Bubble nucleation in micellar solution : A density functional study

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A. Introduction

Sonolysis has recently been proposed for the degradation of surfactants which pollute the environment.[1,2] However, the efficiency of sonolysis depends on many factors such as the physico-chemical properties of the surfactant,[3,4] the frequency of ultrasound,[5] and the presence of micelles.[1,2,6] In the process of sonolysis, the surfactant solution is subjected to ultrasonic radiation which induce rapidly chaning pressure pulses. The bubbles form during the negative pressure cycle of the sound wave and begin to grow in the oscillating sound field till these bubbles become unstable and suddenly collapse, producing extreme conditions of temperature and pressure at the center of the imploding bubble. The surfactant molecules, which accumlate at the vapor-liquid interface of the bubbles, undergo various chemical reactions under these extreme conditions.

The rate of formation of the macroscopic bubbles in the aqueous surfactant solution under a negative pressure is controlled by the rate of bubble nucleation.[7] The latter depends on (1) the kinetics including the rates of diffusion of surfactant and solute molecules and (2) the thermodynamics, i.e., free energy of critical bubble formation. In this paper, we study free energetics of bubble nucleation using statistical mechanical density functional theory.[8,9] Our approach is based on the density functional model of micellar solution developed by Talanquer and Oxtoby.[10] There is some experimental evidence to suggest that micelles may enhance the rate of bubble formation during sonolysis.[6] By exploring the free energy surface in the vicinity of equilibrium clusters such as critical bubble nuclei and stable micelles, we

seek for a theoretical explanation for this experimental observation. We also study the effect of attractive interactions among the molecules on bubble nucleation. Thus, our work may lead to better understanding of some of the factors that affect the efficiency of sonolysis.

B. Density functional method

We employ a simple two-component model of nonionic surfactant solution developed by Talanquer and Oxtoby.[10] In this model, which is based on interaction site formalism of molecular fluids,[11] the solvent is represented by a monatomic molecule A and the amphiphile is represented by a diatomic molecule C. The solvent molecule is a single hard core spherical particle with diameter σ. The amphiphile molecule consists of two tangent hard core spheres, each with diameter σ, i.e., the two spherical atoms in the amphiphile are connected by a rigid bond with bond length equal to σ. The attractive interactions between the particles are treated in a mean-field fashion and are modeled as follows,

$$\phi_{ij}^{att}(r) = \begin{cases} 0 & (r \leq \sigma) \\ -4\epsilon_{ij}(\sigma/r)^6 & (r > \sigma), \end{cases} \tag{1}$$

where, $i, j = 0,1,2$ and r is the distance between the interaction sites i and j. Here, the subscript '0' refers to solvent particle, and the subscripts '1' and '2' refer to solvophilic and solvophobic site of the amphiphile, respectively.

In particular, the Helmholtz free energy of this surfactant solution is a functional of local average densities of the interaction sites and is approximated as given in Ref. 10. The stationarity condition of the Helmholtz free energy determines the density profiles $\rho_i(\mathbf{r})$ of the inhomogeneous cluster such as the bubble cluster or the micellar aggregate in equilibrium with the surrouding surfactant solution at constant temperature T, volume V, and the number of particles. These density profiles are then used to calculate all the relevant properties of the equilibrium clusters.

In particular, we are interested in calculating the reversible work of formation of the bubble cluster and the micellar aggregate that are in equilibrium with the metastable surfactant

solution in an open system. This quantity is given by the excess in the grand potential Ω of the system containing an equilibrium cluster relative to its value Ω_h of the metastable homogeneous phase,

$$\Delta\Omega[\rho_i(\mathbf{r})] = \Omega[\rho_i(\mathbf{r})] - \Omega_h. \tag{2}$$

In addition, we also calculate the excess number of amphiphilic molecules C relative to the homogeneous phase[10]

$$i_C = \int d\mathbf{r}[\rho_1(\mathbf{r}) - \rho_C] = \int d\mathbf{r}[\rho_2(\mathbf{r}) - \rho_C] \tag{3}$$

and the excess number of solvent particles A relative to the homogeneous phase

$$i_A = \int d\mathbf{r}[\rho_0(\mathbf{r}) - \rho_A]. \tag{4}$$

For a bubble cluster, i_A is negative and i_C represents the number of amphiphilic molecules adsorbed at the vapor-liquid interface of the critical bubble. For a given i_C, the size of the bubble cluster is given by the value of i_A. For a micellar aggregate, i_C may be regarded as the number of amphiphilic molecules in the micelle. In our discussion on the free energy surface in the next section, we have considered i_A and i_C as reaction coordinates. It is therefore assumed that the time scales characterizing change of i_A and i_C are much larger than those of other degrees of freedom.

The properties of the surfactant solution depends sensitively on the relative values of the energy parameters ϵ_{ij} in Eq. (1), which determine the attractive interaction between the molecules. Talanquer and Oxtoby[10] have combined these parameters into four groups, namely, ϵ_{CC}, ϵ_{AC}, α^*_{AC}, and α^*_{CC}. The energy parameters ϵ^*_{CC} and ϵ^*_{AC} determine the bulk phase diagram and other homogeneous phase properties of the binary mixture.[10] The other two parameters α^*_{AC} and α^*_{CC} control the amphiphilic properties of the diatomic molecule C and have no effect on the bulk phase diagram and other homogeneous phase properties.[10] In this work, we examine five sets of values for the energy parameters ϵ^*_{CC} and ϵ^*_{AC} as shown in Fig. 1.

C. Results and Discussion

As the pressure on the surfactant solution is lowered below the vapor-liquid coexistence pressure, to a negative value, i.e., as the surfactant solution is stretched, it becomes metastable and bubbles nucleate. We studied the properties of micellar aggregates and critical bubble nuclei forming in metastable surfactant solution under such conditions.

In particular, we studied the variation of $\Delta\Omega$, i_C, and i_A of the equilibrium clusters with respect to the mole fraction ϕ of the surfactant in the surrounding solution at a given temperature and pressure. We found that the work of formation $\Delta\Omega$ of critical bubble nucleus is lower in a surfactant solution than that in a pure solvent for all values of ϕ. Moreover, as ϕ increases, i_C increases and work of formation of the critical bubble decreases. This is expected since the presence of surfactant molecules at the vapor-liquid interface of the critical bubble reduces its surface free energy. We also found that for a certain range of ϕ, critical bubble nuclei and micellar aggregates exist simultaneously in equilibrium with the metastable surfactant solution. This points to the possibility that in this range of mole fractions, micelle may form first, which then evolves to form the critical bubble.

We studied the above possibility in more detail by considering the free energy surface of the model system as shown in Fig. 2. The points M1, M2, and B1 in this figure correspond to the critical micelle, the stable micelle, and the critical bubble, respectively. The critical micelle M1 represents the free energy barrier of the formation of the stable micelle M2 from the homogneous surfactant solution.[10] The rest of the points represent the non-extremum clusters and their free energies are estimated using an approximate mapping scheme.[12] From this figure, we anticipate that there is a broad valley connecting M2 to B1, and hence if the process of critical bubble formation is driven by the free energetics alone, the stable micelle at M2 may evolve to form the critical bubble B1. This is indicated by the arrow pointing from M2 to B1. The free energy barrier of this process (i.e. M2–B1) is $\beta\Delta\Omega_{td} = 67.9$, where $\beta = 1/k_B T$ and k_B is the Boltzmann's constant. The critical bubble B1 may also evolve directly from the homogeneous surfactant solution, as indicated by the arrow pointing from

the origin to B1 in Fig. 2. The free energy barrier of bubble nucleation in this process (i.e. O–B1) is $\beta\Delta\Omega_{hs} = 76.1$. The free energy barrier of bubble nucleation in a pure solvent at the same pressure is $\beta\Delta\Omega_s = 90.7$.

Now let us consider the kinetic aspects of bubble formation from the stable micelle. In a real surfactant solution, size of the surfactant molecule is much larger than that of the solvent molecule, and hence the solvent molecules are likely to diffuse much faster compared to surfactant molecules. If this scenario holds for the present model, then the stable micelle at M2 is likely to form a bubble cluster along the pathway represented by the arrow pointing from M2 to B2 in Fig. 2. The free energy barrier of bubble nucleation in this process (i.e. M2–B2) is $\beta\Delta\Omega_{kn} = 74.5$. However, in the present model, the size of the amphiphilic molecule is similar to that of the solvent molecule, and hence the kinetic consideration discussed above will not be relevant. Further, the relative probability of the kinetic pathway (i.e. M2–B2) to to the thermodynamic pathway (i.e. M2–B1), which is $\exp[-\beta(\Delta\Omega_{kn} - \Delta\Omega_{td})]$, is only 0.015. Thus, in the model system we studied, the thermodynamic pathway discussed above is likely to be preferred over the kinetic pathway.

To determine the exact pathways of bubble nucleation on the free energy surface, and hence the role of stable micelles in bubble nucleation, an appropriate rate theory is also needed, but we do not pursue it in this work. Nonetheless, based upon the free energetics alone, we can compare the rate of bubble nucleation associated with different possible pathways. Thus, we find that $\beta\Delta\Omega_{td}$ for (M2–B1) pathway is smaller than $\beta\Delta\Omega_{hs}$ for (O–B1) pathway and both of these quantities are much smaller than the free energy barrier of bubble nucleation $\beta\Delta\Omega_s$ in a pure solvent. Hence, the rate of bubble nucleation in the model surfactant solution is expected to be higher than that in a pure solvent. Moreover, in the range of ϕ where the stable micelles exist in equilibrium with the surfactant solution, bubble nucleation is likely to be further enhanced due to the possible mechanism of bubble nucleation from the stable micelles.

We also studied the effect of pressure on the bubble nucleation in the model surfactant solution. We found that the work of formation and size of the equilibrium bubble clusters

decrease as the pressure is decreased. This is expected because the state of the surfactant solution approaches the spinodal as we lower the pressure. Moreover, as the pressure becomes close to spinodal, (i) the micelles are found to be less stable with respect to dissolution process and (ii) the kinetics associated with evolution of the micelle to the critical bubble is not favorable since the size of the critical bubble (as measured by the excess solvent molecules i_A in the cluster) becomes smaller than that of the micelle, while the number of excess surfactant molecules i_C in the micelle is larger that that in the critical bubble. As a result, there is no enhancement of rate of bubble nucleation in the presence of stable micelles at such pressures.

We now examine the effect of parameters ϵ^*_{CC} and ϵ^*_{AC} on bubble nucleation. These parameters determine the miscibility of the liquid phases of the model system (one liquid phase is solvent-rich and the other is surfactant-rich). For the parameter sets S2 and S4 in Fig. 1, where the liquid phases are more miscible, stable micelles are found to exist over a wider range of mole fractions. Also, the equilibrium concentration and stability of the micelles in the model surfactant solution is higher. Thus, the evolution of the micelle to critical bubble is more likely. For the parameter sets S3 and S5, where the liquid phases are less miscible, stable micelles exist over a narrower range of mole fractions and the equilibrium concentration and stability of the micelles is lower. Hence, in this case, the mechanism of micelle assisted bubble nucleation is less likely to be relevant. Thus, the effectiveness of the suggested mechanism of micelle assisted bubble nucleation is found to correlate with the miscibility of the liquid phases.

ACKNOWLEDGMENTS

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FIGURES

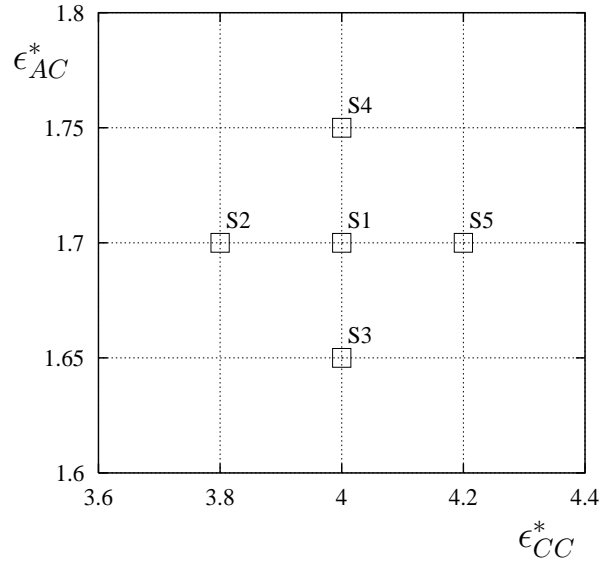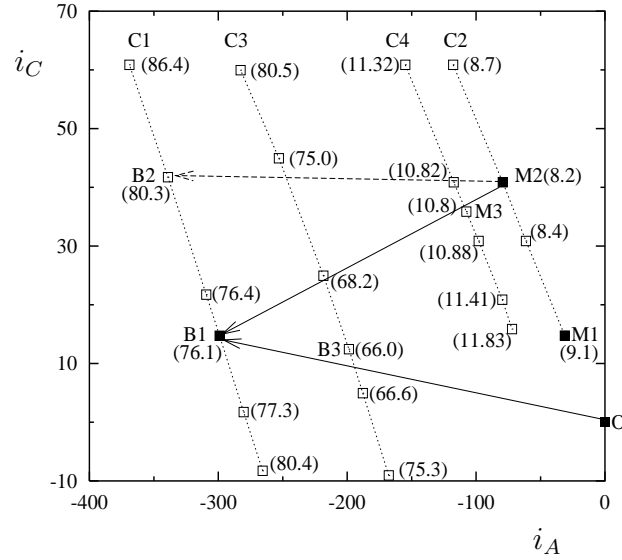
FIG. 1. Parameter sets used for the study.

FIG. 2. The free energy surface at $T^* = kT/\epsilon_{00} = 0.8$, $P^* = \sigma^3 P/\epsilon_{00} = -0.52$, and $\phi = 0.00906$ for the parameter set S1. The numbers in parentheses are free energy of formation of respective clusters, either obtained by a direct calculation or from an approximate mapping scheme.[12] M1 is the critical micelle, M2 is the stable micelle, B1 is the critical bubble, and the rest are non-extremum clusters. The origin $(0,0)$ corresponds to the homogeneous surfactant solution. Arrows show the possible pathways of bubble nucleation.