

## Postscript to the Foregoing Note by O. K. Rice

Henry S. Frank

Citation: *The Journal of Chemical Physics* **14**, 350 (1946); doi: 10.1063/1.1724147

View online: <http://dx.doi.org/10.1063/1.1724147>

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spheres and a dilute gas, for which the communal entropy per mole is only  $R$ , more graphically. If the spheres are very densely packed, under the restrictions noted above a sphere cannot get out of its row and column. (For convenience we restrict ourselves to two dimensions.) On the other hand, consider the situation which may arise in the case of point atoms, as illustrated by Fig. 2. This figure shows a square divided into cells by solid lines, one cell for each atom. If we assume that the atoms may pass the cell boundaries, we can get a situation such as shown in Fig. 2. This may be considered as produced in the main by fluctuations in the top row only. It can also be produced by another set of fluctuations as is indicated by the broken lines. Since the two sets produce indistinguishable configurations, they give rise to only one state of the system. In the case of closely packed spheres, however, the two sets of fluctuations, if they were of the same order of magnitude relative to the free space (therefore taking the molecules out of their individual cells), would, nevertheless, give only small displacements relative to the diameter of the spheres. The two sets of small displacements would give rise in this case to distinguishable configurations. It is, therefore, seen that the closely packed spheres can have a greater communal entropy than the dilute gas, because in the latter case row and column fluctuations interfere and overlap, giving rise to indistinguishable configurations.

Frank has quite properly called attention to the arbitrary nature of communal entropy. It depends upon the size of the "natural" cell which one chooses in the first place, when one assumes that each atom is assigned to its own cell. However, it is agreed that, insofar as possible, the cells should be assigned so that they are of equal size, and completely fill the space available. Then the assignment is easy in the case of a densely packed gas of hard elastic spheres. When the atoms exert forces on each other, it becomes a little more difficult. I made an estimate of communal entropy in this case because I wished later to combine the partition function for a gas of hard elastic spheres with that of a Debye solid in setting up the partition function for a liquid, assuming each part carried its own communal entropy factor. It seemed reasonable to do this if the excitation of communal entropy was comparable in the two cases. Otherwise some special means of averaging might have been necessary. Though the Debye solid was found to have a communal entropy only 77 percent as excited as the dense gas of hard spheres, this did not seem sufficiently different to render any special computation necessary.

In order to make a fair comparison of the communal entropy in the two cases, it seemed necessary to define the "natural" cell for a Debye solid in a manner as nearly analogous as possible with the definition for the hard elastic spheres. If, in the hard-sphere case, all atoms are fixed in position except one, this one has a free volume  $2^3$  times as large as if it were confined to its own cell. It was, therefore, assumed that if all the atoms of a Debye solid were held fixed except one, this one also would move in an effective volume equal to  $2^3$  times its natural cell. It is known that this atom would vibrate with the root-mean-square value of the frequencies of the normal modes. Therefore, it seemed

reasonable to say that a solid in which all atoms moved with this same mean frequency (Einstein model) was one in which the molal entropy was  $3R \ln 2$  times as great as it would be if each atom were confined to its "natural" cell, and the communal entropy of the Debye solid was calculated by comparison with the Einstein model, on this basis. In any event, it seems more "natural" to me to define the "natural" cell by means of an average frequency. Frank prefers the Debye maximum frequency, which seems "artificial" to me. However, nothing can be proved about this. I merely wish to emphasize that I had a real reason for choosing the natural cell as I did in view of the purpose I had in mind.

*Errata to reference 2.* On page 3 of reference 2 (last sentence beginning in the first column) where it reads, "If this result is multiplied by the momentum integral and divided by  $h$ ," replace  $h$  by  $h^N$ . This gives what we have called  $Q^N$  (though in this case it is for a one-dimensional array) and  $Q$  (correctly given by Eq. (1) of reference 2) is the partition function referred to a single atom.

At the end of page 6 and beginning of page 7, it was inadvertently stated "that the partition function per molecule of a Debye solid is  $e^{kT/h\nu_m}$ ." This is the partition function *per degree of freedom* and was used as such.

<sup>1</sup> H. S. Frank, J. Chem. Phys. 13, 478 (1945).

<sup>2</sup> O. K. Rice, J. Chem. Phys. 12, 1 (1944). For some errata see *ibid.* 12, 521 (1944) and the end of this article.

<sup>3</sup>  $Q^N$  is called  $Q$  by Frank; to be consistent with my own Eq. (2) I retain  $Q$  for the partition function referred to a single atom.

<sup>4</sup> L. Tonks, Phys. Rev. 50, 955 (1936).

## Postscript to the Foregoing Note by O. K. Rice

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April 8, 1946

I GREATLY appreciate the opportunity to see Professor Rice's "Note on Communal Entropy" in advance of publication, and to place on record as promptly as possible my agreement with the derivation he has given of the limiting partition function for a simple cubic array of hard attractionless spheres compressed toward the limit of complete mutual contact, and with the conclusion which it establishes, that  $3R$  is the correct theoretical fluctuation entropy for this case, appropriate to the choice of  $l^3(1-\theta)^3/N$  as the elementary cell. Rice's derivation also makes it possible to see where my "superficially straightforward" generalization of the one-dimensional case to three dimensions fails in this application. The latter corresponds, for the present model and for distinguishable particles, to letting each atom permute only with other atoms in the same linear arrays with it in the  $x$ ,  $y$ , and  $z$  directions. A correct method of counting, permitting all  $N!$  permutations, reproduces both Rice's mathematics and his result.

When the system becomes more expanded, the motions become too complicated for simple analytical discussion. There are doubtless several ways of "breaking down" the process by which the fluctuation entropy decreases as  $\theta$  decreases, and the picture given here by Rice is very instructive in throwing light on one of them.

Rice and I have never disagreed on the physical occurrence of a considerable amount of fluctuation entropy in a real solid for which any intuitively "natural" choice of cell size is made. I agree with him completely as to the "naturalness" of choosing a definition of cell size which will be most appropriate to the purpose one has in view. I now agree with him also in accepting as significant the closeness of the agreement between the fluctuation entropy found, for his cell size, in solid argon and the theoretical value  $3R$  which he has established.

### The Tetrahedral $P_4$ Molecule

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April 15, 1946

THE methods developed by Pauling<sup>1</sup> in his treatment of the tetrahedral bond orbitals of carbon (and applied by him and others to a number of individual cases) have been extended and systematized by Kimball<sup>2</sup> into the theory of directed valence. This scheme serves to predict the bond configurations for covalent molecules with remarkable success.

One of the few remaining anomalies is the tetrahedral  $P_4$  molecule (with its analog  $As_4$ ). The bond angles for a trivalent P atom might be expected to be somewhat over  $90^\circ$ , as typical  $p$  bonds, and, in fact, all other compounds which have been investigated show angles in the neighborhood of  $100^\circ$ . Pauling<sup>3</sup> has suggested that the  $P_4$  molecule is merely a strained structure, but the great amount of distortion involved seems to render this explanation improbable. The purpose of this note is to point out a set of orbitals with more suitable bond angles.

The symmetry group of the three bonds extending from one P atom is  $C_{3v}$ , and from group theoretical considerations we can reduce the possible orbitals to  $p^3$ ,  $sp^2$ ,  $pd^2$ ,  $sd^2$ . The bond angles for  $p^3$  are obviously  $90^\circ$ , while for  $sp^2$  and  $sd^2$  they are  $120^\circ$ . The combination  $p_x d_{xz} d_{yz}$ , as for example in the set:

$$\begin{aligned}\psi_1 &= 1/\sqrt{3}\psi_{p_z} + \sqrt{2}/\sqrt{3}\psi_{d_{xz}} \\ \psi_2 &= 1/\sqrt{3}\psi_{p_z} - 1/(6)^{1/2}\psi_{d_{xz}} + 1/\sqrt{2}\psi_{d_{yz}} \\ \psi_3 &= 1/\sqrt{3}\psi_{p_z} - 1/(6)^{1/2}\psi_{d_{xz}} - 1/\sqrt{2}\psi_{d_{yz}}\end{aligned}$$

yields bond angles of  $66^\circ 26'$ . This is the smallest possible angle for orbitals involving  $s$ ,  $p$ , and  $d$  states only. The bond-forming strength (in Pauling's terminology) is 2.29, compared to 1.73 for pure  $p$  orbitals.

Some distortion is still required to compress these angles to  $60^\circ$ , but the strain is not now excessive. The advantage gained in replacing a triple bond by three single bonds may be used to account for the promotional energy required to produce a  $pd^2$  structure from the  $p^3$  ground state, and the stability of  $P_4$  relative to  $P_2$ .

The above explanation sheds no light on the  $60^\circ$  bond angles found in carbon compounds, but it does account for the absence of a tetrahedral nitrogen molecule.

<sup>1</sup> L. Pauling, *Proc. Nat. Acad. Sci.* **14**, 359 (1928).

<sup>2</sup> G. Kimball, *J. Chem. Phys.* **8**, 188 (1940).

<sup>3</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1944), second edition, p. 80.

### Ultra-High Frequency Denaturation of Proteins

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April 18, 1946

ELECTROMAGNETIC waves in the ultra-high frequency range offers a new method for the study of protein-type molecules in the following suggested manner. From dielectric studies it is known that protein molecules are not rotated by frequencies above  $10^7$  cycles per second (below 30 meters). However, atomic and electronic polarization of the proteins do occur at the higher frequencies.

During each half-cycle, polarization on the molecule builds up to a peak and decays to zero. This produces a pulsating strain of twice the frequency of the electromagnetic wave. The pulsating strain will place the molecule in forced vibrations except at a resonant frequency,  $f_r$ , where the molecular energy absorption will rise sharply. The frequency  $f_r$  will depend upon whether the entire molecule vibrates as a two-body oscillator with each half of the mass of the molecule acting as one body or whether a prosthetic group and the remaining portion act as the two bodies. Because of the low strength of the hydrogen cross bonds and the small number required to be broken for denaturation, it is probably that at polarization resonance sufficient energy will be absorbed to denature the protein for the first type of vibration. Denaturation will result for the second type of vibration if the prosthetic group is broken off.

Now let us assume that each protein molecule of our laboratory experience is characterized by a unique energy state. For example, let us suppose that egg albumin has the energy  $E_1$ , and lactoglobulin, the energy  $E_2$  and that each energy state will resonate with one particular frequency. Thus, there will be a frequency  $f_{r1}$  which will denature egg albumin and another frequency  $f_{r2}$  which will denature lactoglobulin. It then follows that each of the proteins, enzymes, viruses, genes, and other protein-like molecules can be denatured by frequencies which are related to their energy states. This would lead to a systematic identification of the molecules by their resonant frequencies.

In this connection it seems that we should not conceive of a large number of lactoglobulin molecules, for example, as having identical energy states. It is perhaps more probable that these molecules have a distribution of energy states, say a normal distribution with the mean state having the energy  $E_2$ . Thus, the question arises as to the sharpness of the effect of the resonant frequency, i.e., how broad is the band of energy states about the mean which will be denatured by  $f_{r2}$ .

We do not know how to determine this band width at present but the concept is of value in setting up biological experiments. Let us assume two proteins, for example, egg albumin and lactoglobulin with mean energy states  $E_1$  and  $E_2$ , respectively, with distributions of states such that the denaturable band of states do not overlap. If we irradiate the two proteins in a common solution with a frequency  $f_{r1}$ , which will resonate with the band of states about  $E_1$ , but does not resonate with the band about  $E_2$ , we can visualize the denaturation of egg albumin without the denaturation of the lactoglobulin. There follows the