for the refractive index of the plate. This gives for the retardation

$$e \left(\mu' - 1 - \lambda \frac{d\mu'}{d\lambda} \right),$$

and for the best thickness of the plate this must be equal to $\frac{1}{2}N\lambda$ or $-\frac{1}{2}\lambda t \frac{d\mu}{d\lambda}$ according as a grating or prism is used to produce the spectrum.

6. We are so much accustomed to regard the homogeneous wave as the simplest element into which all wave-motions may be resolved that we sometimes overlook the fact that the phenomena of white light may all be reproduced by a single disturbance of short duration. There are cases, and the phenomenon of Talbot's bands may serve as a conspicuous example, where the consideration of the combined group yields to a simpler treatment than the resolution into homogeneous waves. I have shown in my paper on "Interference Phenomena" how group velocities may be used to determine the conditions of achromatism. Considerations similar to those used in that paper may perhaps be usefully employed to simplify the treatment of achromatized interference-bands.

II. *On the Variation of Entropy as treated by Prof. Willard Gibbs.* By H. A. BUMSTEAD, Ph.D., Assistant Professor of Physics, Yale University*.

IN the August number of the Philosophical Magazine Mr. S. H. Burbury has discussed certain difficulties which present themselves in Chapter XII. of the "Principles of Statistical Mechanics," by the late Prof. J. Willard Gibbs. Unless I have misunderstood Mr. Burbury's statement, I believe these difficulties may be surmounted, and shall endeavour to give, as briefly as possible, my reasons for this belief. For the sake of brevity I shall assume that the reader has Mr. Burbury's paper before him, and shall refrain from quoting from it unless it seems necessary for clearness of statement.

The first difficulty (which may be more conveniently discussed in terms of the hydrodynamical analogue than in terms of the ensemble of systems) is in regard to Prof. Gibbs's statement that "one may perhaps be allowed to say that a finite amount of stirring will not affect the mean square of the density of the colouring matter, but an infinite amount of stirring may be regarded as producing a condition

* Communicated by the Author.

in which the mean square of the density has its minimum value, and the density is uniform." It seems to me that this statement may be justified as follows:—If, after a certain amount of stirring, we should determine the density of the colouring matter in the liquid, using finite elements of volume sufficiently large, we should find the density sensibly constant in the different elements; but if the elements were chosen small enough (but still finite) some of them would be entirely within the coloured portions and some in the uncoloured portions, and the density in such an estimate would no longer appear to be uniform. If now the stirring were continued, a time would come when these smaller elements would all have the same average density, and so on indefinitely; and no system of finite elements, however small, could be assigned in advance in which the average density could not be made the same for all by a sufficient amount of stirring. In other words, if we are allowed to stir as long as we please, we may use elements (in the estimate of density) as small as we please. That this is what Prof. Gibbs means by his somewhat guarded statement about an infinite amount of stirring, seems plain in the light of the preceding paragraphs in which he discusses the effect of altering the order in which limits are taken. This latter consideration was one of which he not infrequently made use; I recall that he once employed it to reconcile conflicting views as to the interpretation of Fourier's series in a discussion which arose in the columns of '*Nature*' (vol. lix. p. 200).

Although it seems to me that the statement can be thus justified, I nevertheless must agree with Mr. Burbury that the other way of escaping the difficulty, viz. by defining the density by finite elements of volume (or of extension-in-phase) is preferable. If I understand the matter correctly, this is not because there is anything in the structure of the ensemble of systems corresponding to a molecular structure in the liquid, for a system of n degrees of freedom occupies no finite extension in the $2n$ -fold space in which its possible phases lie; but it is because we are unable, owing to the finiteness of our perceptions, to recognize very small differences of phase, just as we are unable to recognize very small differences of position in the analogous case of the liquid. And it is certainly nearer the truth to base the doctrine of the increase of entropy upon the finiteness of our perceptions rather than upon the infiniteness of time. That this was also Prof. Gibbs' opinion I believe is evidenced by the sentence following the one quoted ("one may perhaps be allowed," &c.) in which he says, "We may certainly say that a sensibly

uniform density of the coloured component may be produced by stirring." And it is really this latter form which he uses when he comes to apply the principle, as in the third paragraph on page 154, in which the qualification, "if very small differences of phase are neglected," is of course equivalent to taking finite elements of extension-in-phase. The infinite time idea was, I believe, introduced merely as an alternative (and not a preferable) way of regarding the subject.

Admitting then the possibility of variation of the density-in-phase D in the finite elements through which a moving system passes, Mr. Burbury finds a difficulty in the definition of η in the expression $\bar{D} = N e^{\eta}$. He says, "so long as η remains constant for the same system, we may define η to be the entropy which that system has. . . . But η being now supposed to be variable for the same system, we require a definition." Here I think the whole trend and spirit of Prof. Gibbs' method has been misapprehended; unless I have mistaken his position, Prof. Gibbs would not have admitted that the η for a single system, although exactly determined, corresponds to what we call entropy in bodies met with in nature. So far as he applies his results to thermodynamics, he regards the bodies of nature as corresponding, not to a definite system, but to a system chosen at random out of a properly distributed ensemble; so that it is certain average properties of the ensemble which we observe experimentally, and not the properties of a single system. The average value of η for the whole ensemble (taken with the negative sign) corresponds to the entropy of any body which the ensemble is capable of representing, and we are no more concerned about the η of a single system (except in so far as a knowledge of it may be necessary to get a correct average) than we are concerned with the exact configuration of the system. But it is evident that we may get a sufficiently close value of the average for the whole ensemble by adding, not the η for every system, but the mean values of η for each one of a set of finite elements of extension-in-phase taken sufficiently small. Thus all we are concerned to know is the mean value of η in an element, and hence the equation $\bar{D} = N e^{\eta}$ may still serve as the definition of η , for all necessary purposes, even though D is no longer the exact density at a point but is the mean density throughout an element. Prof. Gibbs' statement in a succeeding paragraph (p. 148) that η "is an arbitrary function of the phase," which Mr. Burbury takes to be a new definition, is, I think, not a definition at all, but the statement of an assumed initial condition in the particular problem which he is then considering.

It is this problem (p. 148) which gives rise to Mr. Burbury's final difficulty, and which leads him to the conclusion that the hypotheses made by Prof. Gibbs concerning the mechanical systems are not sufficient to serve as a basis of rational thermodynamics. Perhaps I may best show why Prof. Gibbs' conclusions seem to me legitimate by restating his demonstration, as I understand it, in slightly different form and with special reference to the objections which have been brought against it. Let us consider an ensemble of systems not in statistical equilibrium. An ensemble is in statistical equilibrium if, during any interval of time, as many systems enter any fixed element of extension-in-phase as leave it during the same interval; the density-in-phase in any fixed element (finite or infinitesimal) does not change with the time. But when the ensemble is not in statistical equilibrium the density in fixed elements of extension-in-phase will vary with the time, and therefore the value of η associated with a fixed finite element (as explained above) will obviously vary. The question is whether the average value, $\bar{\eta}$, for the whole ensemble, as determined by the use of these elements, will increase or decrease with the time. At a certain initial instant t' let the density be distributed in any arbitrary manner throughout the extension-in-phase, that is, *at this instant*, we may consider D (or η) to be given as "an arbitrary function of the phase." Later, of course, it will be a function of the phase and of the elapsed time. With this initial distribution given we may now choose a system of fixed finite elements of extension-in-phase, DV , small enough so that the density may be regarded as sensibly constant throughout any one of them. At a later time t'' (unless the motion in phase is of a highly special and relatively improbable kind) the systems which were together in one element at t' will not all be in a single element. Thus some of the systems which were at t' in the element DV' may now be in the element DV'' , but they will have mixed with them systems which, at t' , occupied other elements, DV_1' , DV_2' , &c. If, now, we ascertain the average density in DV'' and take its logarithm (η), thus assuming that η has a constant value for all the systems in the element, we shall, by Theorem IX. of Chapter XI., get a less value than if we took the actual values of η which the separate systems have. But the actual values of η for the separate systems are those which they have brought with them into DV'' , and are the same which they had in their scattered condition in DV_1' , DV_2' , &c. at the instant t' . Therefore the value of η which we have obtained by averaging the density in the element

DV'' at t'' is less than that based on the same systems as they were at t' ; and, as this is true for every element, the average value of η for the whole ensemble so determined is less at t'' than at t' . This diminution in the average is wholly the result of mixing, in the elements, systems each of which preserves a constant value of η . It may be well illustrated by the hydrodynamical case which Prof. Gibbs uses earlier in the same chapter (p. 146), in which a cylindrical mass of liquid is imagined, one sector of 90° being black and the rest white. If it is given a motion of rotation about the axis of the cylinder, in which the angular velocity is any function of the distance from the axis (except in the highly special case when this function is a constant), "the black and white portions would become drawn out into thin ribbons which would be wound spirally about the axis." At any given instant t' we might choose a system of finite elements of volume so small that the density of the black colour in any one would be constant, either unity or zero; but at a later time the same elements would each contain a mixture of black and white, provided of course that the motion continues long enough.

But the chief difficulty is that the analytical demonstration will work either forward or backward in time, as Mr. Burbury points out. Assuming that the motion of the systems, or of the liquid in the illustration, extends backward in time *uninterruptedly*, we shall inevitably come to a prior time, say t_1 , at which the average η in an element is less than at t' , or at which the black and white portions of the liquid are better mixed than at the later epoch. Prof. Gibbs has not overlooked this fact, and has, I think, given the true solution of the difficulty, although so briefly that the true import of his remarks may easily be overlooked. He says (p. 150) "It is to be observed that if the average index of probability $[\bar{\eta}]$ in an ensemble may be said in some sense to have a less value at one time than at another, it is not necessarily priority in time which determines the greater average index. If a distribution, which is not one of statistical equilibrium, should be given for a time t' , and the distribution at an earlier time t'' should be defined as that given by the corresponding phases*, if we increase the interval leaving t' fixed and taking t'' at an earlier and earlier date, the distribution at t'' will in general approach a limiting distribution which is in statistical equilibrium. The determining difference in such cases is that between a definite distribution at a definite time and the

* Italics are mine.

limit of a varying distribution when the moment considered is carried either forward or backward indefinitely.

“ But while the distinction of prior and subsequent events may be immaterial with respect to mathematical fictions, it is quite otherwise with respect to the events of the real world. It should not be forgotten, when our ensembles are chosen to illustrate the probabilities of events in the real world, that while the probabilities of subsequent events may often be determined from the probabilities of prior events, it is rarely the case that probabilities of prior events can be determined from those of subsequent events, for we are rarely justified in excluding the consideration of the antecedent probability of the prior events.”

Let us consider first the rotating cylinder of liquid. It is quite true, if we imagine the motion to be continued backward in time from the instant when we have the black sector according to the same distribution of angular velocity along the radius, that we shall have the black and white portions more and more drawn out into thin ribbons the further back we go. But that there should have been the nice adjustment of distribution of colouring matter and of angular velocity necessary in order that these ribbons should, at a given instant, resolve themselves into the black and white sectors is exceedingly improbable. In all reasonable probability such a distribution is essentially an initial one, that is one produced by outside causes and not by antecedent motion of the same type; as a matter of fact we do not separate liquids by stirring them.

In the same manner the thermodynamic states of natural bodies which correspond to ensembles not in statistical equilibrium are, except in very improbable cases, produced by external causes. In Chapter XIII., in which Prof. Gibbs considers the effects of external influences upon an ensemble of systems, he shows that an ensemble originally in statistical equilibrium will have that equilibrium disturbed by changes in the “ external coordinates.” This is truly an initial state, and thereafter the mean value of η will decrease* as time goes on; that it would also decrease if we supposed the same motions carried back into the past is of no practical importance since that is not the way in which the existing state of things has arisen. An ensemble may unquestionably be arranged, as to distribution and motion, so that its $\bar{\eta}$ shall increase, but only up to a certain time, after which it will decrease; that such a preliminary arrangement should

* It is to be remembered that it is $-\bar{\eta}$ which is analogous to entropy.

fortuitously occur is exceedingly improbable. If there were something like an attraction in phase between systems with the same values of η , some sorting effect might be expected to occur, but scarcely otherwise; and thus, as it appears to me, instead of requiring an assumption to make η decrease, we should require an assumption to keep it from decreasing.

III. *On Deflexions of the Plumb-line in India.* By Rev. O. FISHER, M.A., F.G.S., Hon. Fellow of Jesus College, Cambridge, and of King's College, London*.

EARLY in 1902 I received, kindly sent to me by the author at the suggestion of my friend Mr. Oldham, Superintendent of the Geological Survey of India, a Report on the attraction of the Himalaya Mountains upon the plumb-line in India †. The observed phenomena led the Surveyors to suspect the existence of what they term a hidden chain of excessive density, traversing India from Balasore near the mouth of the Hooghly to Jodhpur in Rajputana, and underlying Manata and Bhopal. The position of this supposed chain is given in chart No. 6 of the Report. It appears however that, if such a chain exists as to cause deflexion of the plumb-line towards it, its presence ought likewise to be betrayed by its influence upon the pendulum; because gravity ought to be locally increased above it.

Now, in the 'Account of the Great Trigonometrical Survey of India' ‡, we learn that there is no escape from the conclusion that there is a more or less marked negative variation of gravity over the whole of the Indian continent. These variations are tabulated in my 'Physics of the Earth's Crust' §, and it appears that there is a slight increase of density at Kalianpur in latitude $24^{\circ} 7'$, which is in the position of the supposed hidden chain, but at the same time there is another nearly of the same amount at Usira in latitude $26^{\circ} 57'$, so that if the one affect the plumb-line the other ought to do so in the same manner. The deficiency in the vibration number calculated for the sea-level, which is due to diminished

* Communicated by the Author.

† By Major S. G. Burrard, R.E., Superintendent of the Trigonometrical Surveys of India. Dehra Dun, 1901.

‡ Calcutta, 1879. By General Walker.

§ 2nd ed. p. 208.