9}
\end{aligned}$$

Because of the identity of the subsystems the mean m and the variance σ^2 have been taken as the same for each subsystem. The relative fluctuation of additive physical quantities for a system consisting of statistically independent subsystems is thus

$$(\Delta F)_{\text{rel}} = \frac{\sigma}{\sqrt{Nm}} \propto \frac{1}{\sqrt{N}}. \tag{1.5.10}$$

Thus for macroscopic bodies when $N \sim 6.022 \times 10^{23}$ the relative fluctuation tends to zero and the average value of a physical quantity becomes the most probable value. This justifies our use of the statistical averages for the description of a macroscopic body. Any fluctuation from these average values are *extremely rare*. It should be mentioned that for **mesoscopic systems** of modern **nano-materials** the above thermodynamic limit cannot be applied and other techniques have to be used for their analysis.

A concrete physical example of this general result is manifest if we consider a system of N particles in a volume V . We imagine a given region of volume v within V . Let us imagine that n number of particles are in v . Because of statistical fluctuation n will fluctuate and we calculate $(\Delta n)_{\text{rel}}$. We assume that p is the probability of finding a particle in v so that $\frac{v}{V}$ is a very good physical estimate of p . The probability of finding n particle in v is thus the **binomial distribution** $W_B(n, N; p)$ given in § (14.7.2.1) of Mathematical Appendix. Using Equation 14.7.2 and Equation 14.7.3 of Mathematical Appendix, we arrive at the expected result

$$(\Delta n)_{\text{rel}} = \frac{1}{\sqrt{N}} \sqrt{\frac{1-p}{p}}. \tag{1.5.11}$$

1.6 Statistical Fluctuation and Generalized Susceptibility

Statistical fluctuations not only determine the applicability of the methods of statistical physics, it actually gives expressions for different response functions like compressibility, specific heat and thermal conductivity. These response functions control how the system reacts to application of external stimuli like mechanical pressure, thermal energy source and temperature gradient to it. The generic name for these response functions is **generalized susceptibility**. The name has been suggested from response of magnetic systems to external magnetic field.

We consider isothermal compressibility as a prototype of such a generalized susceptibility. As a result of fluctuation of volume V of the system, the number density n of particles changes as a random stochastic process. If ΔV and Δn are these changes and ΔF denotes the resulting change in the free energy, then the general principle states that the probability of volume change by this amount is

$$w(\Delta V) \propto \exp\left(-\frac{\Delta F}{k_B T}\right), \quad (1.6.1)$$

where k_B is the Boltzmann constant. Since F is minimum at equilibrium, so up to the first non-vanishing term

$$w(\Delta V) \propto \exp\left[-\left(\frac{\partial^2 F}{\partial V^2}\right)_T \frac{(\Delta V)^2}{2k_B T}\right]. \quad (1.6.2)$$

This is a Gaussian distribution in ΔV with mean zero and variance (*vide* § (14.7.2.3) in the Mathematical Appendix)

$$\overline{(\Delta V)^2} = \frac{k_B T}{\left(\frac{\partial^2 F}{\partial V^2}\right)_T}. \quad (1.6.3)$$

Using the thermodynamic relationships for pressure $P = -\left(\frac{\partial F}{\partial V}\right)_T$ and the isothermal compressibility $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$ we arrive at

$$\overline{(\Delta V)^2} = k_B T V \bar{V} K_T. \quad (1.6.4)$$

We now calculate the fluctuation in the mean number density $\bar{n} = \frac{N}{V}$ in two ways: first as a fluctuation in volume

$$\overline{(\Delta n)^2} = \left(\frac{\bar{n}}{\bar{V}}\right)^2 \overline{(\Delta V)^2} = \bar{n}^2 \frac{k_B T K_T}{\bar{V}}, \quad (1.6.5)$$

and then as a fluctuation in the total number of particles

$$\frac{\overline{(\Delta N)^2}}{N^2} = \frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{k_B T K_T}{V}. \quad (1.6.6)$$

Einstein showed that if electromagnetic radiation of intensity I_{inc} is incident on a medium in which the number density fluctuates then the incident radiation deviates from the path of the geometrical optics and gets scattered with intensity I_{sc} given by

$$\frac{I_{\text{sc}}}{I_{\text{inc}}} \propto \sqrt{\frac{\overline{(\Delta n)^2}}{\bar{n}^2}}. \quad (1.6.7)$$

The density fluctuation is thus directly measurable by experiments.

The most striking phenomenon of **Critical Opalescence** can be explained as a manifestation of number density fluctuation. When light is scattered by a *real gas* near its critical point, scattering increases enormously. The whole scattering chamber is then filled up with radiation giving a semblance of the surface of the naturally occurring mineral Opal, which is of dazzling milky white texture. This is the origin of the name of the phenomenon. A real gas consisting of interacting particles has $(\frac{\partial P}{\partial V})_T \rightarrow 0$ and thus $K_T \rightarrow \infty$ as $T \rightarrow T_c$ the critical temperature. Thus the scattered intensity $I_{\text{sc}} \rightarrow \infty$ as T approaches the critical temperature T_c .

As we have mentioned connection between Number fluctuation and isothermal compressibility has been taken as a prototype. Similar connection exists for other response functions and fluctuations in corresponding physical variables. Connection between magnetic susceptibility χ and fluctuation of magnetic moment M

$$k_B T \chi = \overline{(\Delta M)^2} \quad (1.6.8)$$

and the **Einstein relation** between heat capacity C_v and fluctuation of energy E

$$k_B T^2 C_v = \overline{(\Delta E)^2} \quad (1.6.9)$$

are two other often-mentioned relations.

1.7 Generalized Ornstein-Zernicke Relation

Ornstein and Zernicke obtained expression for fluctuation of the number density in terms of inter-particle interaction. This gives a microscopic description of statistical fluctuation. We start with the **two-body density-correlation function**

$$n^{(2)}(\mathbf{r}, \mathbf{r}') \stackrel{\text{def}}{=} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') g(\mathbf{r}, \mathbf{r}'). \quad (1.7.1)$$

The inter-particle interaction is incorporated in the inter-particle distribution function $g(\mathbf{r}, \mathbf{r}')$ and a sketch of this function is plotted in Figure 1.7.1. For isotropic systems $g(\mathbf{r}, \mathbf{r}') = g(R)$ where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ and $|\mathbf{R}| = R$. For

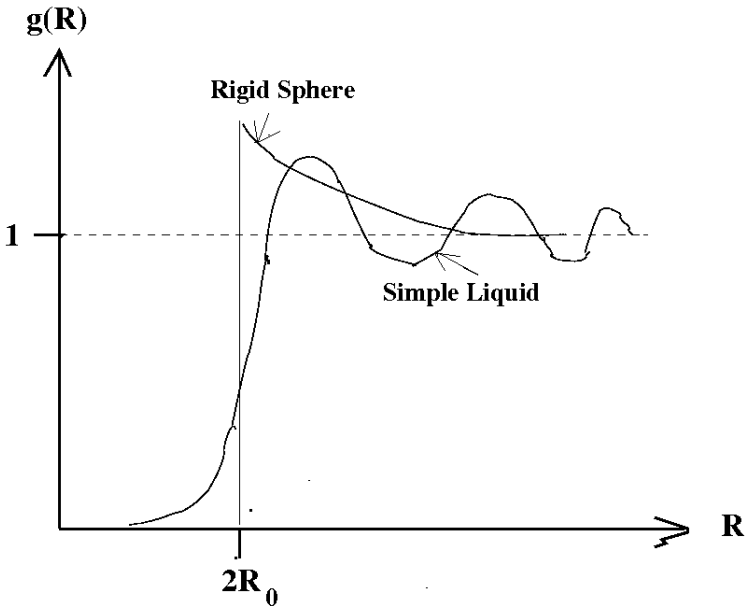


Fig. 1.7.1 A sketch of the inter-particle distribution function $g(R)$ is plotted for hard spheres of radii R_0 and simple liquids with valence electrons in the s and p shells.

non-interacting point particles $g(R) = 1.0$ for all values of R . Obviously as $R \rightarrow \infty$, $g(R) \rightarrow 1$. For systems consisting of rigid spheres of radii R_0 , $g(R) = 0$ when $R < 2R_0$. For simple liquids with valence electrons in the s and p shells $g(R)$ are obtained from X-ray scattering data just above the melting temperature. Again, $n^{(1)}(\mathbf{r})$ and $n^{(1)}(\mathbf{r}')$ are different because of the existence of fluctuation in the medium.

With obvious mathematical operations we obtain

$$\overline{n^{(1)}(\mathbf{r})} = \bar{n} = \frac{\bar{N}}{\bar{V}}, \quad (1.7.2)$$

$$\overline{n^{(2)}(\mathbf{r}, \mathbf{r}')} = \bar{n}^2 g(R), \quad (1.7.3)$$

$$\begin{aligned} \int \int \left[\overline{n^{(2)}(\mathbf{r}, \mathbf{r}') - \bar{n}^2} \right] d^3\mathbf{r} d^3\mathbf{r}' &= \bar{n}^2 \int \int [g(R) - 1] d^3\mathbf{r} d^3\mathbf{r}' \\ &= \bar{n}^2 V \int [g(R) - 1] d^3\mathbf{R}. \end{aligned} \quad (1.7.4)$$

We now express the number density and the two-body density correlation function in terms of Dirac Delta functions (§ 14.2 of the Mathematical Appendix)

$$n^{(1)}(\mathbf{r}) = \sum_j \delta(\mathbf{r}_j - \mathbf{r}), \quad (1.7.5)$$

$$n^{(2)}(\mathbf{r}, \mathbf{r}') = \sum_{j \neq k} \delta(\mathbf{r}_j - \mathbf{r}) \delta(\mathbf{r}_k - \mathbf{r}'), \quad (1.7.6)$$

$$\overline{n^{(1)}(\mathbf{r})} = \overline{\sum_j \delta(\mathbf{r}_j - \mathbf{r})}, \quad (1.7.7)$$

$$\begin{aligned} \overline{n^{(2)}(\mathbf{r}, \mathbf{r}')} &= \overline{\sum_{j \neq k} \delta(\mathbf{r}_j - \mathbf{r}) \delta(\mathbf{r}_k - \mathbf{r}')} \\ &= \overline{\sum_{j,k} \delta(\mathbf{r}_j - \mathbf{r}) \delta(\mathbf{r}_k - \mathbf{r}') - \sum_j \delta(\mathbf{r}_j - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}')} \\ &= \bar{n}^2 - \delta(\mathbf{r} - \mathbf{r}') \overline{\sum_j \delta(\mathbf{r}_j - \mathbf{r})} = \bar{n}^2 - \bar{n} \delta(\mathbf{r} - \mathbf{r}'). \end{aligned} \quad (1.7.8)$$

We can now calculate

$$\begin{aligned} \int \int \left[\overline{n^{(2)}(\mathbf{r}, \mathbf{r}') - \bar{n}^2} \right] d^3\mathbf{r} d^3\mathbf{r}' &= \int \int \left[\bar{n}^2 - \bar{n} \delta(\mathbf{r} - \mathbf{r}') - \bar{n}^2 \right] d^3\mathbf{r} d^3\mathbf{r}' \\ &= \bar{N}^2 - \bar{N} - \bar{N}^2. \end{aligned} \quad (1.7.9)$$

Comparing Equation 1.7.4 and Equation 1.7.9 we obtain for the fluctuation

$$\frac{(\overline{\Delta N})^2}{\bar{N}^2} = \frac{(\overline{\Delta n})^2}{\bar{n}^2} = \frac{1}{\bar{N}} \left(1 + \bar{n} \int [g(R) - 1] d^3\mathbf{R} \right) \quad (1.7.10)$$

and the **Ornstein-Zernicke Relation** for isothermal compressibility

$$K_T = \frac{1}{k_B T} \left(\frac{1}{\bar{n}} + \int [g(R) - 1] d^3\mathbf{R} \right). \quad (1.7.11)$$

For a **perfect gas** of non-interacting point particles $g(R) = 1$ and we arrive at the well-known relation $K_T = \frac{1}{nk_B T}$.

We shall later see in § 7.1 that the expression $\int [g(R) - 1] d^3\mathbf{R}$ appears also in the second virial coefficient of *real gases*.

1.8 Problems

Problem 1.1. Write down the Mathematical Condition that ‘none of the levels in Figure 1.2.2 is isolated’. Prove that in this case at equilibrium $p_1 = p_2 = p_3$.

Problem 1.2. Draw the phase trajectory of a particle of mass m executing a one dimensional simple harmonic motion of frequency ω .

Problem 1.3. Prove Equation 1.5.9.

Problem 1.4. Prove Equation 1.5.11.

Problem 1.5. For a real gas satisfying the Virial Equation of state $P = \frac{Nk_B T}{V} \left[1 + B(T) \frac{N}{V} \right]$ obtain the expression for $\frac{(\Delta N)^2}{N^2}$.

Problem 1.6. Calculate the isothermal compressibility K_T , when the inter-particle distribution function is given by

$$g(R) = \begin{cases} 0, & \text{for } 0 \leq R \leq 2R_0 \\ g_0 \exp(-k_0 R) & \text{for } 2R_0 \leq R \leq \infty. \end{cases} \quad (1.8.1)$$