ENTROPY OF MOLECULAR LIQUIDS

***Doç.Dr.Handan GÜRBÜZ**

MOLEKÜLER SIVILARIN ENTROPİSİ

ÖZET

Basit sıvıların entropi ve yapısı katı kürelerden oluşmuş bir sistem ile yeterli ölçüde modellenebilir.En azından erime noktası civarında, verilen bir yoğunlukta istiflenen katı küreler ile entropi ölçülmüştür.Daha karmaşık sıvılar için katı küre modeli en iyi model olmasa da moleküllerin şeklinin entropi değeri üzerinde nasıl etkili olduğu incelenebilir. Bu çalışmanın amacı konveks parçacıklardan oluşan bir sistem için entropinin, parçacıkların şekillerinden nasıl etkilendiğini incelemektir.Bulunan sonuçlar erime noktası civarında birkaç diatomic (N_2 ,O_2 ,Br_2 ,F_2) sıvı için entropinin tahmin edilmesinde kullanılmıştır.

**Yıldız Teknik Üniversitesi, Fen-Edebıyat Üniversitesi Öğretim Üyesi*

SUMMARY

The entropy and structure of simple liquids may be adequately modelled by a system of hard spheres. It appears that, at least near the melting point, the entropy is measured by the way the hard spheres pack at a given density.

More complicated liquids are not necessarily best modelled by hard spheres and it may be of some interest to find out how the shape of the molecules affects the value of the entropy.

İt is the purpose of this work to investigate how the entropy of a system of convex bodies is affected by their shape.The results will be used to predict the entropies of a few diatomic (N_2, O_2 , Br_2 , F_2) liquids near their melting points.

1. INTRODUCTION

Good progress has been made in the study of liquids by assuming that they behave like a system of hard spheres held together by mutually attractive forces. It will be shown that the entropy of non-conducting liquids does not depend explicity on the attractive forces and is thus the same as for a system of hard spheres, provided that the size of the spheres is correctly chosen. It has also been shown that for liquid metals the entropy can be written as $S_{Hs}{}^{+}S_{elec}$, where S_{Hs} is the entropy of a system of hard spheres and S_{elec} is an electronic contribution to the entropy[l]. The success of this approach was to suggest using systems of hard non-spherical bodies to predict the entropies of molecular liquids where the inter molecular repulsive forces may not be best modelled by hard spheres.To calculate the entropy of a single component fluid of N hard bodies with number density n, an equation of state must first be found.The method used was developed by Reiss et al.[2] for hard spheres and extended to convex bodies in general by Gibbons [3],[4].

He proposed an approximate equation of state for particles of arbitrary shape, based on the scaled particle model.

The results will be used to predict the entropies of a few diatomic liquids near their melting points.

2. THEORY

The basic idea behind the Scaled Partide Theory (SPT) is that progress can be made in calculating the thermodynamics of the system by calculating the work necessary to add to it one extra particle.This work can be thought of as the work necessary to create a volume, free from particles, large enough to slip in the extra one.A cavity is defined as a volume in the liquid which does not contain any molecular centres.An approximate equation of state for a one component fluid is given by,

$$\frac{\beta P}{n} = \frac{1}{1-n\eta} + \frac{1}{3}\frac{\bar{R}^{2} A^{2} n^{2}}{(1-n\eta)^{3}} + \frac{\bar{R} A n}{(1-n\eta)^{2}} \tag{1}$$

where $\bar{R}$, A and V are the radius averaged over all orientations, the surface area and the volume of the indivudial particles respectively and P is the pressure, ß=l/k_BT the Boltzmann factor.

The entropy of a system of N hard convex bodies of the same size and shape with number density n was obtained by substituting equation of state (1) in to the relation [5].

$$\frac{\beta F}{N} = \int_0^n n^{-1}\left(\frac{\beta P}{n} - 1\right) dn + \ln\left(n\Lambda^3\right)^{-1} - 1 \tag{2}$$

which gave,

$$\frac{\beta F}{N}=\frac{-\gamma^2}{6(1-n\eta)^2}+\frac{1}{1-n\eta}\left(\gamma-\frac{\gamma^2}{3}\right)+\left(\frac{\gamma^2}{6}-\gamma\right)-\ln(1-n\eta)+\ln\left(n\Lambda^3\right)^{-1}-1 \qquad (3)$$

$\gamma = RA / V$ is a dimensionless number that is dependent only on the shape of the particle and $\Lambda = \frac{h}{(2\pi mk_BT)^{1/2}}$ de Broglie's thermal wavelengt.

From the Helmholtz free energy F, the entropy of the system S, was obtained using the relation F= U - TS.The internal energy U was taken to be that of an ideal gas, that is

$$U/N=3/2k_BT \qquad (4)$$

For a real system there exists a rotational contribution to the internal energy not included in eq.(4) which will add to the entropy of system.This rotational entropy will be worked out seperately.Thus ignoring the rotational contribution from eq.(3),

$$\frac{S}{Nk_B}=\frac{\gamma^2}{6(1-n\eta)^2}\frac{1}{1-n\eta}\left(\gamma-\frac{\gamma^2}{3}\right)+\left(\gamma-\frac{\gamma^2}{6}\right)+\ln(1-n\eta)+\frac{5}{2}\ln\left(n\Lambda^3\right)^{-1} \qquad (5)$$

On inspection of eq.(5) it can be seen that depends only on γ and packing fraction η. The ideal gas entropy is given by,

$S_{ideal}/Nk_B = 5/2 - \ln(n\Lambda^3)^{-1}$, $S / Nk_B = S_{ideal} / Nk_B + S_{XS} / Nk_B (\gamma,n,\eta)$

where S_{XS} is called the excess entropy and is given by,

$$\frac{S_{xs}}{Nk_B}=-\frac{\gamma^2}{6(1-n\eta)^2}-\frac{1}{1-n\eta}\left(\gamma-\frac{\gamma^2}{3}\right)+\left(\gamma-\frac{\gamma^2}{6}\right)-\ln(1-n\eta) \qquad (6)$$

Thus the shape of the particles will have a profound effect on S_{XS} .For a sphere γ=3 and S_{XS} is written as follows,

$$\frac{S}{Nk_B}=\frac{3}{2}\left(1-\frac{1}{(1-n\eta)^2}\right)+\ln(1-n\eta)$$

which is the excess entropy predicted using the Percus-Yevick compressibility equation of state.The total entropy of the system S_{tot} is thus given by $S_{tot} = S_{XS}+S_{rot}+S_{ideal}$ where S_{rot} is the rotational entropy.

Having obtained an equation for S_{XS} it was decided to see how it varied with number density and with shape.To do this use was made of Gibbons' paper in which he tabulates R,A and V for several shapes.γ was then found for each shape and graphs were drawn of S_{XS} against η with the volume of the individual particles taken as unity.The results are given in a later section (Figure 1**).**

3.APPLICATION OF THE THEORY

The above results applied to a system of spherocylinders were used to predict the entropy of real diatomic liquids at the melting.The method used is shown below using nitrogen as an example.

To calculate S_{XS} for a system of spherocylinder values for γ, V and η are needed.The values of R, A and V for the spherocylinder are given below [6], [7],

$$\bar{R} = \frac{L+4a}{4}\,;\, A = 4\pi a^2 + 2\pi aL\,;\, V = \frac{4}{3}\pi a^3 + \pi a^2 L \qquad (7)$$

To apply these results to nitrogen an appropriate size for the spherocylinders must be found.The length L was taken as the distance between the atomic centres which is obtainable from spectroscopy data.The length a poses more of a problem.A method used by Kihara[6] is to adjust a until he obtains agreement between his predicted value for the second virial co-efficient of a gas and its experimental value of several temperatures.However the second virial co-efficient is difficult to measure and is not usually known very accurately.Kihara's for nitrogen, a=1.74Å does show that we should expect a value for a much larger than the atomic radius, 0.71Å.Ionic radii chosen using this method will be used in this work that follows.

For nitrogen then the radius a was taken as 1.74Å and the length L as 1.1Å..Using eq. (7), γ and V were found to be γ=3.104, V=3.105x10^{-23} cm^{-3}.

To find the number density n the density p of the liquid at the melting point was used p=Nm/V = nm, where m is the mass of a molecule, V is total volume.

For nitrogen p=0.810g/cm^2 and the molecular weight M=28.0134 giving a mass in grammes of 46.502x10^{-2} and a value for n of 1.742x10^{22}.

Substituting these values into eq.(6) gives S_{XS}/Nk_B= - 6.647.Using the temperature of the melting point T and the values given above, packing fraction η can be found and hence S_{ideal} for nitrogen the melting point is 63.1 K and S_{ideal}/Nk_B=9.188.

These calculations were repeated for O_2 , Br_2 and F_2 using the values tabulated below as data [8] , [9].

Table1. To tabulate the data

Substance	Valency	Radius (a) Å	Interatomic distance (L) Å	Density at melting point(ρ) g/cm^3	Molecular Weight (M)	Melting Point K
N_2	3	1.74	1.10	0.810	28.01	63.1
O_2	2	1.32	1.20	1.142	32.00	54.1
Br_2	1	1.96	2.29	1.661	159.80	266.1
F_2	1	1.33	1.40	1.108	38.00	55.2

To find the total entropy of the systems the rotational entropy must be found. The rotational entropy of the particle can be obtained from the rotational partition function Z_r using the relation [10],

$$S_{rot} = k_B\left(\ln Z_r + \beta \bar{E}_r\right) = k_B\left(\ln Z_r - \beta\frac{\partial \ln Z_r}{\partial \beta}\right)$$

where $\bar{E}_r$ is the ensemble average of the rotational energy.Therefore for N molecules,

$$S_{rot} = R\left[\ln\left(\frac{k_B T}{2Bch}\right)+1\right] \qquad (9)$$

where R is the Gas constant, I the moment of inertia of the molecule and h is given by h=h/2π .Equation (8) can be rewritten in terms of the spectroscobic rotational constant B as,

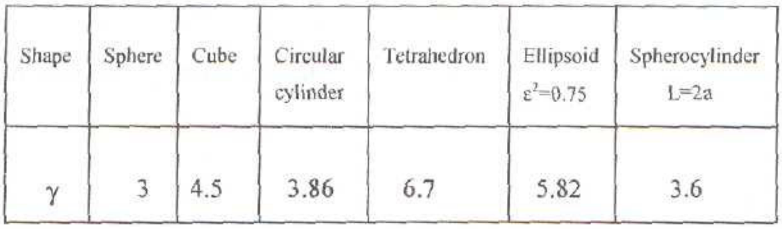
$$S_{rot} = R\left[\ln\left(\frac{I}{\beta\hbar^2}\right)+1\right] \qquad (8)$$

where B is given by $B=h/8\pi^2 cI$ and c is the speed of light, h the planck constant.Knowing I S_{rot}, can be found from (8).For nitrogen $I=1.393\text{x}10^{-39}$.

RESULTS AND CONCLUSIONS

γ's for several shapes are tabulated in Table2.In this work we are presenting the results of S_{xs} for these shapes in figure 1.

Table2. γ values for several shapes

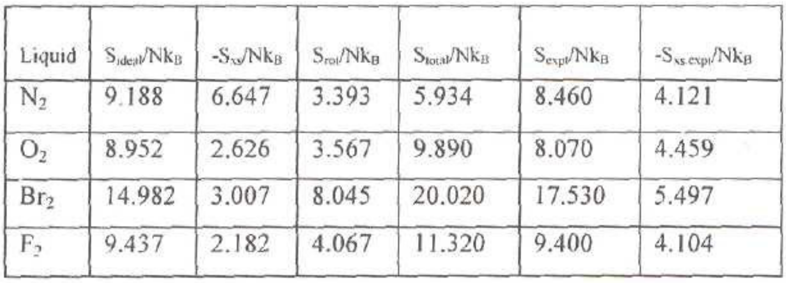


Shape	Sphere	Cube	Circular cylinder	Tetrahedron	Ellipsoid $\varepsilon^2=0.75$	Spherocylinder L=2a
γ	3	4.5	3.86	6.7	5.82	3.6

In the case of systems of ellipsoids we have used the eccentricity ε -or,more precisely, ε^2 - rather than the length to breadth ratio, as a measure of their departure from spherical symmetry [11].We have taken for ellipsoids $\varepsilon^2=0.75$ and for spherocylinders the length as twice its radius.

The comparison of the entropy of diatomic liquids with systems of hard spherocylinders with the same mass shape and number density to be presented in Table3.

Table3. The comparison of the entropy for diatomic liquids.



Liquid	S_{ideal}/Nk_B	$-S_{xs}/Nk_B$	S_{rot}/Nk_B	S_{total}/Nk_B	S_{expt}/Nk_B	$-S_{xs\,expt}/Nk_B$
N_2	9.188	6.647	3.393	5.934	8.460	4.121
O_2	8.952	2.626	3.567	9.890	8.070	4.459
Br_2	14.982	3.007	8.045	20.020	17.530	5.497
F_2	9.437	2.182	4.067	11.320	9.400	4.104

Excess-experimental entropy is given by $S_{xs,expt} = S_{expt} - S_{ideal} - S_{rot}$.The shape of bodies in a hard body system has a fairly jarge effect on its entropy.This effect increases with number density and always reduces the total entropy. The results of the comparison between a fluid of spherocylinder and a real liquid are different.Even taking account of the 10 percent error in S_{expt}, does not bring any of the liquid entropies into agreement with the predicted results S_{total}.Further there seems to be no correlation between the magnitudes of S_{xs} and $S_{xs,expt}$.For example the magnitude of S_{xs} for N_2 is different from the other S_{xs}'s but for N_2 $S_{xs,expt}$, shows no such prominence.

An explanation for the above results may be that the wrong radius a for the particles was chosen, so that $(\partial F/\partial \eta) \neq 0$.

However for nitrogen the value chosen for arrived at independently agreed fairly well with Kihara's estimate.Incidently calculations using Kihara's radius for nitrogen predict a result for the entropy even further from S_{expt}. If further work is done in this area it may be better to use for the value of a the radius which minimises the free energy rather than an emprical radius.

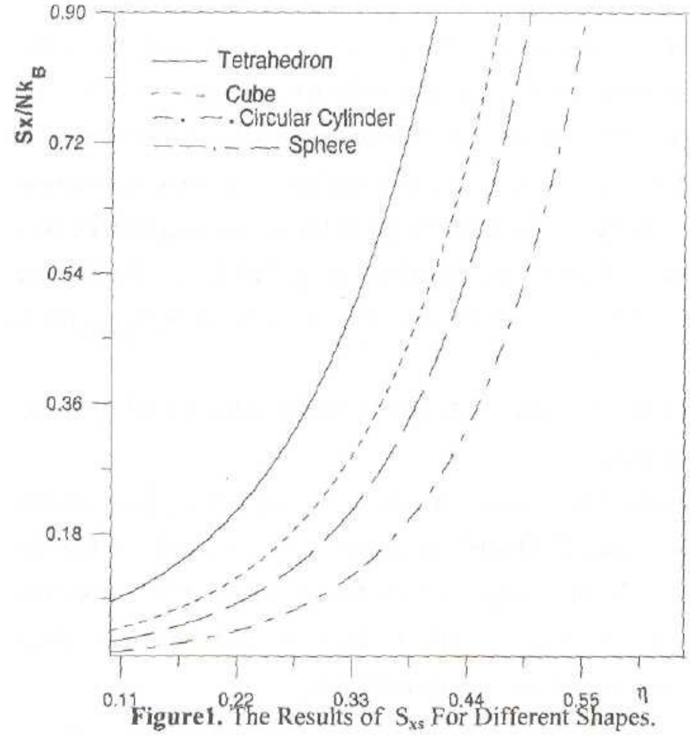


Figure1. The Results of S_{xs} For Different Shapes.

REFERENCES

1 M. Silbert, I.H. Umar, M. Watebe and W.H. Young, J. Phys. F, Metal Phys. **5** (1975) 1262.
2 H. Reiss, H.L. Frisch and J.L. Lebowitz, J. Chem. Phys. **31** (1959) 369.
3 R.M. Gibbons, Mol. Phys. **17** (1969) 81.
4 R.M. Gibbons, Mol. Phys. **18** (1970) 809.
5 M.A. Cotter and D.E. Martire, J. Chem. Phys. **52** (1970) 1909.
6 T. Kihara, Rev. Mod. Phys. **25** (1953) 831.
7 J.A. Barker and D. Henderson, Rev. Mod. Phys. **48** (1976) 587.
8 "CRC Handbook of Chemistry and Physics" 49 th ed. (1968).
9 "The Practising Scientists Handbook" (1978).
10 Fundamentals of Statistical and Thermal Physics, Mc Graw Hill (1965).
11H.N. W. Lekkerkerker, Ph. Coulon, R.Van Der Haegen and R. Deblieck, J. Chem. Phys., **80**(1984)3427.