COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 23 ANNÉE 1976

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by

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Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Calculation of the Total Interaction Energy and Surface Energy of Liquid Droplest in Microscopic Sizes

Timur HALICIOĞLU

ABSTRACT

A method is developed to calculate the total intermolecular potential energy, E_D, of spherical droplets of simple liquids as a function of the droplet's radius. Numerical values of E_D are calculeted for droplets of liquid Argon with radii between 10–250 Å (i.e., containing 10^2–10^6 atoms). It is found that for droplets containing less than 10^5 atoms to estimate any quantity related to the energy (such as potential energy, surface energy etc.) the use of macroscopic bulk properties of the liquid is inadequate. The variation of the surface energy with respect to the droplet's size is also calculated.

INTRODUCTION

In the study of a vaporization-condensation process the most peculiar situation occurs when the liquid phase is in the form of small droplets. The properties of very small droplets are of importance especially in problems related to homogeneous nucleation [1–9]. The main problem, here, is to find how the thermodynamic properties vary as the size of the droplet diminishes down to very small dimensions. However, there is as yet no sound theory to estimate the thermodynamic quantities of very small droplets; and the subject is quite contoversial [6–10].

Recently, various attempts have been made to estimate -numerically- the total potential energy of clusters (microcrystallites) of atoms, or molecules, from pair interractions [2, 11, 12]. Because of the computational difficulties, however, there has not been any work done for clusters containing more than 10^3 molecules, nor for droplets of liquids.

In this work, a method is developed to calculate the total intermolecular potential energy, E_D, of spherical droplets of simple liquids using Lennard-Jones type pair interactions. The method takes the geometry of the system into consideration and provides the possibility of computing the total potential energy of droplets of simple liquids up to macroscopic sizes.

As an example the values of E_D are calculated for varying sizes of droplets of liquid Argon. It is found that droplets containing less than 10^5 atoms can be considered as microscopic and accordingly, the use of macroscopic quantities to estimate the potential energy (and related quantities) of such small droplets is shown to be inadequate. Furthermore, an estimate of the surface energy of microscopic droplets of liquid Argon is also obtained as a function of the droplet's size.

Model and Theory

A droplet is considered as a "central" molecule surrounded by shells of molecules. In each shell molecules are assumed to be distributed uniformly (providing a complete spherical symmetry). If the internuclear distance between the central molecule and a molecule located in the i th shell is denoted by r_i, we further assume that the relation

$$1. \qquad \frac{r_i}{r_1} = \sqrt{i}$$

holds, as in an assembly of close packed spheres [11, 13]. Now, the total number of molecules, N_T, in a given droplet can be expressed as:

$$2. \qquad N_T = 1 + \sum_i^s N_i$$

Where, N_i represents the average number of molecules located in the i'th coodination shell, and s is the number of the outermost coodination shell. Accordingly, the total potential energy, E_D, of the droplet due to the interaction among molecules is:

$$3. \qquad E_D = \tfrac{1}{2} \left(e_o + \sum_i^s N_i e_i\right)$$

where, e_o denotes the potential energy of interaction of the central molecule with all the other remaining molecules, and e_i is the

potential energy of interaction between a "reference" molecule located in the i'th coordination shell and the other N_T–1 molecules in the droplet. For a "reference" molecule located within the surface region of the droplet the value of e_i should be different from e_o.

Now, we will first consider a macroscopic droplet and estimate the average numbers, N_i, and distances, r_i, of molecules on the coordination shells, then, these will be used in calculating E_D for microscopic droplets by means of Eq.3.

A. *Macroscopic Droplets.* In the case of a droplet of macroscopic size (i.e., $N_T \leftrightarrow \infty$) the number of molecules in the surface region is negligibly small, if compared with the total number of molecules in the droplet. Accordingly, for any macroscopic assembly the difference between e_i and e_o can be ignored (as though there were no surfaces). Therefore Eq.3 may be written in the following form:

$$4. \qquad E_D = \frac{N_T}{2} e_o \text{ (for } N_T \text{ very large)}$$

Considering pairwise additivity of the potential, the term e_o can be calculated from:

$$5. \qquad e_o = \sum_i^s N_i . u(r_i)$$

where, $u(r_i)$ denotes the pair potential energy between two molecules at an internuclear distance, r_i. To calculate $u(r_i)$ for simple liquids the Lennard-Jones pair potential may be used:

$$6. \qquad u(r_i) = 4\varepsilon \left(\left(\frac{\sigma}{r_i} \right)^{12} - \left(\frac{\sigma}{r_i} \right) \right)^6$$

where, ε and σ are the energy and distance parameters, respectively. Combining Equations 4,5 and 6 one obtains:

$$7. \qquad e_o = 4\varepsilon N_1 \left(\frac{\sigma}{r_i} \right)^6 \left(\sum_i^s \frac{N_i}{N_1} \left(\frac{r_1}{r_i} \right)^{12} - \sum_i^s \frac{N_i}{N_1} \left(\frac{r_1}{r_i} \right)^6 \right)$$

Here, the term N_i/N_1 is considered to be a geometrical factor, and can be calculated from the geometry of an assembly of close packed spheres (†). Accordingly, for macroscopic droplets (i.e., $s \to \infty$), the terms within the summation signs of Eq.7 approach limiting values. From the geometry and considering Eq.1 we obtain:

$$\lim_{s\to\infty} \sum_i^s \frac{N_i}{N_1}\left(\frac{r_1}{r_i}\right)^{12} = 1.011 \text{ and } \lim_{s\to\infty} \sum_i^s \frac{N_i}{N_i}\left(\frac{r_1}{r_i}\right)^{6} = 1.204$$

The number of molecules in a spherical droplet is given by:

$$8. \qquad N_T = \frac{4\,\pi\,R^3}{3\,v_m}$$

where, R denotes the radius of the droplet, and v_m is the volume of one molecule in the liquid phase. (Here, v_m is calculated as the weight of one molecule divided by the bulk density of the liquid). For droplets of macroscopic sizes R may be taken as equal to r_s. Therefore, considering Equations 1, 2 and 8 we obtain:

$$9. \qquad N_1 = \frac{4\,\pi\,r_1^{\,3}}{3\,v_m}\;\frac{\sqrt{s^3}}{\sum_i N_i/N_1}$$

Now, for a macroscopic droplet using Equations 7 and 9 one can calculate N_1 and r_1 in terms of e_o, v_m, ε and σ (*). For liquid Argon, Krypton and Xenon numerical values of N_1 and r_1 are calculated and given in Table I, with corresponding experimental values. The value of e_o is calculated from the experimental value of E_D, the cohesive energy, [16] by means of Eq. 4. Numerical

(†) Bernal [14] and Scott [15] have shown that simple liquids can be well represented by "Random Close Packed" spheres. In their model, if we compare the ratio N_i/N_1, (the average number of spheres in the i'th coordination shell divided by the average number of nearest neighbors) with the analogous ratio, N_i^c/N_1^c, for an assembly of close packed spheres, we find that up to i=4, the value of N_i/N_1 may be considered to be equal to the value of N_i^c/N_1^c. This region -which coincides with the short range order of liquids- is the most important region in the energy calculations. (See Reference 11.)

(*) The term $\frac{\sqrt{s^3}}{\sum N_i/N_1}$ in Eq. 9 for the limit $s \to \infty$ converges to $\frac{9}{\pi\sqrt{2}}$.

values of E_D, v_m, ε and σ that are used in the calculation are tabulated in Table II.

B. *Droplets in Molecular Dimensions.* In the case of microscopic droplets the number of molecules located in the surface region is no longer negligible compared with the total number of molecules. Therefore, to calculate the total energy, Eq. 3. should be used, which considers molecules on each shell separately. Of course, every molecule in the droplet has its own coordination shells. Let us name the coordination shells around the "central" molecule as "central coordination shells" and the coordination shells around and other reference molecule as "reference coordination shells" (π). Depending on the location of a reference molecule some of its "reference coordination shells" should be cut by the surface of the droplet. As a result, in those coordination shells there should be a decrease in the average number of molecules. (See Figure I.) Accordingly, the interaction potential energy, e_i, of a molecule located in the i'th "central coordination shell" may be calculated in the following way:

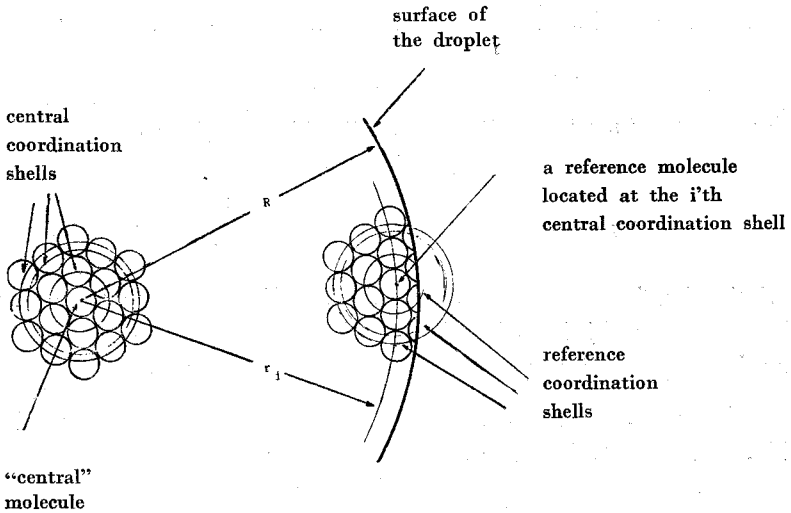

Figure 1. *"Central" and "Reference" Coordination Shells*

$$10. \qquad e_i = \sum_{j}^{s} a_{ij} N_j u(r_j)$$

π According to the model, molecules are uniformly distributed over the "central coordination shell". In calculating e_i, similarly, molecules in any "reference coordination shell" are assumed to be uniformly distributed.

Where, α_{ij} N_j is the average number of molecules in the j'th "reference coordination shell" of a molecule located in the i'th "central coordination shell". The factor α_{ij} can take values $0 < \alpha_{ij} \leq 1$, depending on the location of the reference molecule. If the "reference coordination shell" is not disturbed by the surface of the droplet then, $\alpha_{ij} = 1$; otherwise $\alpha_{ij} < 1$.

The factor α_{ij} may be calculated in various ways. For example, if we assume that molecules in each coordination shell are distributed uniformly over the entire surface, for the j'th "reference coordination shell", which is cut by the surface of the droplet, we may write:

$$11. \qquad \alpha_{ij} = \frac{S_P}{S_T}$$

where, S_T denotes the total surface area of the j'th "reference coordination shell", $S_T = 4\,\pi r_j^2$; and S_P represents the portion of S_T included by the droplet. Accordingly, α_{ij} is given by (*):

$$12. \qquad \alpha_{ij} = \frac{(R/r_i)^2 - (\sqrt{i}-\sqrt{j})^2}{4\sqrt{ij}} \quad \text{if} \quad \frac{R}{r_1} < (\sqrt{i}+\sqrt{j})$$

$$\alpha_{ij} = 1. \qquad \text{if} \quad \frac{R}{r_1} \geq (\sqrt{i}+\sqrt{j})$$

Obviously, for small i the values of α_{ij} differ from unity only for larger values of j; but, for a large i (for a reference molecule in the surface region) almost all α_{ij}'s will be smaller than 1.

Now Eq. 3 can be used to calculate the total potential energy, E_D, of a droplet. As an example, droplets of liquid Argon are considered. The numerical values of E_D are calculated for various droplet sizes. Calculation is carried out for droplets containing up to 10^6 Argon atoms. The results are tabulated in Table III. The change in $-E_D/N_T$ versus R is shown in Figure II. The curve

(*) The radius of the droplet, R, is defined according to Eq. 4 for very small droplets R is not always equal to r_s –as it was assumed for macroscopic droplets. The surface area of a droplet is consi dered as the surface area of a sphere having the same volume as $N_T\, v_m$. [2]

approaches asymptotically to the macroscopic value (**), $e_\infty = -1.05 \times 10^{-13}$ ergs, shown with the broken line.

Table III Calculated Values of E_D and E_s for Various Droplet Sizes of Liquid Argon

Droplet's radius R (Å)	Average number of molecules in the droplet N_T	Total potential energy of interaction $-E_D$ (ergs/droplet)	Energy per molecule in the droplet $-E_D/N_T$ (ergs/molecule)	Surface energy E_s (ergs/molecule)
9.02	65	4.1395×10^{-12}	0.6386×10^{-13}	4.1992×10^{-14}
17.92	509	4.2754×10^{-11}	0.8402×10^{-13}	2.1835×10^{-14}
27.04	1749	1.5932×10^{-10}	0.9111×10^{-13}	1.4742×10^{-14}
35.87	4084	3.8693×10^{-10}	0.9475×10^{-13}	1.1102×10^{-14}
54.08	13993	1.3771×10^{-9}	0.9842×10^{-13}	0.7438×10^{-14}
108.15	111927	1.1421×10^{-8}	1.0204×10^{-13}	0.3814×10^{-14}
180.29	518489	5.3667×10^{-8}	1.0351×10^{-13}	0.2347×10^{-14}
243.44	1276483	1.3285×10^{-7}	1.0408×10^{-13}	0.1778×10^{-14}

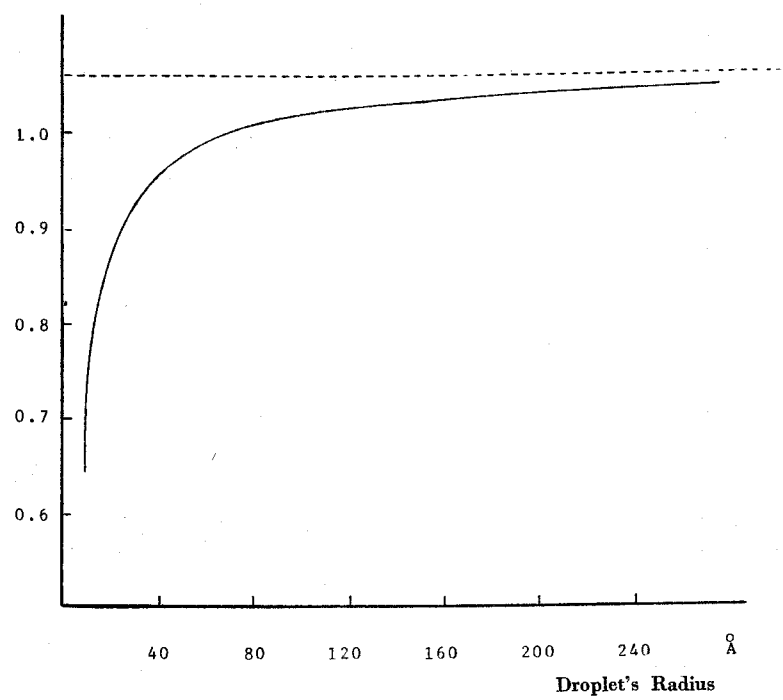

Figure 2. *Interaction Potential Energy per Atom versus the Droplet's Radius*

(**) Here, e_∞ is calculated as the molecular cohesive energy, i.e., cohesive energy/N_T. Note that for infinitely large droplets we have $e_\infty = e_0/2$.

From the values of the total potential energy for droplets of various sizes one can also calculate the surface energy of droplets as a function of their radii. The surface energy, E_s, of a droplet of N_T atoms is defined as the difference between the energy of these N_T atoms in the droplet and the energy of N_T atoms in the bulk liquid [2, 11]. Accordingly;

13. $$E_s = E_T - N_T e_\infty$$

The values of E_s are calculated for droplets of liquid Argon, and tabulated in the last column of Table III. Also the variation of E_s versus the droplet's radius is given in Figure III.

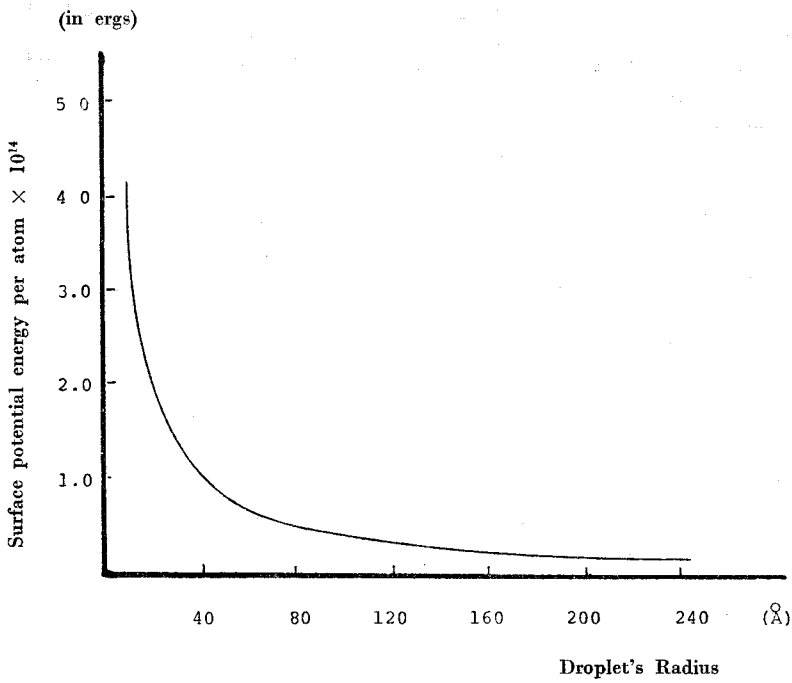

Figure 3. *Variation of the surface potential energy per atom as a function of the droplet's radius.*

DISCUSSION

The model which is used in this work to represent liquid droplest agrees quite well with the nature of the liquid state.It considers no lattice structure. The assumption of the uniform distribution of atoms –or molecules– on each coordination shell (that

provides a spherical symmetry around a reference atom) facilitates the compitational procedure greatly.

The method enables us to calculate the average value of the microscopic quantities, N_1 and r_1, of a liquid, and the potential energy of a liquid droplet of given size. With the Lennard-Jones parameters, only the energy of vaporization and the density of the liquid are necessary to estimate the numerical values of N_1 and r_1. The geometry of the close packed spheres is used to obtain only the value of N_i/N_1 (the ratio of the average number of atoms in the i'th shell to the average number of nearest neighbors) for liquid droplets. This is found to be a very good approximation, especially within the short range order of simple liquids. The calculated values of N_1 and r_1 for liquid Argon, Krypton and Xenon are found to be in good agreement with the experimental measurements.

The calculation of the total potential energy, E_D, for various sizes of droplets of liquid Argon indicates that liquid droplets containing more than 10^5 atoms may be considered as macroscopic and the potential energy –or any quantity related to it– can be estimated using macroscopic (bulk) values. For smaller droplets, however, the extrapolation of macroscopic quantities down to droplets containing less than 10^5 atoms is inadequate.

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ÖZET

Küçük küresel sıvı damlacıklarında toplam çekim potansiyeli E_D'nin damlacık yarı çapının bir fonksiyonu olarak hesaplanması için yeni bir metod geliştirildi. Sıvı Argon'un 10–250 Å yarı çaplarındaki (yani 10^2–10^6 Argon atomu ihtiva eden) damlacıkları için E_D'nin sayısal değerleri hesaplandı. 10^5 atomdan daha az atom ihtiva eden damlacıklar için herhangi bir termodinamik miktarın (mesela, toplam potansiyel enerji, yüzey enerji gibi) doğrudan doğruya makroskopik özelliklerden hesaplanmasının hatalı olacağı gösterildi. Ayrıca yüzey enerjinin damlacık yarı çapı ile değişimi de incelendi.

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Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı Ankara, Turquie.

Ankara Üniversitesi Basımevi. Ankara – 1976