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Analysis of the Motion Process of Bulk Nanoparticles Based on EDU and Time Series Stationarity

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Keywords: Stability, MA (q) model, Coarse-grained particles, Uniformity, Correlation

Abstract: As the name implies, bulk phase nanobubbles exist under bulk phase conditions. Bulk phase here generally refers to liquid phase environment, and nano bubbles refer to bubbles with a diameter less than 1 micron. It has unique physical properties such as small size and large relative surface area, and has broad application prospects in many fields, such as agriculture, surface cleaning, water purification, ore flotation, drug transportation and so on. The nanobubbles suspended in the liquid are in Brownian motion under the action of thermodynamics, resulting in a nearly spherical structure, which makes it difficult to directly detect many physical properties. There have been many theoretical models about the physical mechanism of nanobubble stability, such as linear tension model, dynamic equilibrium theory, high density theory and magazine theory. But these theories explain only part of the results, so they are not universally accepted. Molecular dynamics simulation method can be used to obtain the dynamic process of bulk phase nanobubbles at the scale of 100 nanometers. This method can prove the stable dynamic process of bulk phase bubbles, which is helpful to explain some physical properties of nanobubbles and explain the reason why they can be stabilized for a long time. We use gas phase equilibrium and thermodynamic methods to investigate whether the nanobubbles are stable under the conditions of temperature and pressure changes, and found that no matter the temperature or pressure changes, the impact on it is minimal.

1. Introduction

1.1. Background

Bulk nanobubbles, as the name implies, are nanobubbles that exist under bulk conditions. The bulk here generally refers to a liquid environment, and nanobubbles refer to bubbles with a diameter less than 1 micron [1]. It has unique physical properties such as small size and large relative surface area, and has broad application prospects in many fields, such as agriculture, surface cleaning, water purification, ore flotation, drug transportation, etc. The nanobubbles suspended in the liquid are in a state of Brownian motion under the action of thermodynamics, resulting in a nearly spherical structure, which makes it difficult to directly detect many physical properties. Regarding the physical mechanism of the stability of nanobubbles [2-3], there have been many theoretical models, such as linear tension model, dynamic equilibrium theory, high density theory, and magazine theory.

But these theories can only explain part of the experimental results, so they cannot be accepted by

everyone. The molecular dynamics simulation method can be used to obtain the dynamic process of bulk nanobubbles at the 100-nanometer scale. This method can prove the stable dynamics of bulk bubbles, help explain some of the physical properties of nanobubbles and explain their long-term stability reason.

1.2. Restatement of the Problem

In order to solve those problems, we will proceed as follows:

- **Question 1** According to the data, through the analysis of a large amount of data, it is judged whether the density distribution of the coarse-grained particles at the interface is uniform.
- **Question 2** By constructing a suitable mathematical model, test the relationship between the density distribution of coarse-grained particles in different regions with time and the correlation between the density of different regions.
- **Question 3** According to data analysis and appropriate model selection, determine the relationship between the volume of the interface formed by coarse-grained particles and the change over time.
- **Question 4** Consult a large number of related documents to further explore the effect of changing temperature and pressure on bubble size

1.3. Our Work

1) Import the data into MATLAB, build each group of data in 3D coordinates, conduct preliminary analysis on the data and make basic conjecture.

2) It is concluded that in x, Y and Z coordinate directions, the number of coarse-grained particles conforms to normal distribution. According to our model, it is concluded that the particles are uniformly distributed on a plane approximately as a sphere in space.

3) Make statistics on the number of particles in the eight regions divided, and get the change of density of each region in space with time.

4) Calculate the relation between volume and time of each group of data and establish a model to prove its correlation.

5) Search a large number of materials and literature, and through the analysis of relevant literature [4-7], use the model to find out the relationship between bubble volume and temperature and pressure, and conduct data processing.

2. Assumptions and Justification

To simplify the problem and make it convenient for us to simulate real-life conditions, we make the following basic assumptions, each of which is properly justified.

- **Assuming that all data sources are reliable and the data is true and accurate**. If the data source is unreliable and the data is not true and accurate, our investigation will be meaningless.
- **Assuming that all data sources are reliable and the data is true and accurate**. If you consider bulk nanobubbles from a microscopic point of view, many elements and limitations need to be considered. Our existing tools cannot reach this level.
- **Assuming that coordinate data after the order of** 10^{-10} **has no effect on the model**. If the coordinate data after the order of 10^{-10} is not considered, the graphics formed by the interface can be regarded as a standard ball.
- **Assuming that the volume of the four water molecules model has no effect on the bubble size**. If the influence of the volume of the four water molecules model on the bubble size is considered, the forces and gaps between the water molecules also need to be considered, which will greatly

increase the workload. For simple analysis, it is not considered.

- **Assuming that the gas composition inside the bubble as a single-component ideal gas**.
- **Assumed that the influence of water vapor inside the bubble on the model is ignored**.

3. Notations

Table 1: Main parameters

Symbols	Description	Unit
T	Temperature	℃,K
P	Pressure	pa
V	Volume of a single bubble	nm^3
V	Gas chemical potential	J
k_H	Reduced Henry Coefficient	Dimensionless
k_B	Boltzmann constant	Dimensionless
R	Gas constant	Dimensionless

Main parameters are shown in Table 1.Where we define the main parameters while specific value of those parameters will be given later

4. Model and Results

4.1. Analysis and Processing of Raw Data

We import the given coordinate data at 0ns into MATLAB, establish a three-dimensional coordinate system, and express the coordinates of each point in three-dimensional coordinates.
As shown in Figure 1. It can be seen intuitively that the coarse-grained particles at the interface form a sphere-like surface.

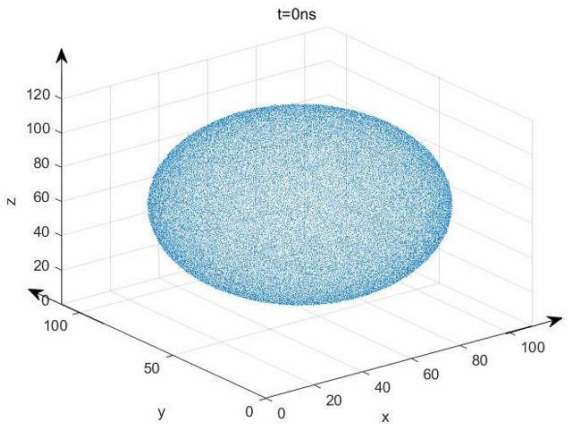

Figure 1: Data coordinate graph at 0ns

As shown in Figure 2, the three-dimensional spherical surface was observed from different viewing angles, and it was found that the pictures obtained from XOZ, XOY, and YOZ had the same shape and were all circular. Therefore, we take the maximum mean value in the xyz direction as the circle center coordinates. The coordinates of the center of the circle can be obtained by processing the data through Excel. Center coordinates: (59.98, 59.98, 59. 96).
Based on 3.1 data analysis, we boldly guess that the density distribution of coarse-grained particles at the interface is uniform [8]. Import the given data into EXCEL, arrange the coordinates in ascending order,

and make the particle distribution density curve in the direction, as shown in Figure 3, Figure 4 and Figure 5. We can intuitively see that X, Y, and Z all obey the normal distribution.

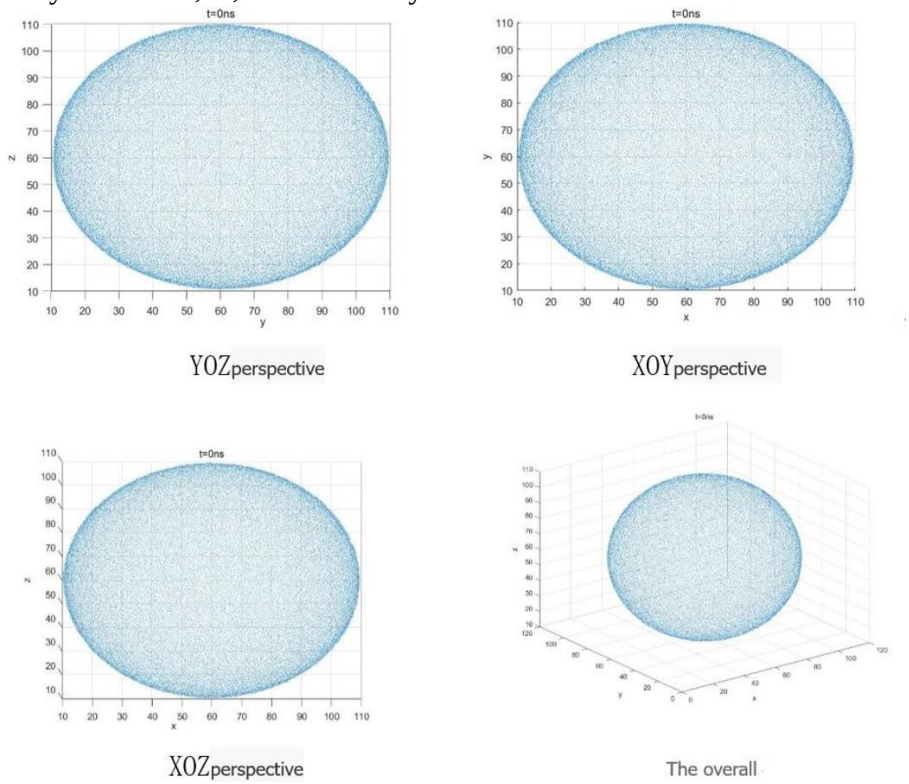

Figure 2: Observe pictures from different perspectives

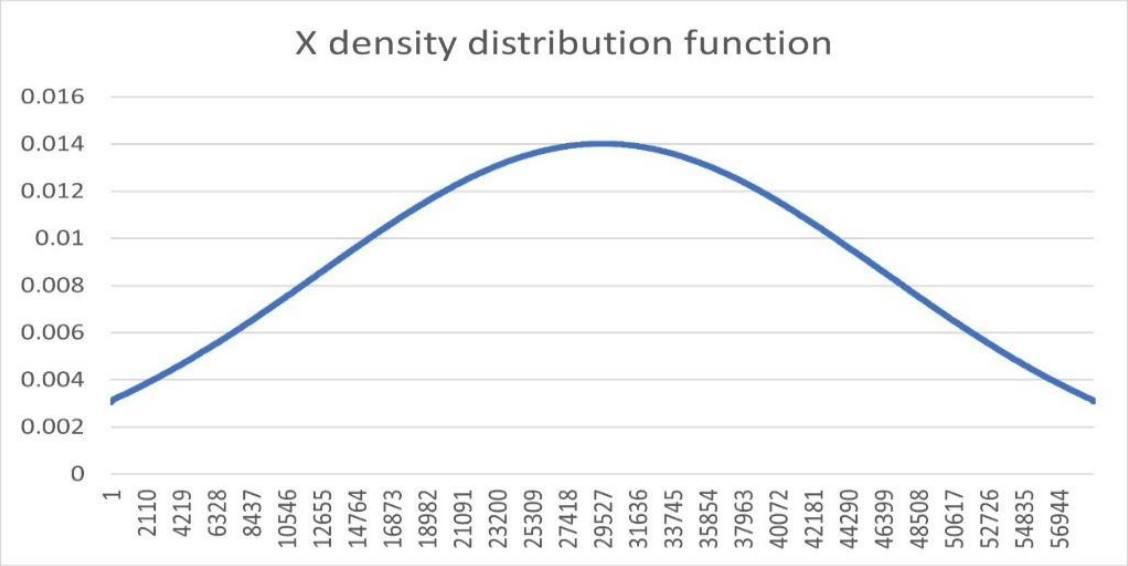

Figure 3: X density distribution chart

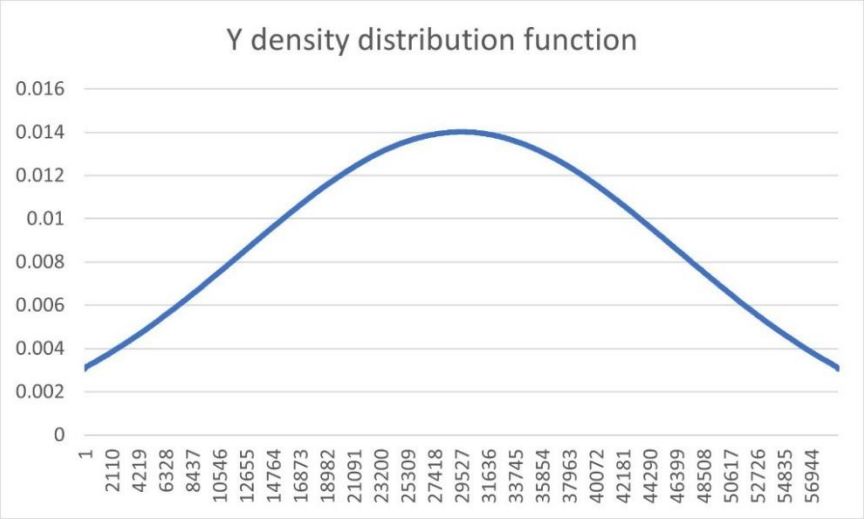

Figure 4: Y density distribution chart

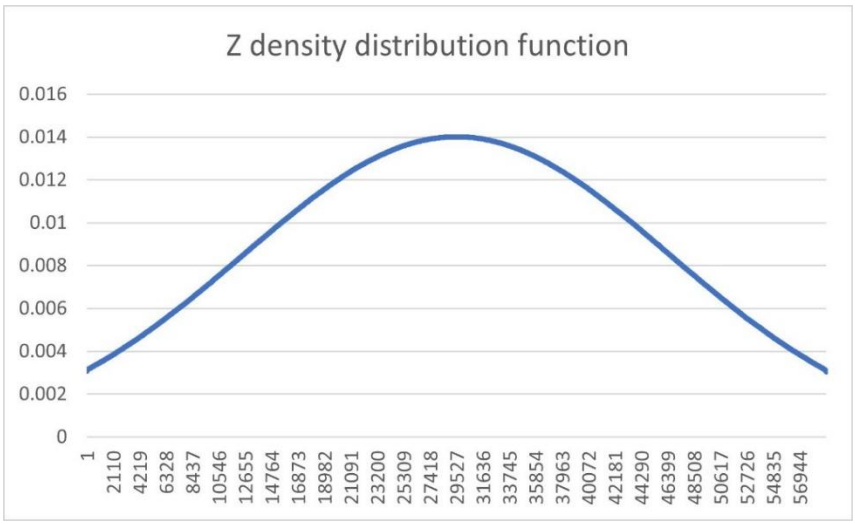

Figure 5: Z density distribution chart

By formula

$$\mu = \frac{1}{n}\sum_{i=1}^{n} X_i \qquad (1)$$

Without considering the influence of data below 10−10 on the model, the sample X mean value is 60.

By formula

$$S^2 = \frac{1}{n-1}\sum_{i=1}^{n}(X_i - \mu)^2 \qquad (2)$$

Without considering the influence of data below 10−10 on the model, the standard deviation of the sample is obtained 28.

From the above data, it can be seen that the particle distribution in the X-axis direction respectively obeys X～N(60,28). By repeating the above calculation process, we can get: Y～N (60,28),Z～N(60,28), and their distribution can be denoted as:

$$f(X) = \frac{1}{60\sqrt{2\pi}} e^{-\frac{1}{2}(\frac{x-60}{28})^2}$$

$$f(Y) = \frac{2}{60\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{Y-60}{28}\right)^2}$$

$$f(Z) = \frac{1}{60\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{Z-60}{28}\right)^2} \quad (3)$$

$$f(X,Y,Z) = f(X)f(Y)f(Z) == \frac{1}{60\sqrt{2\pi}} e^{\left[-\frac{1}{2}\left(\frac{X-60}{28}\right)^2+\left(\frac{Y-60}{28}\right)^2+\left(\frac{Z-60}{28}\right)^2\right]}$$

$$f(X,Y,Z) = \frac{1}{60\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{r}{28}\right)^2} \quad (4)$$

That is, f(X, Y, Z) is a constant, and the overall probability is only related to the radius, which proves that the particles are uniformly distributed at the interface.

In addition, since the densities of different regions are equal, there is no correlation.

4.2. Time Series Stationarity Model

4.2.1. Make a Guess

In order to further explore the time-varying nature of the density of coarse-grained particles at the interface, we divided the area surrounded by the coarse-grained particle interface into eight quadrants, as shown in Figure 6.

Establish a rectangular coordinate system with the ball centered as the coordinate origin, divide the ball into eight parts, and count the number of particles in each quadrant over time. The statistical results are shown in Figure 7, and the number of particles in each area is basically stable.

Figure 7 is obtained through MATLAB statistical data and analysis. It can be seen from the figure that the number of particles in each quadrant fluctuates continuously around its mean value of 7380. Therefore, we boldly guess that the time series is stable, and the density distribution of coarse-grained particles in different regions does not vary. Change of time.

Our time series data is generated based on the process of bulk nanobubble motion, and the motion process can be obtained by MATLAB simulation. After visualizing the data, it can be seen intuitively that the density of coarse-grained particles in different regions does not change with time, which further verifies our conjecture.

4.2.2. Time Series Stationarity Proof

Based on the proof of 3.2, the coordinates of the points generated on the interface during the movement of the nanobubbles are generated randomly, so our time series are generated by this random process.

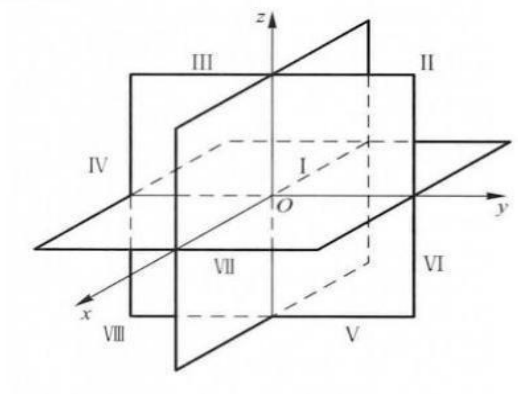

Figure 6: Area division

1) From the question, it is assumed that the number of coarse-grained particles at different moments is conserved, so the average value E (X_t) = 7380 is only related to the division of regions and does not change with time.

2) The variance Var (X_t) is obviously only related to whether the division of the region is accurate, and it is the amount that is determined not to change over time after the division of the region.

3) Auto-covariance: $cov(X_i, X_{i+k})$ = E[($X_i - \mu$)($X_{(i+k)} - \mu$)] = E($X_i X_{i+k}$)-7380^2. Ob-viously, E ($X_i X_{(i+k)}$) is the amount of data only related to k, and has nothing to do with time. Therefore, the autocovariance is a quantity that has nothing to do with time.

From the above analysis combined with the conditions of the stationarity of the time series, it can be known that the time series generated by the random process is stable, that is, the density distribution of coarse-grained particles in different regions does not change with time.

Generally, the time series of any variable can be described by the autoregressive process. But in the practice of model analysis, in order to simplify the workload of estimating parameters, we certainly hope that the parameters in the model are as few as possible. Therefore, it is necessary to introduce the moving average process MA (q).

4.2.3. MA (Q) Model Stability

The MA (q) model is as follows.

$$X_t = \sum_{i=1}^{q} \beta_i \varepsilon_{t-i} \tag{5}$$

It can be established as long as the following conditions are met.

$$E(x_t) = 0, var(x_t) = \delta^2 \sum_{i=s}^{q} {\beta_i}^2, cov(x_t, x_{t-s}) = \delta^2 \sum_{i=s}^{q} \beta_i \beta_{i-s} \tag{6}$$

Since the sum of its series is a finite series sum to q, MA (q) is always stable.

From Figure 7, we can see that the time series generated by substituting our data into the same proof that the random process is stable.

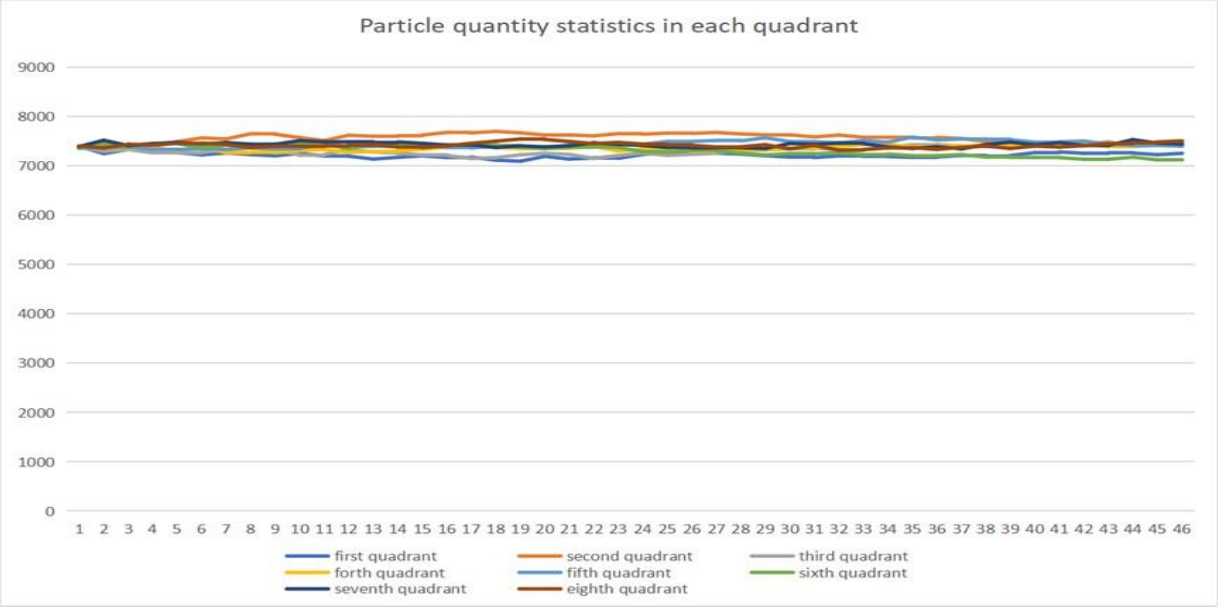

Figure 7: Changes in the number of particles

5. The Relationship between the Interface Formed By Coarse-Grained Particles and the Volume Enclosed By Time

5.1. Relationship Prediction

The simulation of the motion diagram of bulk nanoparticles with time-varying images from 0 to450 ns in the file figures/ movefig.gif shows that the interface of coarse-grained particles and the enclosed volume are basically the same over time. Therefore, we boldly predict that the interface formed by the granulated particles and the volume enclosed by it will not change over time.

5.2. Predictive Test

Based on the assumption of 2.1: the data after the order of10−10 will not be considered. Combining Figure 2 of 4.1, the interface formed by the coarse-grained particles can be deduced from the same diameter as a standard sphere. Take the maximum and minimum values in the X direction as a and d, respectively; the maximum and minimum values in the Y direction as b and e; and the maximum and minimum values on the Z axis as c and f, respectively.

By formula

$$D = [(a - d + (b - e) + (c - f)]/3 \quad (7)$$

We can get D.

By formula

$$V = (\pi D^2)/6 \quad (8)$$

We can get V.

Mathematical analysis of the data by matlab obtains the variation of the boundary volume of the coarse-grained particle with time as shown in Figure 8.

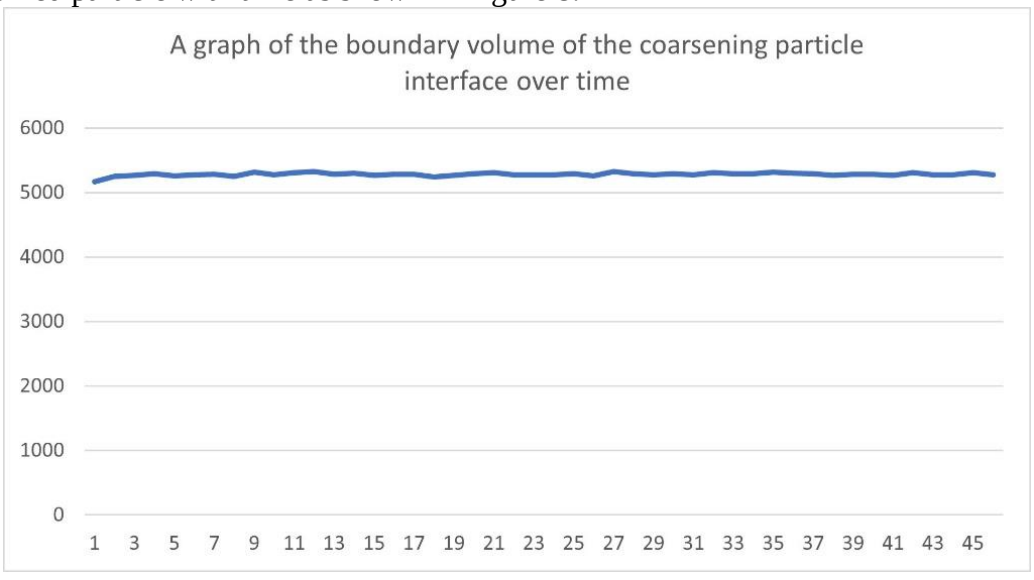

Figure 8: Graph of volume change over time

It can be seen from the figure that the volume enclosed by the interface formed by coarse-grained particles is basically unchanged over time. The reason for the deviation is affected by the assumption 3 of 2.1.

6. Explore the Effect of Changing Temperature and Pressure on Bubble Size

6.1 Thermodynamic Analysis Process

There is a phase equilibrium between the gas in the bubble and the dissolved gas in the solution, that is, the gas in the bubble dissolves into the circumferential solution, and the rate of gas evolution from the solution to the bubble reaches equilibrium. In thermodynamics, this balance needs to meet the following conditions:

$$\mu_{gas} = \mu_{sdution} \tag{9}$$

That is, the chemical potential of the gas inside the bubble is equal to the chemical potential of the gas in the solution. Taking into account our assumptions, the above formula can be simplified to:

$$\mu_{gas}(T,P) = \mu^{\theta} + RTln\frac{P}{P\theta} \tag{10}$$

In the above formula, T is the temperature, P is the pressure of the gas, and R is the gas constant. The chemical potential of the gas in the corresponding solution is:

$$\mu_{solution}(T,P) = \mu^{\theta}(T) + RTln\frac{P_{x,B}}{P^{\theta}} + RTln(x_B) \tag{11}$$

In the above formula, kx is the Henry coefficient of the gas component, and xB is the mole fraction of the gas in the solution. The phase balance requirements (11) and (12) are equal. The two equations are subtracted and simplified:

$$RTln\frac{P}{k_B k_B} = 0 \tag{12}$$

At the same time, the additional pressure of the curved liquid surface can also be expressed as,

$$\Delta P = \frac{\gamma}{r} = 0$$

$$P = P_{atm} + \frac{\gamma}{r} = 0 \tag{13}$$

In the above formula, r represents the radius of curvature of the bubble, and r represents the interface energy of the gas-liquid interface. Substitute (14) into (13),

$$RTln\left(\frac{P_{atm}+2\gamma}{rk_B x_B}\right) = 0 \tag{14}$$

We call (13) and (15) the phase equilibrium equations of bubbles. When this equation is established, the bubble is in a static phase equilibrium state. When the left side of the equation is greater than 0, the chemical potential of the gas inside the gas pool is greater than the chemical potential of the gas in the solution, and the bubbles will dissolve. When the left side of the equation is less than 0, the chemical potential of the gas inside the bubble is less than the chemical potential of the gas in the solution, and the bubble will grow larger. In addition to the phase equilibrium, there is also an infiltration phenomenon at the position of the three-phase line where the bubble is in contact with the solution. This equilibrium can be described by Youngs equation. In the above equation, γSG represents the interface energy of the solid-gas interface, γLGrepresents the interface energy of the solid-liquid interface, and $\theta_c$represents the contact angle. The above equation is only valid for an ideal solid surface. For the actual solid surface, there is a contact angle hysteresis. At this time, the contact angle $\theta_c$is within a certain range, expressed as,

$$\cos(\theta_A) < \frac{\gamma SL-\gamma SG}{\gamma LG} < \cos(\theta_R) \tag{15}$$

In the above formula,θ_A is the advancing contact angle, andθ_R is the receding contact angle.

6.2 Prediction Based on Bubble Phase Equilibrium and Thermodynamic Analysis

By consulting a large number of literatures [9-10], assuming that there is a bubble in phase equilibrium, the formula can be obtained:

$$\Delta\mu = RTln\left(\frac{P}{kx}\right) = 0 \tag{16}$$

Differentiate P, T, and x respectively:

$$\frac{\partial\mu}{\partial P} > 0$$

$$\frac{\partial\mu}{\partial T} = \frac{\partial\mu}{\partial k}\frac{\partial k}{kT} < 0$$

$$\frac{\partial\mu}{\partial x_B} < 0 \tag{17}$$

The second equation uses the chain rule. For gases, the Henry coefficient decreases with the temperature once and is less than zero. The derivative is used to judge the influence of the environment on the bubble balance: when the temperature increases and the pressure decreases, the effect on the nanobubbles is small.

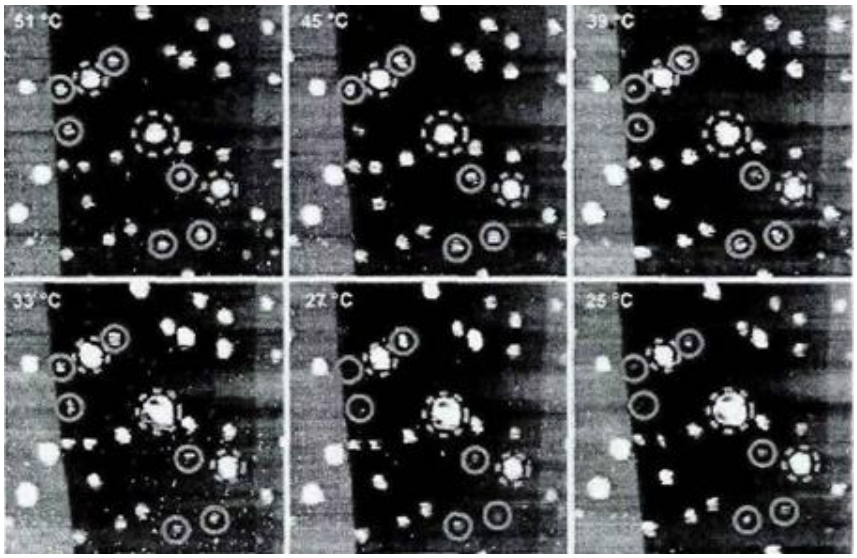

Figure 9: Graph of volume change over time

What happens if the size of the bubble is reduced to the nanoscale? The literature studies the influence of temperature, pressure, and gas saturation in the solution on the stability of nanobubbles [11-12], but the author's position is different, and the final conclusion may be slightly different. As shown in Figure 9, the earliest research on the influence of temperature factors on bubble stability is the nanobubbles generated on mica, the height of which does not change much with temperature, but the lateral width has a large effect on temperature. This is slightly different from the results obtained on graphite, where the morphology of nanobubbles on graphite changes little with temperature. Although the results are slightly different, in general, temperature changes have little effect on the stability of nanobubbles, and the generated nanobubbles will not disappear due to temperature fluctuations.

For the macroscopic bubbles of the solution, if the pressure of the environment is lowered, the bubbles will grow up immediately, which is exactly what we see when we open the lid of the soda

bottle. But what will the result be for nanobubbles? Borkent et al. studied whether nanobubbles can serve as the nucleation center of micron-sized bubbles and grow into micron-sized bubbles under reduced pressure. The result is negative. Which means that the nanobubbles are still stable under the conditions of pressure fluctuations. In the end, can the nanobubbles be dissolved in the degassed solution? We have explored this problem in experiments; finally found that the nanobubbles are almost insoluble in the degassed solution. As shown in Table 2.

Table 2: Experimental result

External environment	Parameter changes	Influence	Stability
Temperature rise	k decreases	Bubble growth	Little impact
Reduce the pressure	P decreases	Bubble growth	Little impact

In addition, we found:

- The dissolution kinetics of nanobubbles is determined by the very slow molecular exchange rate on the gas-liquid interface, rather than the mass transfer in the solution.
- The substance inside the nanobubbles has a very high dynamic viscosity and is similar to a semi-solid substance.

7. Conclusion

7.1 Advantages of the model

- The article has established a reasonable and scientific mathematical model based on a correct and clear analysis of the meaning of the question.
- The model building method is simple and easy to implement and easy to implement.
- The model has a reliable mathematical foundation through rigorous data analysis of MAT-LAB.

7.2 Disadvantages of the model

- All the data we obtain is a large amount of statistical data. If there is a certain error in the data, it will have a certain impact on the conjecture and analysis.
- We make the assumption that the bubble is a standard spherical shell. In practice, the interface of the nano-bubble is approximately spherical. If the assumption is not true, the calculated volume will have a certain error
- In the hypothesis, we make the assumption that the factors that affect the selection can fully reflect the size change of the bubble, and have no effect on the subsequent simulation, and the consideration of too few factors is inconsistent with the actual situation.
- Because the size of coarse-grained particles is smaller than that of nanobubbles, we approximate the coarse-grained particles to one point, ignoring the impact of their size and various properties. If there is an impact, some changes in physical quantities will also be ignored by us.

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