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Part I

"ANGULAR DISTRIBUTION OF THE LIGHT SCATTERED BY RANDOM COILS"

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Part I

ANGULAR DISTRIBUTION OF THE LIGHT SCATTERED BY RANDOM COILS* **

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In many problems, it is assumed that a Gaussian Coil (i.e. a coil with a large number of elements without correlations in their orientations) can be replaced by a spherical distribution of points around the center of gravity. Usually this is characterized by the probability function $4\pi r^2 w(r)dr$, which gives the probability of finding an element of the chain at the distance r from the center of gravity.

As a first approximation, one uses the Gaussian probability function, which can be written

$$w(r) = \left(\frac{9}{\pi b^2 N}\right)^{3/2} \exp - \frac{9r^2}{b^2 N} \qquad (1)$$

In this expression, b is the length of the statistical elements of the chain and N their number.

Recently Isihara[1] and Debye and Bueche[2] have given a more accurate expression based on the theory of Markoff chains:

$$w(r) = \int_0^1 \left\{\frac{2}{9} b^2 N \left[u^3 + (1-u)^3\right]\right\}^{-3/2} \exp - \frac{9r^2}{2b^2 N \left[u^3 + (1-u)^3\right]} du \qquad (2)$$

This expression cannot be integrated in closed form and Debye and Bueche give only expansions in power series.

It seems interesting to use these functions to calculate the angular distribution of the light scattered by random coils and to compare these with the classical expression obtained by using the distribution function for distances separating pairs of elements.[3] For this purpose one can show that for N points, distributed with spherical symmetry, each being at the distance r_i from the center-of-mass, the angular distribution of the light scattered is given by the expression:

$$P(\Theta) = \left[\sum_i \frac{\sin \mu r_i}{\mu r_i}\right]^2 \quad \text{with } \mu = \frac{\pi}{\lambda'} \sin \Theta/2, \tag{3}$$

where Θ is the angle between the incident and scattered beams and λ' the wave length of the light in solution. Now if the probability function $w(r)$ is known, one can write:

$$P(\Theta) = \left[\int_0^\infty w(r) \frac{\sin \mu r}{\mu r} 4\pi r^2 \, dr\right]^2 \tag{4}$$

Using this equation, it is possible to calculate the values of $P(\Theta)$ with the function (1) or (2).

In the first case Hermans[4] has shown

$$P(\Theta) = \exp(-u/3) \quad \text{with } u = \mu^2 \frac{b^2 N}{6} \tag{5}$$

In the second case, the integration is performed by inverting the order of integration; it is found that $P(\Theta)$ is given by the very simple expression

$$P(\Theta) = \frac{\pi}{u} \exp(-u/6) \left[\Theta\left(\frac{\sqrt{u}}{2}\right)\right]^2 \tag{6}$$

where Θ is the well-known probability integral

$$\Theta(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2)\,dt \tag{6'}$$

To compare these two functions and the usual Debye function:

$$P(\theta) = \left[u - 1 + \exp(- u)\right] 2/u^2 \tag{7}$$

we plot in Fig. 1 the reciprocal values $P^{-1}(\theta)$ as functions of u, because it is the usual form of the experimental date. One can see that, though they have the same initial slope, there are substantial differences. The two functions (5) and (6) differ the least; this is not surprising since they are obtained using the Eqs. (1) and (2) which as Debye and Bueche showed are very similar. But the discrepancy between these two functions and the function (7) is considerable for large values of u. The asymptotic behavior of $P(\theta)$ is not at all the same in the different cases.

Isihara has obtained the first two terms in the series expansion of $P(\theta)$ by integrating the expression (2) termwise: he observes that these are very similar to the first two terms of the series expansion of $P(\theta)$ given by Eq. (7). However, it is clear that the first few terms are inadequate to describe the behavior of the function at large values of the argument.

Accepting function (7) as the true result for a Gaussian chain, this discrepancy can only be explained by the approximations involved in the assumption that the molecule can be treated, through $w(r)$, as spherically symmetrical. Specifically, this function does not give the probability of relative positions of the segments of the molecule, but only the probability of finding them at the distance r from the center of mass. The large discrepancy obtained in calculating the angular distribution of the scattered light by this method shows that most of the configurations of Gaussian chains are far from possessing spherical symmetry and that perhaps the use of the distribution function (2) in other problems could also lead to inaccurate results.

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2. P. Debye and F. Bueche, J. Chem. Phys. 20, 1337 (1952)

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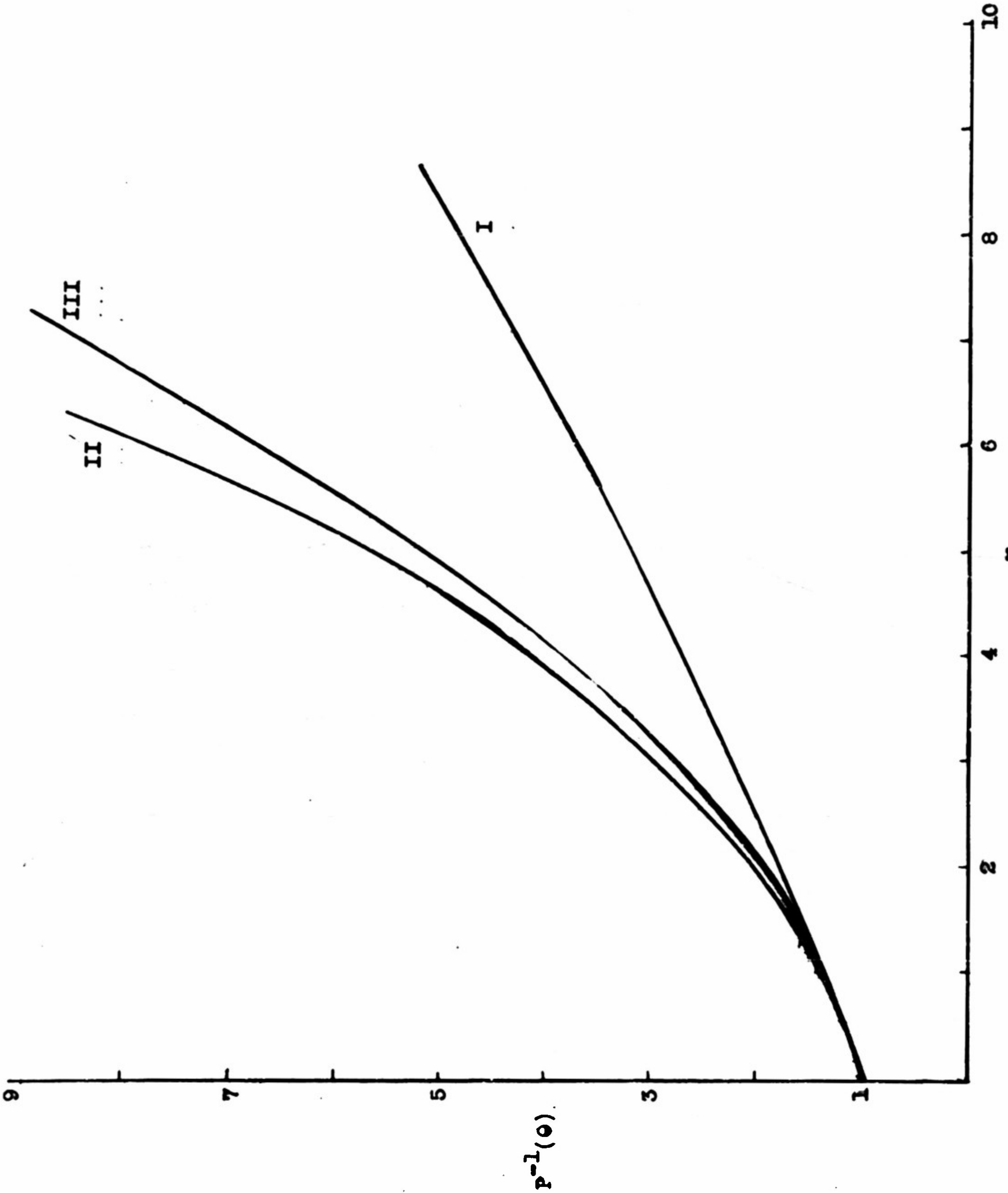

Fig. 1. $P^{-1}(\Theta)$ as a function of $u = \mu^2(b^2N/6)$ in different cases. Curve I--the usual value from Eq. (7); curve II--assuming a Gaussian distribution of elements around the center of mass; Eq. (5); curve III--assuming the Debye distribution (2) around the center of mass; Eq. (6).