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On Communal Entropy and the Theory of Fusion

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The concept of "communal" entropy, introduced by Hirschfelder, Stevenson and Eyring, is further discussed in this paper. It appears from both theoretical and empirical considerations that the entropy of fusion of simple solids is *not* primarily concerned with the excitation of communal entropy. A discussion is given of the nature of communal entropy and its manner of excitation.

IN a recent paper Hirschfelder, Stevenson and Eyring¹ have introduced the concept of "communal" entropy, and have made the hypothesis that the principal contribution to the entropy of fusion of the simplest type of solid is due to the appearance of communal entropy. While they claim to have supported this hypothesis through certain experimental data, they have not given any very definite theoretical argument to sustain it. In view of the attractiveness of such an easily visualizable picture of the process of fusion some further analysis of the situation appears desirable. Unfortunately this analysis does not tend to confirm the hypothesis, at least in the simple form proposed by Hirschfelder, Stevenson, Eyring, and makes it at least improbable that the excitation of communal entropy plays any very important role in the phenomenon of fusion.

In order to make this analysis clear, it seems best to go back to first principles. We shall start with the consideration of a perfect gas. We shall suppose that we have one mole of atoms (let N be the number of atoms) confined in a volume V , this volume to be divided by partitions into r equal cells of volume V/r , each containing N/r molecules. Then we may set up the space part of the phase integral by raising V/r to the N th power and multiplying by the number, $N!/(N/r)!^r$, of arrangements of N molecules in r cells with N/r molecules in each cell, allowing for all possible exchanges of molecules from one cell to another. Thus we get a contribution, S_V , to the entropy

$$S_V = k \ln \frac{N!}{(N/r)!^r} \left(\frac{V}{r} \right)^N = k \ln N! - kr \ln (N/r)! + kN \ln (V/r), \quad (1)$$

¹ Hirschfelder, Stevenson, and Eyring, *J. Chem. Phys.* **5**, 896 (1937).

where k is the Boltzmann constant. Evaluating the factorials by the Stirling approximation

$$S_V = kN(\ln N - 1) - krN(\ln (N/r) - 1) + kN \ln (V/r) = R \ln V, \quad (2)$$

where R is the gas constant. It is seen that this result is independent of the number of cells into which our volume is divided. However, this assumes that N/r is large enough to permit the use of the Stirling approximation. If, however, r should be equal to N , so that there is just one molecule in each cell, then the Stirling approximation would no longer be valid and we would have to set $(N/r)! = 1$. We would then get

$$S_V = R(\ln V - 1) \quad (3)$$

and the entropy of one mole of gas would be less by an amount R . If, then we removed the partitions the entropy would increase by R , the "communal" entropy, just as stated by Hirschfelder, Stevenson and Eyring.

Let us investigate a little more closely the reason for this difference in entropy when we have partitioned the system into N cells. It arises because we have assumed that there is *exactly* one molecule in each cell. To change this situation we do not need to remove the partitions, but only to make an opening so that molecules can pass freely from one cell to another. Then, while the average number of molecules per cell is still one, there will be some cells with two or more molecules, and others with no molecules, and the number of molecules in any cell will change from time to time. It is the introduction of this possibility of fluctuations which causes the increase of R in the entropy. If, and only if, the cells were large enough so that they contained enough molecules to make

fluctuations unimportant, opening the partitions would make no difference.²

In the case of a solid or liquid the situation is different in that the molecules themselves occupy most of the space and there is a relatively small free volume available for their motion. Since any molecule is excluded from the region immediately surrounding the center of another molecule, the question arises as to how effectively the free volume can be shared under various conditions due to fluctuations in the positions of the molecules. In other words, under what circumstances does the excitation of communal entropy occur? The answer of Hirschfelder, Stevenson, and Eyring may best be given in their own words: "As the system expands a point is reached when the neighbors no longer interlock and our partitions have just disappeared. At this point if a hole appears at anywhere in the system it can be transferred (made available) to any other point in the system without appreciable activation energy compared to kT . The system under such circumstances is a liquid. Thus a system on melting acquires communal sharing of volume and with it a communal entropy R ." It is thus seen that they believe that the acquisition of communal entropy depends upon the ability of the molecules to change places among themselves.

However, the question of the sharing of the communal entropy has been definitely answered in one rather special, idealized case,³ that of a one-dimensional gas consisting of solid, elastic, nonattracting spheres constrained to move along a fixed straight line of length l . If these spheres have a diameter of σ and there are N of them, then the available volume in the phase space is just the same as if there were N point molecules moving along a line of length $l - N\sigma$. Since $l - N\sigma$ corresponds to the free volume in this case, it is seen that this free "volume" appears to be

² It is interesting that the incorrect evaluation of the factorial of a small number by use of Stirling's approximation is equivalent to allowing for fluctuations when they actually are excluded. It is to be noted that we refer here to the Stirling approximation in the less exact form,

$$\ln x! = x(\ln x - 1),$$

not the form,

$$\ln x! = \ln (2\pi)^{1/2} + (x + \frac{1}{2}) \ln x - x,$$

which holds reasonably well for much smaller values of x .

³ Tonks, Phys. Rev. **50**, 955 (1936).

completely shared. It is seen, further, that the sharing of the free volume is complete no matter how small $l - N\sigma$ may be; no question of ability of the molecules to exchange positions^{3a} comes into the picture, and there is no evidence whatsoever that a very condensed and closely packed state of the system (as in the solid state) is at all inimical to the complete sharing of the free volume. The main point is that the molecules should be able to move back and forth enough to use all the available space.

Some difficulties arise when it is attempted to extend this to two or three dimensions. We might, for example, consider a two-dimensional square array composed of spherically symmetrical molecules arranged in lines. Lines of touching or nearly touching molecules extend in two directions at right angles to each other. However, since fluctuations can occur in either direction, some of these lines will be badly distorted or broken, thus complicating the situation. A recent observation by Gurney and Mott⁴ enables us to avoid this difficulty. These authors showed that it is not necessary to consider a large number of molecules in order to get fairly accurate results. Thus if the space is divided into cells which contain exactly five molecules the communal entropy is nearly two-thirds excited (provided the sharing of free volume^{4a} is complete), and if the cells contain 27 molecules the communal entropy is 90 percent excited. Let us consider a cell containing 9 molecules, as shown in Fig. 1. In as small a cell as this no molecule will be able to get much out of line, nor will the molecules in one row

^{3a} It is necessary to distinguish between the phrase, "change positions," and the phrase, "exchange positions." By a *change* in position we simply mean that the molecule moves away from its point of equilibrium; by *exchange* of position we mean that a definite rearrangement occurs so that the molecules have different neighbors than they did before the exchange. In calculating the phase integral for the linear system Tonks included all possible arrangements resulting from exchanges of position, as must be done in the Boltzmann statistics, and this has nothing to do with communal entropy. The question of importance for us is whether or not, in any given system, it is necessary in order for the communal entropy to be excited, that such exchanges should actually be able to occur in the course of the motion of the system as time goes on. It is the contention of the present paper that it is not necessary, but, if we understand them correctly, Hirschfelder, Stevenson and Eyring believe it is necessary.

⁴ Gurney and Mott, J. Chem. Phys. **6**, 222 (1938).

^{4a} Here, of course, we refer to the free volume *within* the cell containing only the five molecules.

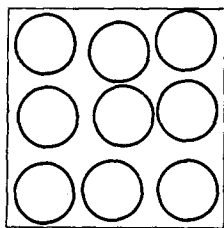


FIG. 1. A group of nine in cubic packing.

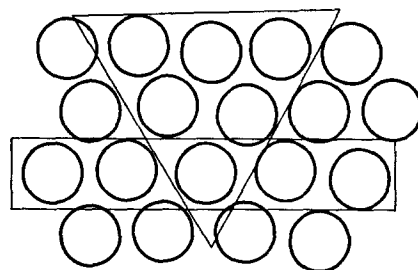
interfere much with the motions of a molecule in an adjacent row. Thus the motion of the x and y coordinates of a molecule may be taken as independent of each other. This will be an especially good approximation if the free volume is relatively small; it is seen then from Tonks' calculation³ that the available phase space is the same as if point-molecules occupied an area equal to $(l - N^{1/2}\sigma)^2$, where $N^{1/2}$ is the number of molecules per row and, as before, this may be interpreted as meaning that the free "volume" is completely shared. This can be extended to three dimensions.

With a triangular (close-packed) arrangement of spheres in two dimensions the situation is geometrically much more complicated, and it is not possible to give as satisfactory a discussion. It is not necessary, however, to consider a triangular array, such as shown in Fig. 2. We could, perhaps, consider as many as five molecules in a row to be in a single cell, there being, then, a fixed distance of motion in the y direction (perpendicular to the line of atoms) and sharing of free volume would occur due to the motion in the x direction. However, the motion in the x direction would, in reality, be affected by the positions of the molecules in the adjacent rows (notice that the boundary of the cell intersects adjoining atoms), and it is, furthermore, more difficult to formulate an expression for the free volume, making it hard to say whether this free volume is shared or not. However, and this is again the important point, there is no reason to believe that the degree of sharing of the free volume depends very much on the possibility of the molecules exchanging positions or on the relative size of the free volume as compared with the total volume. The closer the molecules are packed the nearer the adjacent row of molecules will be; thus the adjacent rows can interfere with each other more, but, on the other hand, less displacement in each row is

required in order to effect a complete sharing of the free volume. Again the situation will not be very different in three dimensions.

The model we have used for a closely packed aggregate of spherical molecules suffers further in that it does not too closely resemble a real aggregation, since it neglects the forces of attraction and does not reproduce the forces of repulsion too well. Any discussion of the subject, to be at all complete, should include a consideration of these real molecular forces, but such a treatment promises to be very complicated. It is true that these forces may tend to cause a freezing out or, perhaps better, a "squeezing out" of communal entropy at small volumes. The excitation of communal entropy depends upon the ability of the molecules to change^{3a} their positions; in other words, it must be possible for fluctuations to occur. Now fluctuations cause some molecules to approach each other while the distance between others increases. If the volume of the liquid is fairly large the approach of molecules means a decrease of potential energy, while the increase of the distance between them means an increase of energy. These two processes cancel each other's effects to some extent so fluctuations of the system do not represent states of particularly high energy. On the other hand, at small volumes, where the average intermolecular distance places neighbor-

FIG. 2. Close packing, showing a triangular group of six and a linear group of five, in their appropriate cells.



ing molecules near the minimum of their mutual potential energy curve, any considerable change in distance will mean an increase in potential energy, so that fluctuations are thereby discouraged. However, this hindrance to the sharing of free volume would gradually fall off with increasing volume; just where it would cease to be effective we cannot be sure, and there is no way to connect it definitely with the process of fusion, and certainly there is nothing to indicate

that just the excitation of communal entropy is the principal contribution to the entropy of fusion, though it may contribute to some extent. Furthermore, if it is necessary to take complicated considerations regarding the intermolecular forces explicitly into account, the concept of communal entropy loses much of its meaning, and becomes more or less fused with ordinary entropy. It is my belief that the change with volume is more rationally presented as a continuous function of the volume, the nature of the function being the result of a combination of causes.⁵

I believe that the empirical evidence supports this point of view. It is true, as Hirschfelder, Stevenson, and Eyring have pointed out, that there are many substances whose entropy of fusion is approximately R . However, when we consider the entropy at various pressures, we note a continuous change in its value. Thus the entropy of fusion of argon, melting at 83.9°K and a pressure of 1 kg/cm² is 3.13 entropy units, while melting at 192.9°K and 6000 kg/cm² it is 1.35 entropy units.⁶ Somewhere between it is just R , but I see no reason to suppose that the hypothesis of Hirschfelder, Stevenson, and Eyring should hold better at one temperature and pressure than another.

QUANTIZATION AND THE FREEZING-OUT OF COMMUNAL ENTROPY

From the above discussion it might appear that, at least if intermolecular forces could be neglected, communal entropy should always be excited, but it may readily be seen that it must "freeze out" at low temperatures, in much the

same way that other types of entropy freeze out, because the system is quantized. If we consider a system of spherically symmetrical molecules (e.g., rare gas atoms) at absolute zero, we can think of each molecule as being in its own special quantum state. These quantum states do not differ in the actual value of the energy, but only in their position in space. They are, nevertheless, perfectly distinct states and represent perfectly distinct regions in phase space, and obviously, no two molecules can occupy the same quantum state; hence communal entropy must be frozen out at the absolute zero.

It will be noted that in this discussion we have treated each molecule as though it were alone in its energy level, and have neglected the effect of the interactions of the molecules. This, however, will cause no error in the entropy at absolute zero; the entropy is as low as it can be in any case, and the system *as a whole* has just $N!$ energy levels of equivalent energy (corresponding to all possible exchanges of the N molecules if we use Boltzmann statistics, which is satisfactory for our purposes).

It is not easy to say at exactly what temperature this freezing-out of the communal entropy will occur. Since a substance like argon acts practically like a classical system at its melting point, it seems altogether doubtful that this process can be intimately connected with the phenomenon of fusion.

In closing it may not be without interest to note that the idea of communal entropy may be used to get the relation between the entropy of a solid and a hypothetical ideal gas at very low temperatures in a very direct way, and may thus serve as a means of obtaining the Sackur-Tetrode constant of the gas on the basis of the third law of thermodynamics.

⁵ Rice, J. Chem. Phys. 5, 492 (1937); and see the accompanying paper, J. Chem. Phys. 6, 472 (1938).

⁶ Bridgman, Phys. Rev. 46, 930 (1934).