

c-axis and the nearest Cl atom of the upper one is 3.48Å and therefore there is possibility of formation of a weak bond between these two atoms. A similar bond may exist also between the Sb atom of the upper molecule and the Cl atom of the lower molecule. In fact the crystal consists of such vertical rods of molecules passing through the corners and the centres of faces of the unit cell.

The four new lines given in table 1 are due to intermolecular oscillations in such 'rods', the line 102.0 cm^{-1} being probably due to torsional oscillation about the *c*-axis in which both the bonds mentioned above are involved. The line 76 cm^{-1} may be due to an angular oscillation of the molecule about the horizontal Sb-Cl bond and the other two lines may be due respectively to such oscillations about a horizontal axis bisecting the angle between the other two Sb-Cl bonds and the three-fold axis of the molecule.

The liquid state probably consists of dimers formed in the same way as in the crystal. In that case in ω_2 the bonding of one of the Sb-Cl bonds is less than that of the other two free bonds and therefore the mode becomes asymmetric to the three-fold axis and the Raman line becomes totally depolarised. In ω_1 no such influence of the intermolecular bonds is expected.

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ON THE METHOD OF MEAN VALUES AND CENTRAL LIMIT THEOREMS

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In the usual method* of mean values (Darwin and Fowler 1922), as in the theory of singular series of Hardy and Littlewood (Bellman 1961) for Waring problems

*In the text of the note, these will be referred to as the usual method and the modified method

of Number Theory, the calculus of residue is used in the formulation of the problem and then, it is evaluated by the method of steepest descent. In the modified method* (Khinchin 1949); from same basic ideas, same results are obtained by the application of a central limit theorem. Apart from the approximation techniques, the difference between these two methods lies in the use of the characteristic function (i.e., the Fourier transform) in the latter in place of the partition (generating) function in the former. Koppé (1949) showed that the same results can also be obtained directly by use of Fourier transforms with a suitable method of approximation. Thus, these two methods appear to be related by a sort of mathematical (formal) equivalence which should be analysed. This note shows clearly the close mathematical similarities of those two methods.

In statistical mechanics, to each energy state ϵ_k of a constituent of an assembly known from mechanics (classical or quantum), a probability (weight), p_k , is associated. The energy of the j th constituent of an assembly of N particles at a complexion is a random variable X_j . The main problem is to find out the distribution so that $E = \sum_j X_j$ corresponds to the observed value, E_0 , and then to find out average values of physical quantities.

In usual method, from partition functions (generating functions of distributions) of constituents, the partition function of the entire assembly is obtained in a convenient form. In a central limit theorem, from characteristic function of X_j 's, the characteristic function (and so the distribution) of the standardised sum of X 's is determined in convenient form. Now, the characteristic function, $C(t)$ is obtained from the generating function $G(z)$ by replacing z by e^{it} . At this step, thus, the two methods are essentially similar.

After this, calculations of averages are routine works and same in the both. In the usual method, the starting point is written by the residue theorem as

$$P(n) = \frac{1}{2\pi i} \oint_C \frac{G(z) dz}{z^{n+1}} \quad (1)$$

where C is a contour within the circle of convergence of the power series of $G(z)$, the generating function of the assembly, and $P(n)$ is the probability of getting $\sum X_j = n$. In central limit theorem, it is written by the inverse Fourier transform as

$$P(n) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{itn} G(e^{it}) dt \quad (2)$$

The integrand of (2) can be written from that of (1) by direct substitution of e^{it} by z . Within the circle of convergence of the power series of $G(z)$, it has nonsingularity, and so the integrand of (1) has only one pole at the origin. Now, in cases, occurred in physics, the radius r , of convergence is 1 or ∞ (Schrödinger 1947).

Now, in the region, $|z| < r$, the contour C can be deformed continuously. In the case $r > 1$, by deformation of C to $|z| = 1$, the integral (1) can easily be expressed in the form (2); only the limit of integral is from $-\pi$ to π in place of $(-\infty, \infty)$. But, in Khinchin proof (1949) for a central limit theorem, it is seen that the actual comes from the interval,

$$\left(\frac{\log N}{B_N^{\frac{1}{2}}} \quad \frac{\log N}{B_N^{\frac{1}{2}}} \right)$$

where B_N is the variance of the joint distribution. If X_j 's are independent random variables with the same variance σ^2 , then $B_N = N\sigma^2$ and $\log N/B_N^{\frac{1}{2}} = \frac{\log N}{N^{\frac{1}{2}}\sigma} =$ a small quantity for large N , and thus, the above interval is contained in the interval, $(-\pi, \pi)$

In case, $r = 1$, some special considerations are necessary.

But in the usual method, in actual evaluation, C is taken as a circle with the centre at origin and passing the col. $z = \xi$ of the integrand of (1). Then, from considerations of steepest descent of the integrand, C is replaced by a line through the col. $z = \xi$ and parallel to the imaginary axis from $\xi - i\infty$ to $\xi + i\infty$. In (2), the integration is to be taken along the line from $-\infty$ to $+\infty$. Of course, actual actual contribution in (1) comes from a very close neighbourhood of the point $z = \xi$ and that in (2), of the point $t = 0$. Thus, the only difference between these two methods under considerations is only in the choice of contours.

The problem of the deformation of the contour is purely mathematical. The above discussion also suggests an interesting converse problem: 'What will be the form of the partition function for which the above deformations of contour are permissible and what is its physical significance?' These investigations will be taken later (Dutta 1968).

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