

# Surface tensions and stress tensors of liquid and solid clusters by molecular dynamics

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**Abstract.** Surface tension and pressure (stress) tensors of Lennard-Jones clusters, in the size range 200 ~ 2700 atoms/cluster, formed from evaporating liquid droplets were calculated in a Molecular Dynamics simulation. Icosahedral clusters have a much larger surface tension than decahedral, fcc, and hcp ones, meanwhile asymmetric icosahedral clusters have a lower surface tension. Fcc and hcp clusters have a very small surface tension. Decahedral clusters have a surface tension closer to that of fcc and hcp ones than to that of icosahedral ones, though both icosahedral and decahedral structures have five fold symmetry axis. Binary component clusters have a higher surface tension than single component ones.

**PACS.** 36.40.-c Atomic and molecular clusters – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 68.03.Cd Surface tension and related phenomena – 82.20.Wt Computational modeling; simulation

## 1 Introduction

Surface tension  $\gamma$  (or surface energy) is usually pointed out as an important term in the stability of small particles and clusters. However, its values are not so often considered in atomistic scale calculations, particularly for system including a curved surface. A reason for the lack of such calculation may be that no good way is available to calculate the surface tension of clusters. Surface tension can be calculated from the pressure tensors in the normal and tangential directions ( $p_N(r)$  and  $p_T(r)$ , respectively) at  $r$  as

$$\gamma = \frac{1}{S} \int_0^\infty 4\pi r^2 [p_N(r) - p_T(r)] dr, \quad (1)$$

where  $r$  is the distance from the center and  $S$  is the surface of tension [1]. Calculation scheme of the local pressure tensor on the atomistic scale was presented by Irving and Kirkwood in 1950 [2] and reformulated by Schofield and Henderson in 1982 [3]. There is, however, a theoretical problem on the uniqueness of integration contour used in the calculation of the pressure tensor in the local volume [4]. We have recently presented a way to avoid somehow this theoretical problem to calculate the local pressure tensor in the liquid droplet by Molecular Dynamics (MD) simulation [5, 6].

Surface tension can be an index to measure how large strain is included in clusters. An example is provided by icosahedral and decahedral clusters, which do not exist in

the bulk because of larger strain for larger clusters. We have shown the existence of a structural transition from icosahedral to a mixture of decahedral, fcc and hcp clusters by increasing the cluster size in MD simulations, in which a lot of Lennard-Jones (LJ) clusters with different sizes ( $N = 200 \sim 2700$  atoms/cluster) were produced by cooling liquid droplets through evaporative and further thermostatic processes [7]. The transition size was about 450 for single component clusters and 550 for binary component clusters. During the simulations many asymmetric or defective clusters were formed. The similar asymmetric or defective clusters can be seen also in the simulation of metal cluster formation [11, 12]. But, the amount of asymmetric clusters may be much larger in LJ clusters than in metal ones. Defective and asymmetric metal clusters are also observed experimentally [8, 9].

In this paper, we present the results of the surface tension calculation for clusters of various sizes and structures. The relationship between the surface tension and the asymmetry of clusters will be also shown. All the samples treated here are the same as those analyzed in reference [7].

## 2 Calculations

The two-component LJ potential,  $\phi_{ij}$ , between atoms  $i$  and  $j$  of component  $\alpha$  and  $\beta$ ,

$$\phi_{ij} = 4\epsilon \left\{ \left( \frac{r_{ij}}{\sigma_{\alpha\beta}} \right)^{-12} - \left( \frac{r_{ij}}{\sigma_{\alpha\beta}} \right)^{-6} \right\}, \quad (2)$$

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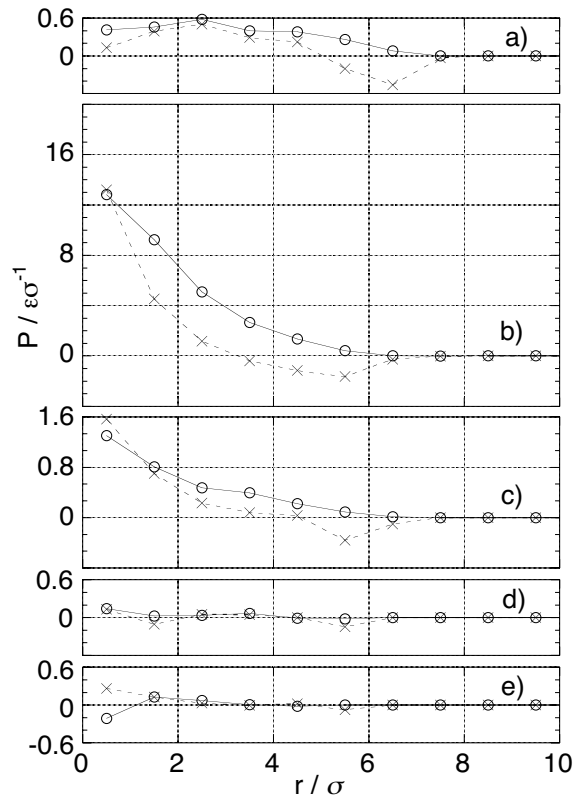
where  $r_{ij}$  is the distance between atoms  $i$  and  $j$ , was used. All variables denoted by  $*$  in this paper are non-dimensional with LJ potential energy  $\epsilon$ , distance parameter  $\sigma_{\alpha\alpha}$  ( $>\sigma_{\beta\beta}$ ), atomic mass, and Boltzman constant. When argon is used as a reference, temperature  $T^* = 1$ , time  $t^* = 1$ , and distance  $r^* = 1$ , correspond to 119.8 K, 2.16 ps, and 0.341 nm, respectively. For the binary component system, atoms having the same mass, the same energy parameter and a smaller size parameter,  $\sigma_{\beta\beta}/\sigma_{\alpha\alpha} = 0.92$ , were randomly added to the system in a 25 % proportion. The distance parameter between the different kinds of atoms is the average value:  $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2$ .

160 single-component and 80 binary-component liquid droplets ( $N = 200 \sim 2700$ ) at  $T^* = 0.6$  were at first prepared under periodic boundary conditions. After an equilibration time of  $t^* = 1,000$ , each liquid droplet formed was put into a free space and the MD calculation was done without any constrain, *i.e.* under the constant energy condition, up to  $t^* = 20,000$ , in order to cool down the clusters by evaporation. Solid clusters at  $T^* \sim 0.4$  were formed. Further cooling by the thermostat was done in order to calculate the physical properties at  $T^* = 0.3$  which corresponds to the estimated temperature, 35 K, of Ar clusters in supersonic expansion experiments. Pressure tensors were calculated by dividing the clusters into spherical layers of thickness equal to 1.0 during MD run for  $t^* = 1,000$  under the constant energy condition around  $T^* = 0.3$ . The details are given elsewhere [6,7]. A time step of  $\delta t^* = 0.01$  was used in all MD calculations.

### 3 Results and discussion

#### 3.1 Pressure profiles

In the liquid droplets, pressure tensors in the normal and tangential directions are equal and uniform in the inner region ( $r^* < 4$  for clusters of  $N \sim 1000$ ) as shown in Figures 1a and 2a. The deviation from this at small  $r$  is due to a lower precision, close to the center. Pressure tensors are found to change at the vapor-liquid interface, that is at  $r^* \sim 6$ . The difference between the pressure tensors in the different directions gives the surface tension according to equation (1) (and surface energy  $= \gamma S$ ). In the case of solid clusters, pressure profile in the clusters are not necessarily uniform because of the inner stress. Perfect icosahedral clusters have different atomic-distances in the radial and tangential directions. They show, therefore, a greater distortion near the center as a result of adjusting the different atomic-distances [10]. Since the inner region is more strongly compressed, the pressure tensors are higher, as expected, when approaching the center as shown in Figures 1b and 2b. For the same reason, decahedral clusters show a higher pressure tensors near the center (Figs. 1c and 2c). However, the inner stress is not as large as in icosahedral clusters, because decahedral clusters can be considered as a structure made of five fcc grains weakly distorted (decahedral clusters have only one five fold symmetry axis meanwhile icosahedral clusters



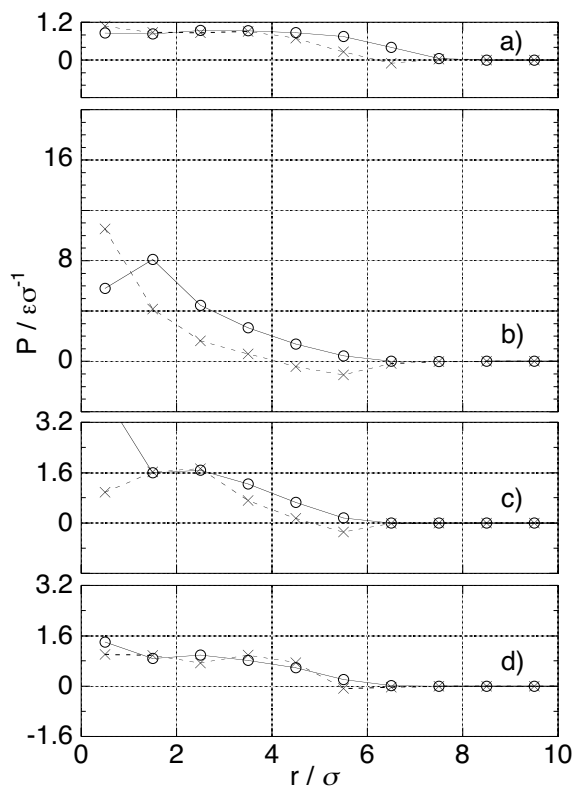
**Fig. 1.** Normal and tangential pressure tensor profiles in single component clusters of (a) liquid droplet at  $T^* = 0.6$ , and (b) icosahedral ( $N = 1052$ ), (c) decahedral ( $N = 1123$ ), (d) fcc ( $N = 864$ ), and (e) hcp ( $N = 799$ ) clusters at  $T^* = 0.3$  formed from liquid droplets by cooling.

have six). Thus, decahedral clusters may be produced in the same size range as fcc clusters (at least  $N < 2700$ ) [7]. The pressure profiles shown in Figures 1 and 2 correspond to rather symmetric clusters taken from a lot of clusters produced by MD simulation with different initial sizes and configurations.

Fcc and hcp clusters exhibit small pressure tensors as shown in Figures 1d, 1e and 2d. In the single component clusters, the pressure is close to zero, since all atomic distances between neighbors are almost equal in fcc and hcp clusters. They are rigorously equal in pure crystals. Random mixture of atoms with different sizes introduces some distortion in solid clusters, leading to higher pressure tensors in the binary-component clusters.

#### 3.2 Surface tension

Surface tensions of clusters (80 single component and 80 binary component clusters) of different sizes and structures formed by evaporation from liquid droplets are shown in Figure 3. They were calculated by equation (1) using equimolar dividing surfaces as  $S$  instead of the surface of tension. Icosahedral clusters show surface tensions higher than those of any other structures as expected from their structure which undergoes an inner stress as described in Section 3.1. The surface tension increases with



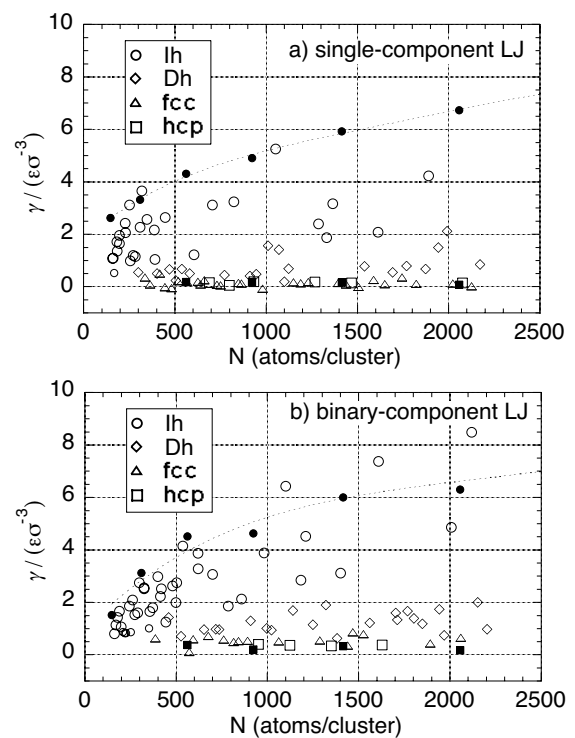
**Fig. 2.** Normal and tangential pressure tensor profiles in binary component clusters of (a) liquid droplet at  $T^* = 0.6$ , and (b) icosahedral ( $N = 1100$ ), (c) decahedral ( $N = 1062$ ), and (d) fcc ( $N = 864$ ) clusters at  $T^* = 0.3$  formed from liquid droplets by cooling.

increasing size, but does not exceed that expected from the perfect icosahedral structures, except in the case of a few binary component clusters. Above the transition size of structures ( $N = 450$  for single component and  $N = 550$  for binary component clusters [7]), clusters with smaller surface tension, *i.e.* decahedral, fcc and hcp ones, are produced. Despite of the five-fold symmetry, decahedral clusters have a surface tension only slightly higher than that of fcc and hcp structures. Such a small surface tension may originate the similar production rate of decahedral and bulk-structure clusters (fcc and hcp) [7].

It can be also noticed from Figures 3a and 3b that the surface tension of binary component clusters is higher than that of the single component clusters in any structures. A random mixture of the different size atoms produces some distortion in solid clusters, giving the higher surface tension as it gives higher pressure tensors.

### 3.3 Asymmetric clusters

In TEM observations of small clusters, symmetric structure clusters are generally observed, because they are more stable than asymmetric structure (at least, at 0 K). However, some asymmetric clusters are experimentally observed and also obtained in some MD calculations [11, 12]. This is partly because of time limitation which prevents



**Fig. 3.** Surface tension of various size clusters of (a) single component and (b) binary component at  $T^* = 0.3$ . Filled circles and squares show that of the ideal icosahedral and fcc clusters, respectively. Broken lines smoothly connect the filled circles.

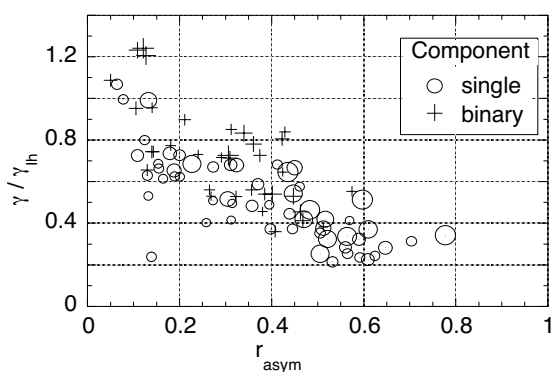
the clusters from changing into the most stable structures with higher activation energy. There might be another reason for the production of asymmetric clusters. They have a lower surface tension (surface energy) than symmetric ones as shown in Figure 4, in which the relative surface tension is plotted against the relative position  $r_{asym}$  of the icosahedral center,  $r_{Ih}$ , which is measured from the center of mass, as defined as

$$r_{asym} = \frac{r_{Ih}}{R}, \quad (3)$$

where  $R$  is the radius of the cluster. The relative surface tension is plotted as a relative value against those expected from the ideal icosahedral clusters shown by a broken line in Figure 3a. This lower surface tension observed in asymmetric clusters implies that they are more easily formed than the symmetric ones.

## 4 Conclusion

Pressure profile and surface tension were calculated for various size clusters formed from liquid droplets by evaporation. Icosahedral clusters showed a much larger surface tension than decahedral, fcc, and hcp ones. The difference in the formation process of icosahedral, decahedral, and fcc/hcp clusters are somehow explained by the surface tension. The formation of asymmetric clusters may be due to the lower surface tension than symmetric clusters.



**Fig. 4.** Relative surface tension as a function of the relative position of the Ih center for various size clusters. Mark size is proportional to the cluster size.

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