Fluctuations :-

' Deviation from mean values"

They are generally small. Study of these fluctuations is of great physical interest because of following reasons —

1) It enables us to develop a mathematical scheme with the help of which the magnitude of the relevant fluctuations, under a variety of physical situations can be estimated.

In a single-phase system the fluctuations are thermodynamically negligible and is quiet important in multi-phase systems. In the latter case, a high degree of spatial correlation among the molecules of the system which gives rise to phenomena of "Critical opalescence."

2) It provides a natural framework for understanding physical phenomena like "Brownian motion". The mechanism of the Brownian motion is used in formulating, a given physical system which is not in a state of equillibrium, finally approaches a state of equilibrium", while, "a physical system, which is already in a state of equillibrium, persists to be in that state.

3) The study of fluctuations, as a function of time, leads to the concept of "correlation functions" which play an important role in relating the dissipative properties of a system, such as viscous resistance of a fluid or the electrical resistance of a conductor, with the microscopic properties of the system in a state of equilibrium.

Spatial Correlations in a fluid :->

OR

Correlation of space time dependent fluctuations :—

The particles constituting a homogeneous isotropic system are equally likely to be at any point 'r' in the space. Under the condition that the positions of all the other particle in the system are completely arbitrary. There exists, a definite amount of correlation between the simultaneous positions of r_1 and r_2 of the two particles.

To study these correlations, the configurational distribution function $F_N(r_1, ---, r_N)$ satisfy the normalization condition.

$$\int_V F_N(r_1, ---, r_N) d^3r_1, --- d^3r_N = 1 \qquad ①$$

Integrating $F_N(r_1, --r_N)$ over the coordinates. $r_2, ---, r_N$ and multiplying the result by N,

Single-particle distribution function

$$F_1(x_1) = N \int_V F_N(x_1, \ldots, x_N) d^3x_2 \ldots d^3x_N = n(x_1)$$

$$\tag{2}$$

The function $F_1(x_1)$ represents the particle density at the pt. x_1 for a homogeneous system. The two-particle distribution function is defined as

$$F_2(x_1, x_2) = N(N-1) \int_V F_N(x_1, \ldots x_N) d^3x_3 \ldots d^3x_N$$

$$= n^2 g(x) \tag{3}$$

Here, $x = (x_2 - x_1)$. Eqn ③ defines the pair distribution function $g(x)$ of the system; The product $g(x) d^3x$ determines the probability of finding a particle in the volume element d^3x around the pt. x when we have already a particle at the point $x = 0$.

In the absence of spatial correlations, $g(x)$ is identically equal to unity; for real systems, $g(x)$ is generally different from unity. It is then introduce a function $v(x)$

$$v(x) = g(x) - 1 \tag{4}$$

as a measure of the degree of spatial correlation in the systems, The function $v(x)$ is generally referred to as the pair <u>correlation function</u>. In the absence of spatial correlation $v(x)$ would be identically equal to zero.

Consider a macroscopic region V_A in the fluid and evaluate the mean square fluctuation in the number N_A of the particles occupying this region.

Introducing a function $\mu(x)$ such that $\mu(x) = 1$ (or 0) according as the point x lies inside (or outside) the region V_A. The fluctuation in N_A is given by

$$N_A = \sum_{i=1}^{N} \mu(x_i) \qquad\qquad\qquad ⑤$$

where summation goes over all the N particles of the system.

$$\bar{N}_A = \sum_{i=1}^{N} \int_V \mu(x_i) F_N(x_1, ---, x_N)\, d^{3N}x$$

$$= \int_V \mu(x_1) F_1(x_1)\, d^3x_1$$

$$= \int_{V_A} F_1(x)\, d^3x \qquad\qquad ⑥$$

Substituting from ②, for a homogeneous system we obtain

$$\bar{N}_A = n V_A \qquad\qquad\qquad ⑦$$

Next we have

$$N_A^2 = \sum_{i=1}^{N} \mu(x_i) \sum_{j=1}^{N} \mu(x_j)$$

$$= \sum_{i \neq j} \mu(x_i) \mu(x_j) + \sum_{i} \mu(x_i) \qquad\qquad ⑧$$

For all i, $\mu(x_i)\mu(x_i) \equiv \mu(x_i)$

Accordingly, $\overline{N_A^2} = \bar{N}_A + \sum_{i \neq j} \int \mu(x_i) \mu(x_j) F_N(x_1, ---, x_N) d^{3N}x$

$$= \bar{N}_A + n^2 V_A \int_{V_A} g(x)\, d^3x \qquad\qquad ⑨$$

Combining ⑦ and ⑨ we have.

$$\frac{\overline{N_A^2} - \bar{N}_A^2}{\bar{N}_A} = 1 + n \int_{V_A} \{g(x) - 1\} d^3x$$

$$= 1 + n \int_{V_A} v(x)\, d^3x \qquad\qquad ⑩$$

Eq^n ⑩ brings out the intimate connection between

(i) the density fluctuations and
(ii) the spatial correlations in any fluid system.

By using the relation.

$$\overline{(\Delta N)^2} = V^2 \overline{(\Delta n)^2} = kT \chi_T N^2/V$$

we obtained.

$$\int v(x) d^3x = \frac{1}{n}\left[(nkT\chi_T)-1\right] \tag{11}$$

For a classical ideal gas, or for a real gas at high temp. and low density, $PV = NkT$;

$$\therefore \chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{P} = \frac{1}{nkT} \tag{12}$$

Accordingly, the space integral of the function $v(x)$ vanishes because in the absence of interparticle interactions and (quantum-mechanical) symmetry effects, there do not exist any spatial correlations among the particles of a given system.

In the region of phase transitions, at the critical pts. the isothermal compressibility of a fluid and the degree of density fluctuations in the fluid become abnormally high. Under these circumstances the correlation function $v(x)$ is given by.

(short ranged) $v(x) \propto \frac{kT}{x} \exp(-x/x^*)$ ⑬

x^* being of the order of mean interparticle distance, becomes long ranged $v(x) \propto \frac{kT}{x}$ ⑭

This spatial correlations among the molecules of a fluid should extend over macroscopic distances is the presence of spatial order in the system.