Clarification of regimes determining sonochemical reactions in solid particle suspensions

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ABSTRACT

Although there has been extensive research on the factors that influence sonochemical reactions in solid particle suspensions, the role that solid particles play in the process remains unclear. Herein, the effect of monodisperse silica particles (10–100 μm, 0.05–10 vol%) on the sonochemical activity (20 kHz) was investigated using triiodide formation monitoring and luminol tests. The results demonstrate that, in the particle size range considered, the sonochemical yields were enhanced in dilute suspensions (0.05–1 vol%), while further particle addition in semi-dilute suspensions (1–10 vol%) decreased the yields. Two regimes, namely the site-increasing regime and sound-damping regime, are identified in respect of the enhancing and inhibiting effects of the particles, respectively, and their dependence on particle characteristics is analyzed. Both regimes are confirmed based on the cavitation erosion test results or cavitation noise analysis. The clarification of the two regimes provides a better understanding of the dominant factors controlling sonochemistry in the presence of solid particles, as well as a guide for sonochemical efficiency prediction.

1. Introduction

Since the advent of inexpensive and reliable ultrasonic generators in the 1980s, power ultrasound in the 20–100 kHz range has been extensively used in water and environmental engineering [1–3]. Instead of interacting directly with molecules to induce a chemical change, the ultrasound causes cavitation, which generates extremely high temperatures (~5000 K) and pressures (~1000 atm) at localized hot spots, forming highly oxidizing species (hydroxyl radicals, -OH) to create sonochemical effects [4]. As an advanced oxidation process (AOP), sonochemistry is a promising tool for the degradation of hazardous chemicals and non-biodegradable materials in wastewater treatment [5,6]. It fulfills the requirements of “green chemistry” [7]. Research on combining it with other AOPs or biological treatments to reduce the cost has been conducted [8–10]. However, most of the laboratory experiments on sonodegradation were performed in pure water, which neglected the fact that the sonochemical process could be affected by the suspended solids in wastewater, including sand grains and microplastics [11]. Therefore, it is crucial to investigate the sonochemical activity in aqueous suspensions of solid particles.

The dependence of the sonochemical activity on the characteristics of the suspended solid particles has garnered research interest since the pioneering work of Lu and Weavers [12], Zhang and Hua [13], and Keck et al. [14] in 2002. These particle characteristics include surface properties (roughness and hydrophobicity), geometric properties (size and shape), and most importantly, the concentration of suspended particles (φp). Stoian et al. [15] compared the impacts of sand particles, spherical glass beads, and cation exchange resins (φp = 1 vol% and similar in size), on the sonochemical activity in a stirred horn-type sonoreactor (20 kHz). The researchers discovered that, although all three types of particles were categorized as hydrophilic, sand particles contributed to higher sonochemical yields owing to their higher roughness values and irregular shapes. It was assumed, based on the crevice model [16], that rough surfaces and irregular shapes facilitate the entrapment and stabilization of gas pockets, which function as nucleation sites and initiate the formation of cavitation bubbles.

The solid particles used in the existing studies encompassed particles of different size ranges (ISO), from clay-sized (<2 μm) [12–14], through silt- and sand-sized (2 μm–2 mm), to gravel-sized (>2 mm) particles [17–19]. Some researchers also reported using solids in powdered form [20–22]. However, the effect of particle size is much debated. Some researchers believed that larger particles are less likely to be trapped at pressure antinodes where cavitation primarily takes place [23], while others argued that sufficiently large particles can mimic a solid wall and...
promote the asymmetric bubble collapse [24]. Tuziuti et al. [25] noticed a rapid increase in sonochemical yields at 42 kHz as the size of alumina particles (20 g/L) increased from 1 to 10 μm, followed by a plateau (no increase) with a further increase in size (10–80 μm). By contrast, Lu et al. [26] suggested that increasing the particle size from 2 to 130 μm could reduce the sonochemical yields at 20 kHz by >10% in silica particle suspensions at the same mass concentration.

Thomas [27] classified particle suspensions into three types according to particle concentration. They are dilute (<1 vol%), semi-dilute (1–25 vol%), and concentrated (>25 vol%) suspensions based on rheology. The values of \( \phi_p \) adopted in previous research cover all three types, but the role of the particles in sonochemical reactions at various \( \phi_p \) is still not clear. Katekhaye and Gogate [28] discovered that the sonochemical yields at 20 kHz were higher in dilute suspensions of titania powder (0.2–0.6 vol%) than in water and increased with \( \phi_p \). They attributed this to the increase in the number of active sites for heterogeneous nucleation, and the catalytic activity of titania [29]. Her et al. [19] studied the sonochemical activity in semi-dilute suspensions of 100-μm inert glass beads (3–12 vol%) at 1 MHz, and reported lower sonochemical yields than in water; the yields decreased with increasing \( \phi_p \). This is consistent with the recent findings of Barchouchi et al. [17] suggesting that the scattering-induced attenuation of ultrasound waves can be related to the inhibited production of reactive free radicals. For sonochemical reactions in concentrated suspensions, it is the rapid growth of apparent viscosity with \( \phi_p \) that might predominate [15]. Microparticles in large quantities could form a barrier that prevents gas or vapor from diffusing through the bubble surface, making it harder for cavitation bubbles to oscillate or collapse [30]. However, extremely high \( \phi_p \) is rarely encountered in the tertiary treatment of wastewater.

Despite all efforts to understand heterogeneous sonochemistry, the mechanisms underlying the demonstrated enhancing yet inhibiting effects of the solid particles were often poorly addressed or inadequately clarified in literature. It is particularly necessary to analyze the relationship between the influencing regimes and sonochemical activity using multiple disciplines and perspectives, including nucleation kinetics and acoustics in multiphase flows. This assists us by clarifying how the particle characteristics influence these regimes and the sonochemical activity, which facilitates the prediction of sonochemical yields in multiphase sonoreactors.

The objective of this study is to examine and clarify the regimes that underlie the enhancement or inhibition of sonochemical reactions in solid particle suspensions. We investigate the effects of the concentration and size of silica microspheres on sonochemical yields, based on KI dosimetry and luminol techniques, and then analyze the experimental results using the parameters characterizing these regimes.

2. Materials and methods

2.1. Silica particles

Monodisperse silica particles were purchased and used with no further purification (Table 1 includes the supplier details). The particle diameters, which were in the same order of magnitude as the size of acoustically generated cavitation bubbles [31], were confirmed using a particle size analyzer (Malvern Mastersizer 2000). All possible combinations of the four sizes (10, 20, 50, and 100 μm) and eight concentrations (0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 10 vol%) of the silica particles were considered in this work.

2.2. Experimental setup

A schematic of the experimental setup is illustrated in Fig. 1. A 20-kHz ultrasonic probe system (VCY–1500, Shanghai Y&Y Sonic) was used to generate ultrasound with an applied power of 250 W. The ultrasonic probe, immersed up to 5.0 cm in the particle suspension, augmented the oscillation displacement amplitude provided by a piezoelectric transducer. An impeller was positioned 2.5 cm from the vessel bottom to ensure that the silica particles were well mixed throughout the cylindrical vessel. The inner radius and height of the vessel were 10.0 and 15.0 cm, respectively. The probe tip and the impeller were positioned symmetrically around the axis of the vessel with eccentricity equal to 0.55. All the tests were performed at minimum impeller speeds required to lift all particles from the vessel bottom; the speeds were determined based on the Zwietering approach [33,34] and are listed in Table 2. The temperature inside the vessel was maintained using a circulating cooling bath and monitored using a real-time sensor.

2.3. Sonochemical experiments

The KI dosimetry was used to provide a quantitative measure of the sonochemical activity. When an aqueous KI solution is sonicated, a fraction of I\(_{-}\) can be oxidized by -OH to give I\(_{2}\). The excess I\(_{-}\) then reacts with I\(_{2}\) to form I\(_{3}\) that absorbs spectrophotometrically at 355 nm [35]. To perform KI dosimetry, KI solution (0.1 M) was prepared by dissolving KI (purchased from Tianjin Bellian Fine Chemical Development Co., Ltd.) in degassed distilled water just before each test. The pH value was initially adjusted to 8 ± 0.2 with KOH (0.1 M, purchased from Chengdu Jinshan Chemical Reagent Co., Ltd.). This is because I\(_{-}\) in acidic

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### Table 1

| Particle size (μm) | Density (10^3 kg m⁻³) | Specific surface area (m² kg⁻¹) | Supplier |
|-------------------|-----------------------|-------------------------------|----------|
| 10                | 2.55                  | 235                           | Shanghai Aladdin Bio-Chem, China |
| 20                | 2.46                  | 122                           | Sigma-Aldrich, USA                |
| 50                | 2.49                  | 48                            | Sigma-Aldrich, USA                |
| 100               | 2.36                  | 25                            | Tokyo Chemical Industry, Japan    |

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\( a \) Density of silica particles was measured using Archimedes’ principle [32].

\( b \) Specific surface area of silica particles is calculated as the total surface area of the particles per unit of mass.

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![Fig. 1. Sketch of the experimental setup. Key: 1: ultrasonic generator, 2: piezoelectric transducer, 3: ultrasonic probe, 4: output tip (emitting surface area: 2.0 cm²), 5: electric motor (maximum speed: 1500 rpm), 6: shaft, 7: pitched blade turbine impeller (diameter: 7.5 cm, pitch angle: 45°), 8: silica particle suspension, 9: glass vessel, 10: cooling bath, 11: readout display, 12: real-time temperature sensor, and 13: supporting rod.](image-url)
solutions are susceptible to oxidation by oxygen gas, and $I_3^-$ in strongly alkaline solutions is more likely to react with $H_2O_2$ (formed by the recombination of $\cdot OH$) to form $I^-$. [36,37]. The silica particles were placed in the vessel, and KI solution was added to a height of 10.0 cm, prior to the sonochemical experiments. Preliminary control tests have revealed that the adsorption of $I_3^-$ on the glass vessel and silica particles was negligible, and the KI solution did not tend to react with air in the mechanically stirred tanks.

The total sonication time for each test was 25 min, and all tests were performed at room temperature ($25 \pm 1^\circ C$). An aliquot (6–7 mL) of solution containing minimal particles was taken every 5 min and then centrifuged (2 min at 2500 rpm). Then the supernatant was transferred into quartz cuvettes to determine the concentration of $I_3^-$; the $I_3^-$ concentration was directly proportional to the absorbance measured using a UV–Vis spectrophotometer (UV754N, Shanghai Aucy Scientific Instrument).

The intensity of the sonochemical reactions under heterogeneous conditions was also visualized using the sonochemiluminescence (SCL) method; SCL images were obtained using a solution of luminol (1 mM, purchased from Shanghai Rhawn Chemical Technology Co., Ltd.) and KOH (0.1 M) in complete darkness [38]. To facilitate SCL observation, a 500 mL transparent glass beaker was used as a substitute for the mechanically stirred vessel, and the cooling bath was temporarily removed. Virtually all the silica particles could be lifted from the bottom of the beaker under the environment of ultrasonic agitation. The shutter speed for the digital camera (EOS 200D II, Canon) was set to 30 s, and the lens (EF 50 mm f/1.8 STM) was switched to the manual focus mode.

3. Results

The measured absorbance was divided by the product of the cuvette width (1.0 cm) and the molar attenuation coefficient (23200 M$^{-1}$·cm$^{-1}$) to determine the concentration of $I_3^-$ generated. The concentration increased linearly with sonication time in the silica particle suspensions similar to the particle-free scenario (Fig. 2 a–c), which is consistent with previous reports [17,36]. When $\phi_p$ was low (0.05 vol%), slightly more $I_3^-$ was detected at every point of time compared with the particle-free scenario; smaller particle diameters ($d_p$) led to higher concentrations of $I_3^-$ (Fig. 2a). When $\phi_p = 1$ vol%, the 10-μm particles caused less $I_3^-$ production than the particle-free scenario, while the 100-μm particles still enhanced the formation of $I_3^-$ (Fig. 2b). Under high $\phi_p$ conditions (10 vol%), adding silica particles of either size reduced the $I_3^-$

![Fig. 2](Image)

Fig. 2. $I_3^-$ production plotted against sonication time for the 10- and 100-μm silica particles at (a) 0.05 vol%, (b) 1 vol%, and (c) 10 vol%; the particle-free scenario is included for comparison. (d) Comparison of the $I_3^-$ formation rates at various particle sizes and concentrations (the dashed line represents the particle-free scenario). All tests were performed in triplicate, and error bars display the standard deviation.
concentration. The concentration at 25 min for the 100-μm particles was over 50% higher than that for the 10-μm particles, which was only half as high as for the particle-free scenario (Fig. 2c). Apparently, the formation of $I_3^-$ depended largely on both $d_p$ and $φ_p$.

Given the linear relationship illustrated in Fig. 2(a)–(c), it is reasonable to assume that the formation rate of $I_3^-$, denoted by $r(I_3^-)$, follows zero-order kinetics (i.e., is independent of sonication time). Consequently, one could estimate $r(I_3^-)$ directly from the gradient of the straight line on a concentration versus time graph. With the increase in $φ_p$, $r(I_3^-)$ exhibited a similar pattern of initial increase and subsequent decrease for all four $d_p$ (Fig. 2d). Compared with the particle-free scenario, the addition of silica particles at $φ_p = 0.05–0.5$ vol% contributed to higher $r(I_3^-)$, while at $φ_p = 1–10$ vol% (except for the 1- vol% suspensions of 100-μm particles), less $I_3^-$ formed. In contrast to the marginal change in $r(I_3^-)$ when $φ_p < 1$ vol%, the decrease in $r(I_3^-)$ was marked at higher $φ_p$. For instance, $r(I_3^-)$ could decrease by 30% with a tenfold increase in $φ_p$ (1–10 vol%) for the 100-μm silica particles.

To characterize the enhancing or inhibiting effects of the suspended solid particles on the sonochemical activity and facilitate the comparison of the research findings obtained under different conditions (e.g., different particle types or ultrasound frequencies), we defined the percentage change in the formation rate as $Δr/r_0$, in which $Δr$ is the variation in the formation rate from the homogeneous system (absence of solid particles) to a heterogeneous system (presence of solid particles), and $r_0$ is the formation rate in the absence of solid particles.

There is a clear distinction between the four particle sizes in terms of $Δr/r_0$, varying with $φ_p$ (Fig. 3a). Under low $φ_p$ conditions (0.05–0.2 vol%), $I_3^-$ formation was enhanced by adding silica particles of either size, and the 10-μm particles had the best enhancing effect. The enhancing effect decreased as silica particles became larger despite a fixed $φ_p$. For example, when $φ_p = 0.1$ vol%, $Δr/r_0$ for the 10-μm particles was 57% greater than the $Δr/r_0$ for the 100-μm particles. However, crucial differences between the large and small particles emerged as $φ_p$ reached 0.5 vol%. It could be observed that $Δr/r_0$ was still increasing for the 100-μm particles, while it was decreasing for the 10-μm particles. Thus, the former soon overtook the latter as being most effective in enhancing $I_3^-$ formation. The intersection point of the curves in Fig. 3(a) indicates that $r(I_3^-)$ appeared independent of particle size at $φ_p ≈ 0.3$ vol%.

When $φ_p = 1$ vol%, the addition of the 10–50-μm silica particles generated less $I_3^-$ compared with the particle-free scenario; by contrast, the 100-μm particles still had an enhancing effect on $I_3^-$ formation, although $Δr/r_0$ was already decreasing (Fig. 3a). In this paper, we define the “critical $φ_p$” as the particle concentration at which the formation rate of the sonochemical yields in the particle suspensions is the same as that in the particle-free scenario. The critical $φ_p$ varied among particle sizes, and the larger particles had higher critical $φ_p$ values (e.g., approximately 0.6 and 1.3 vol% for the 10- and 100-μm particles, respectively). As $φ_p$ increased (2–10 vol%), adding silica particles of all four sizes inhibited $I_3^-$ formation. Smaller silica particles had a stronger inhibiting effect at specific $φ_p$; for example, the absolute value of $Δr/r_0$ for the 10-μm particles was 48% greater than the absolute value of $Δr/r_0$ for the 100-μm particles when $φ_p = 10$ vol%.

Fig. 3(b) illustrates the experimental data generated by other researchers. Although it appears impractical to compare their data with those obtained in this study (Fig. 3a), there are still some striking similarities despite the differences in the characteristics of the suspended solid particles and sonochemical reactors. First, their data follow a similar “first increasing then decreasing” pattern of $Δr/r_0$ against $φ_p$. Second, both the $φ_p$ at which $Δr/r_0$ starts decreasing and the critical $φ_p$ for the 10-μm alumina particles (0.7 and 1.8 vol%) in Ref. [25] are lower than those for the 100-μm glass beads (2.0 and 3.4 vol%) in Ref. [19], respectively, which agrees with our results. Third, the range of the $φ_p$ values illustrated in Fig. 3(b) is a good approximation to that of the 10–100-μm silica particles used in this study. Although $φ_p$ of the 3-μm quartz particles in Ref. [14] was not sufficient to reduce the $H_2O_2$ formation to the level of $Δr/r_0 < 0$ at 206 kHz, the critical condition is predictable at a higher $φ_p$, according to the downward trend. Notably, the highest $Δr/r_0$ of every work shown in Fig. 3(b) is higher than the value in Fig. 3(a). One possible cause might be the higher frequencies used by these researchers (20–206 kHz), which could contribute to a
larger population of cavitation bubbles releasing more radicals [39].

Fig. 4 illustrates the SCL photographs captured with and without silica particles. Luminol molecules reacted with -OH, producing bursts of blue lights whose intensity was associated with the cavitation intensity. For the homogeneous system (Fig. 4a), the bright areas, otherwise known as the “active zones”, were concentrated near the probe tip. The light intensity reduced with increasing distance from the probe tip due to acoustic pressure dissipation [40]. For the heterogeneous system (Fig. 4b), however, the active zones appeared across almost the entire selected area, and the light intensity was predominantly uniform (except for the periphery of the area).

The marked difference in the pattern of SCL emission in Fig. 4 demonstrates the significant role of silica particles in influencing sonochemistry. Additionally, it can be seen from Fig. 3 that large and small values of $\varphi_p$ could result in different phenomena related to the sonochemical activity in heterogeneous systems, and the variation in particle size also makes a difference. The critical $\varphi_p$, which is not a specific value but a range of values, depending on the particle characteristics, proves to be a paramount parameter. Two contrasting regimes, one enhancing sonochemical reactions and the other inhibiting, will be proposed, and discussed in detail in the following section.

4. Discussion

4.1. Effect of increase in nucleation sites

Nucleation in water, the first step in the formation of cavitation bubbles, is heterogeneous in most cases, rather than homogeneous. A typical example of preferential sites for heterogeneous nucleation, the “weak spots”, is the gas-filled micro-crivaces on the surfaces of the solid impurities or container walls [41]. Once silica particles are added into water, there will be an increase in the number of nucleation sites, thereby lowering the threshold for cavitation inception [42] and promoting the formation of cavitation bubbles (and thus -OH). This provides a logical explanation for the enhancement of the sonochemical reactions in the solid particle suspensions based on the kinetics of nucleation.

The most common quantitative model for nucleation kinetics is the classical nucleation theory (CNT) model, which was originally established by Volmer and Weber [43] nearly a century ago and is rooted in Gibbs’s thermodynamics. The CNT model predicts the rate of heterogeneous nucleation, $r_n$, using the following equation (Eq. (1)) [44]:

$$r_n = \rho Z \exp \left( -\frac{\Delta G^*}{k_B T} \right)$$

where $r_n$ is the number of nuclei formed in a unit sample volume per unit time; $\rho$ is the number density of sites for heterogeneous nucleation and is expressed in units of (number of sites)/(volume); $Z$ is the Zeldovich factor; $j$ is the rate at which molecules attach to the nuclei; $\Delta G^*$ is the energy barrier that governs nucleation at a surface, and $k_B T$ is the average thermal energy with $k_B$ the Boltzmann constant and $T$ the absolute temperature. The main difficulty in applying this theory lies in the lack of knowledge about the surface properties of every single particle, on which the nuclei form. Solid particles vary in size and structure; therefore, we would expect the nucleation sites to be distributed randomly and the nucleation barrier $\Delta G^*$ to vary between nucleation sites.

In the strictest sense, $r_n$ could be determined with a single nucleation site that can be tested using identical conditions many times or with identical sites located in separate sampling units. However, this is seldom achievable in practice [45]. Thus, it seems reasonable to make assumptions about the surface properties with respect to the probability distribution of the “effective” nucleation sites (i.e., sites where the nuclei formed can eventually evolve into active vapor bubbles). Given the monodispersity of the suspended silica particles in this work, we assumed that any part of the particle surface had an equal likelihood of containing an “effective” nucleation site. The site-specific nucleation rate (defined as $J_s = \rho_s / SA$), consequently, would remain unchanged; $SA$ is the total surface area of the solid particles in a unit volume of the suspension. That is, with a fixed $SA$, the number of nucleation sites remained constant. In addition, heterogeneous nucleation could be characterized by a single barrier height among the nucleation sites based on our assumption about the particle surface [44].

Upon replacing $\rho_s$ in Eq. (1) with the product of $J_s$ and $SA$, it can be assumed that the formation rate of the nuclei would be largely dependent on $SA$:

$$SA = SSA\frac{d\varphi_p}{dp} = f(\varphi_p, d_p)$$

where SSA is the surface-area-to-volume ratio defined as the total surface area per unit volume of solid particles (distinct from the specific surface area shown in Table 1). This ratio decreases as the particle size increases (without changing shape). $SA$, which is directly proportional to $\varphi_p$ and inversely proportional to $d_p$, appears to be an important indicator of the capability of the total suspended solids in a specified volume to increase nucleation sites. However, although both the 0.5-vol% suspensions of 10-μm particles and the 5-vol% suspensions of 100-μm particles had an identical $SA$ of $3 \times 10^3 \text{ m}^{-1}$, the former enhanced $I_3^-$ formation while the latter inhibited $I_3^-$ formation, compared with the particle-free scenario (Fig. 2d). In addition, for $\varphi_p = 0.5$ vol%, smaller silica particles contributed to less $I_3^-$ formation despite their higher $SA$ (Fig. 3a). Both pieces of evidence necessitate thorough investigation into the circumstances (especially the range of $\varphi_p$) required for enhancing sonochemical reactions by increasing the number of nucleation sites.

Wide discrepancies can be seen between high and low $\varphi_p$ for all four $d_p$ for the relationship between $\Delta r_t / r_0$ of $I_3^-$ and $SA$ of the silica particles (Fig. 5a). The relationship exhibits a strong positive correlation for the 0.05-0.2-vol% suspensions of the 10- and 20-μm particles, and the 0.05-0.5-vol% suspensions of the 50- and 100-μm particles. The key factor controlling $I_3^-$ formation could be the increase in the number of nucleation sites, which might lead to more collapsing bubbles and enhance sonochemical yields. The highest $\varphi_p$ for the large particles under this site-increasing regime is greater than that for the small particles. This implies that, with the increase in $\varphi_p$, the enhancing effect of the site-increasing regime on $I_3^-$ formation is offset and overridden by an inhibitory effect at an earlier stage for the smaller particles whose $SA$ values are higher. When $SA = 0.6 \times 10^3 \text{ m}^{-1}$, $\Delta r_t / r_0$ for the 10-, 20-, and 50-μm particles is approximately the same (8.6–9.3 %); however, for the 100-μm particles, it has already dropped to <2.0 %, indicating the important, but not decisive, role the site-increasing regime plays in influencing sonochemical activity. No significant correlations are apparent between $\Delta r_t / r_0$ and $SA$ under higher $\varphi_p$ conditions (i.e., $\varphi_p > 1$ vol%), and $\Delta r_t / r_0$ leans toward negative values as the $SA$ becomes larger. This phenomenon signifies the nullification of the enhancing effect produced by the growth of effective sites for heterogeneous nucleation.

Similar findings were reported by Barchouchi et al. [17], who investigated the role of glass beads (between 8–12 μm and 6 mm) on the $I_3^-$ production at 575 kHz. The researchers concluded that, with the increase in $SA$, the sonochemical activity first remained unchanged (i.e., $\Delta r_t / r_0 \approx 0$) and then markedly decreased after $SA$ exceeded a critical value, irrelevant of the particle size and the frequency. These results are interesting from a comparative point of view. First, the minimum value of the experimental $\varphi_p$ used by Barchouchi et al. [17] was 0.0061 vol%, which is much lower than the $\varphi_p$ used in the present study (0.05 vol%). Although the addition of glass beads could barely influence the sonochemistry under such low $\varphi_p$ conditions, the limited experimental data available in their study might have led to an inadvertent omission of the influence of the site-increasing regime. Second, their critical $SA$ and $\varphi_p$ were (0.02–0.06) $\times 10^3 \text{ m}^{-1}$ and 0.04 vol%, respectively, both lower
than those used in this study (1.0 × 10³ m⁻¹ and 0.6–1.3 vol%) This may be attributed to the higher frequencies utilized in their study. Third, their Δν/ν₀ did not correlate well with SA above the critical area value, which is similar to the data in Fig. 5(a).

The existence of the site-increasing regime is also sonochemically verifiable by the SCL photographs in Fig. 4. Unlike the concentrated active zones in the particle-free scenario (Fig. 4a), the presence of silica particles induced a uniform light intensity distribution (Fig. 4b), implying that cavitation occurred in a relatively uniform manner throughout the liquid. This SCL pattern resulted from the stirred suspension of silica particles (in violent unsteady-state motion), each having an approximately equal probability of offering sites for nucleation. This is generally consistent with the work of Son et al. [18], who detected peak intensities of SCL in particle-free systems but none upon the addition of 75-μm glass beads.

Apart from sonochemical methods, cavitation erosion (CE) detection is an alternative way of evaluating the intensity of ultrasonic cavitation [46] because the shock waves and micro-jets formed during the asymmetric scenario and the regime that determines sonochemical reactions in semi-dilute suspensions of solid particles. The inhibitory effect of particle addition on sonochemical activity will be analyzed in Section 4.2.

4.2. Effect of ultrasound attenuation

When ultrasound waves propagate through a lossy medium, there is always thermal consumption of energy due to viscous attenuation. For heterogeneous media, obstacles in the path such as rigid particles also scatter ultrasound waves in all directions, resulting in further dissipation of energy [51]. Therefore, if silica particles are added into an ultrasonic cavitation field in adequate quantities, there will be a reduction in the amplitude and intensity of ultrasound waves, thereby making it more difficult for cavitation inception to occur and cavitation bubbles (and -OH) to form. This offers a rational explanation for the inhibition of sonochemical reactions in suspensions of solid particles based on the acoustic of solid–liquid two-phase mixtures.

Two groups of theories have been principally developed to determine the relationship between acoustic properties (e.g., ultrasound speed and attenuation) and the characteristics of the heterogeneous system (e.g., particle size distribution and concentration). One is the scattering theory, including the model proposed by Epstein and Carhart [52] and Allegre and Hawley [53], in which only a simple superposition of the contribution of each particle was considered, and some “multiple scattering” revisions [54,55]. The other is the coupled phase theory (CPT) based on two-phase hydrodynamic equations, which inherently integrates “multiple scattering” [56]. The popular CPT model established by Atkinson and Kytömaa [57], which applies when wavelengths (72.5 mm herein) ≫ d₀, is adopted in this study. The model defines the imaginary part of a complex-valued wavenumber as the attenuation parameter in a more concise form elsewhere (Eq. (3)) [58]:

\[
\alpha \approx -\frac{\omega}{2} \sqrt{\left(\frac{\rho^p \Delta \rho}{\rho^p \rho^l}\right) - 1} \frac{A}{A^2 + (1-B)^2} = f(\phi_p, d_p) \tag{3}
\]

where ω is the angular frequency, κ and ρ denote the bulk modulus and density of either the solid particles (subscript p) or the liquid (subscript l), respectively; the quantities Φ, Ψ, and ρs are given by Φ⁻¹ = ψρψ⁻¹ + (1 - ψρ)κ⁻¹, Ψ = ψρψ + (1 - ψρ)ρs, and ρs = (1 - ψρ)ρψ + ψρρl, respectively; and the dimensionless parameters A and B are defined as (Eqs. (4) and (5)):

\[
A = \frac{9\rho_l\left(1 + 2\delta/d_p\right)\delta/d_p}{2\rho^p (1 - \phi_p)} \tag{4}
\]
Fig. 6. (a) 3D color map of the attenuation coefficient $|\alpha|$ covering the entire range of particle size and concentration ($\phi_p$) herein; and (b) its absolute value ($|\alpha|$) as a function of $\phi_p$ for various particle sizes ($\phi_p < 10$ vol%). The inset in Fig. 6(b) depicts $|\alpha|$ as a function of $\phi_p$ for the 10-µm particles ($\phi_p < \phi_m \approx 64$ vol%).
1.1 vol%, which is similar to the critical size might also lead to a regime shift, which was not observed in this investigation. It is, therefore, necessary to characterize the two regimes consistent to interact with cavitation bubbles but could increase the noise, while 500-μm particles decreased the cavitation noise levels. The authors explained that such large particles could barely remain suspended consistently to interact with cavitation bubbles but could increase the total number of nucleation sites. This implies that altering the particle size might also lead to a regime shift, which was not observed in this investigation. It is, therefore, necessary to characterize the two regimes with a wider range of \( d_p \) and \( \phi_p \) in future work.

Notably, the three outlier points above the dashed line in Fig. 5(a) were not discussed when addressing the two regimes because neither appears to have a decisive influence. These three cases signify the gradual transition from one regime into the other, i.e., the process of one regime offsetting or overriding the other, with the variation in \( \phi_p \). The two regimes are fundamental to elucidating the contradictory effects of the suspended solid particles on sonochemical activity.

5. Conclusions

Based on the sonochemical analysis conducted in silica microparticle suspensions, we proposed and examined two contrasting regimes, namely the site-increasing regime and the sound-damping regime, which are likely to control sonochemical reactions in heterogeneous systems. The summary of the key findings is as follows:

(a) With the increase in \( \phi_p \) from 0.05 to 10 vol%, the sonochemical yields initially increased gradually and then decreased suddenly. The overall effect of adding solid particles on the sonochemistry changed from being enhancing to inhibiting as \( \phi_p \) exceeded a critical value (~1 vol%). At a specific \( \phi_p \), the extent of the effect also differed between various \( d_p \) (10-100 μm). Smaller particles had stronger enhancing effects at low \( \phi_p \) or stronger inhibiting effects at high \( \phi_p \).

(b) The sonochemical yields in dilute suspensions were higher than those in the particle-free solutions due to the increase in the number of nucleation sites. Smaller particles in larger quantities contributed to even higher yields due to higher nucleation rates. According to the CNT model, the nucleation rate is directly proportional to the total particle surface area, to which the sonochemical yields correlated strongly. The uniform distribution of the light intensity in SCL images validates this site-increasing regime.

(c) Further addition of solid particles in the semi-dilute suspensions led to lower sonochemical yields than in the particle-free solutions because of the greater damping of the ultrasound by the scattering effect. The sonochemical yields correlated well with the attenuation, which increases with an increase in \( \phi_p \) and a decrease in \( d_p \) within our experimental range, according to the CPT model. This sound-damping regime can also be validated by analysis of the cavitation noise signals in heterogeneous media.

The results presented here describe the important roles that solid particles enact in sonochemical reactions and provide appropriate clarification regarding the influencing regimes. The new insights into these regimes and their transitions could prove useful in predicting sonochemical yields in solid–liquid two-phase flow systems, such as the sonochemical degradation of pollutants in solids-containing wastewater. Future work should focus on the validation of these regimes with a wider range of particle sizes, concentrations, and surface properties.

CRediT authorship contribution statement

Kunpeng Su: Conceptualization, Investigation, Formal analysis, Writing – original draft.
Jianhua Wu: Funding acquisition, Supervision.
Dingkang Xia: Visualization, Methodology, Data curation, Formal analysis, Writing – review & editing.
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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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