Molecular, Surface, and Continuum Issues in the Capture of Bacteria Particles by Solid Aerosols

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ABSTRACT

In this study, we develop the design parameters required to remove airborne biological particles by impact with scavenging aerosols. The conditions for capturing airborne biological particles for a head-on collision are determined as a function of each particle's mass, radius, incident velocity, and modulus of elasticity, the attractive or repulsive force between them, and the binding energy created during impact. Estimates of the radii of bacteria particles that can be captured are determined as a function of the material parameters, binding energy, and kinetic energy of the interacting particles. Surface chemistry approaches for creating desired scavenger materials are identified. Molecular simulations of the interaction between the scavenger and bacteria particles offer a cost-effective manner of computing such factors. Designing surface chemistry to strengthen the boundary interactions is crucial to maximizing scavenger capability. Weak van der Waals and pair-wise electrostatic interactions may not be sufficient to capture particles with an upper range of kinetic energy.

Keywords: bacteria, impact theory, scavenging, surface chemistry, van der Waals

1 INTRODUCTION

The purpose of the study is ultimately to delineate the limits of design parameters that would be required to scavenge the range of chemical and biological particles effectively. A likely mode of delivery for chemical or biological particles is an airborne cloud of micron-sized dry particulates (e.g., anthrax) or liquid aerosols (e.g., chemical or biological particles). One proposed response to such an attack is the rapid airborne deployment of a substance that effectively scavenges the chemical or biological particle and removes it from the atmosphere [1,2]. For the scavenger to be effective, it must stick to the particle upon collision. The conditions for sticking are determined by each particle's mass, radius, incident velocity, and modulus of elasticity, the attractive or repulsive force between the particles, the binding energy created during impact, and, to a lesser extent, the dissipation modes of the kinetic energy in an inelastic collision.

In this initial phase of the study, we outline the basic assumptions in the simplest order-of-magnitude analysis of the particle-scavenger interactions to determine the conditions for sticking during a head-on collision. In this paper, we describe the conditions for the worst-case scenario: the attractive force between the particles is short range and of minimal magnitude, there is a long-range repulsive force, and the particles have a significant kinetic energy for the atmospheric conditions. Both the particle and the scavenger are assumed to be spheres whose macroscopic interactions can be described by impact theory [3]. Long-range repulsive forces can arise from electrostatic interactions from particles with a significant net charge. At the microscopic level, the particle surfaces are assumed to consist of identical "atoms" spaced 3 Å apart. The surface interactions are then described in terms of van der Waals pair potentials between the surface layers of atoms on each macroscopic particle. The attractive force thus described represents a lower bound on the real surface chemistry.

This model provides a simplified framework in which more realistic treatment of the particles, their dynamics, and their surfaces can be readily developed. Extending the simulation to cover the range of particle aspect ratios, trajectories, and distribution of kinetic energy is straightforward mechanics. The key to optimizing the performance of scavenger particles, however, will be a more realistic description of the surface chemistry to maximize the sticking coefficient to biological particles while maintaining the ability to be dispersed readily.

2 AEROSOL CAPTURE WITH IMPACT

In this section, we develop the general physical and chemical principles for scavenging relatively small (1- to 5-μm radius) aerosols by larger (tens of micron radius) scavenger particles. This applies, for example, to removing a bacterial particle cloud created in the lower atmosphere by laying down a scavenger cloud on top of the bacterial cloud [1,2]. The scavenger particles, being much heavier, will fall to the ground relatively rapidly and will collide with many particles on the way down. The trick is to get these particles to stick together. Head-on collisions are assumed. We do not attempt to determine the effective capture cross section since such a determination requires the analysis of non-head-on collisions.

For treating the worst-case scenario, we assume the presence of a long-range repulsive force, such as that which can arise if the particles carry like-net-charges. At close range, the van der Waals attractive forces dominate. The range of attractive surface forces is tens of Angstroms and is quite small in comparison to the radii of the micron-size particles [4]. If r is the distance between the centers, the energy associated with bringing them together is $E_{\text{int}}(r)$. In this study, we assume the existence of a maximum value, $E_{\max}$, at the range $r_{\max} > R_1 + R_2$, associated with a repulsive force, and a minimum value, $E_{\min}$, which occurs essentially at the point of impact, $r_{\min} \cong R_1 + R_2$. These are shown in Figure 1. $E_{\text{int}}(r)$ depends on the radii of the interacting aerosols and the electro-chemical characteristics of their surfaces [4].

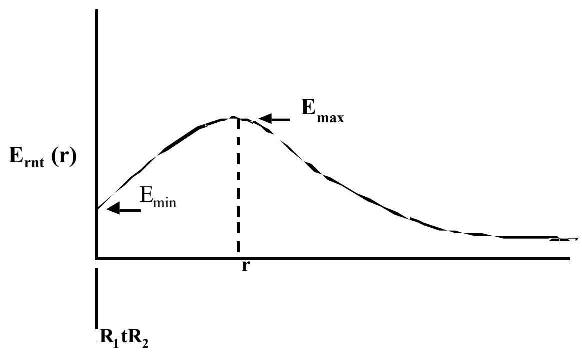

Figure 1: Energy Diagram Before Impact

The kinetic energy available for the collision is $K = \mu_r V_{rel,\infty}^2 / 2$, where $\mu_r = m_1 m_2 / (m_1 + m_2)$ is the reduced mass, m_1 and m_2 are the masses of the particles, and $V_{rel,\infty} = V_{1,\infty} + V_{2,\infty}$ is the relative velocity (assuming the particles are initially approaching one another). It is apparent that the first condition for sticking is that the kinetic energy available for a collision has to be greater than the maximum repulsive energy. We require

$$K = (\mu_r V_{rel,\infty}^2 / 2) > E_{\max} \quad (1)$$

When Eq. (1) is not satisfied, an elastic rebound will occur at $r > r_{\max}$ before the particles hit one another. When Eq. (1) is satisfied, the kinetic energy available for impact at $r_{\max}$ is reduced to $K - E_{\max}$. As the particles begin to approach each other, there is a gain in kinetic energy, $E_{\max} - E_{\min}$, between the distances $r_{\max}$ and $r_{\min}$. The kinetic energy available for impact is then $K - E_{\min}$. Solving the equations of motion for the interacting particles in the range $r_{\max}$ to $r_{\min}$ determines the velocities V_1 and V_2 at the point of impact. The relative velocity at impact, $V_{rel} = V_1 + V_2$, is less than $V_{rel,\infty}$ and is determined from the equation $(\mu_r V_{rel}^2 / 2) = K - E_{\min}$.

Reference 3 provides an analysis of the impact of two spheres when only elastic deformation is considered. Plastic deformation and other loss mechanisms are neglected. This provides a less optimistic basis for sticking because something less than the impact kinetic energy will be available for rebound. If the forces acting on the interacting particles are derived from energy-conserving potentials, capture will not occur. Irreversible energy-loss mechanisms are needed to ensure that the rebound kinetic energy after impact (i.e., when the particles just begin to disengage) is less that the kinetic energy available for impact, $K - E_{\min}$.

Let the rebound kinetic energy after impact be written as

$$K_b = K - E_{\min} - E_{loss} \quad (2)$$

The energy lost during the impact engagement is E_{loss} . For the smaller particle to be captured, it must not be able to get over the energy hump, $E_{\max} - E_{\min}$, on the way out. Capture will occur when $K_b < E_{\max} - E_{\min}$. By combining Eq. (2) and Eq. (1), we get the following condition for capture:

$$E_{\max} < K < E_{\max} + E_{loss} \quad (3)$$

Given that $K > E_{\max}$ (so that it satisfies the conditions that impact will occur), the range of kinetic energies available for capture is E_{loss} . This condition may pose serious limitations on scavenging in situations where the spread in kinetic energies is large and E_{loss} is small. For example, if ΔK is the natural spread in kinetic energy in the environment, the fraction of particles that will be scavenged, f_c , is approximated by $f_c \approx E_{loss} / \Delta K$.

Figure 2 shows the conditions during impact [3]. The particles close in on one another a distance, x . Under conditions normally considered for scavenging, we expect E_{loss} to be small because the kinetic energy available for the collision will be small. In this case, the compression will be small, resulting in minimal opportunity for energy losses because of plastic flow and other mechanical mechanisms.

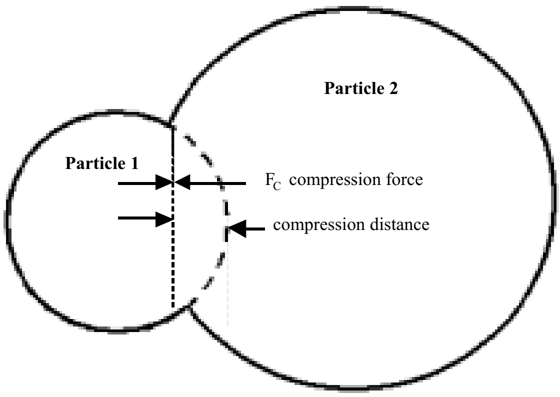

Figure 2: Interacting Particles During Impact

Without plastic flow and other mechanical loss mechanisms, such as vibrational dissipation of the kinetic energy, a complete rebound will occur. Therefore, for capture to occur, we must look for other than purely mechanical forces and/or create additional energy barriers.

Creating strong chemical bonds during the impact process would ensure capture (sticking). For our order-of-magnitude analysis of the weakest possible sticking coefficient, however, we treat the surface attractive forces as van der Waals pair potentials. Let E_{bind} be the total attractive energy created during the impact. Using Eq. (3) and equating E_{bind} with E_{loss} give the following condition for capture:

$$E_{\max} < K < E_{\max} + E_{bind} \tag{4}$$

We will derive an expression for E_{bind} based, in part, on the impact model in Reference 3. We briefly review the main features and equations of the model and express the results using our notation. The reader should refer to Reference 3 for the basic derivation.

The instantaneous compressive force, F_c, is related to the closing distance, α, via the equation

$$F_c = n\alpha^{3/2} \quad \text{(a)}, \qquad n = \frac{4S_{eff} R_{eff}^{1/2}}{3\pi} \quad \text{(b)} \tag{5}$$

In the foregoing expression, S_{eff} is the effective modulus of elasticity in tension and compression, and R_{eff} is the effective radius. They are defined by the following expressions:

$$\frac{1}{S_{eff}} = \frac{1-\nu_1^2}{\pi S_1} + \frac{1-\nu_2^2}{\pi S_2} \quad \text{(a)}, \qquad R_{eff} = \frac{R_1 R_2}{R_1 + R_2} \quad \text{(b)} \tag{6}$$

S_1 and S_2 are the respective values of the modulus of elasticity for each particle, and ν_1, ν_2 are the respective Poisson ratios. They are typically about 0.3.

The radius of the contact surface is $a_c = R_{eff}^{1/2}\alpha^{1/2}$, and the contact area, A_c is

$$A_c = \pi\, a_c^2 = \pi\, R_{eff}\,\alpha \tag{8}$$

The maximum depth of penetration, $\alpha_{\max}$, and one-way time to reach the maximum depth, τ, are

$$\alpha_{\max} = \left(\frac{5\mu_r V_{rel}^2}{4n}\right)^{2/5} \quad \text{(a)}, \qquad \tau = \frac{1.47\alpha_{\max}}{V_{rel}} \quad \text{(b)} \tag{9}$$

We assume that the number of binding sites, N_{bind}, created during the impact is proportional to the contact area. If N_b^a is the number of binding sites per unit area, we have

$$N_{bind} = N_b^a A_c \tag{10}$$

Let ε be the energy per binding site. The maximum binding energy, E_{bind}, occurs when $A_c = \pi R_{eff}\alpha_{\max}$.

$$E_{bind} = N_b^a \varepsilon\pi R_{eff}\alpha_{\max} = N_b^a \varepsilon\pi R_{eff}\left(\frac{5\mu_r V_{rel}^2}{4n}\right)^{2/5} \tag{11}$$

Using previous definitions, we get $E_{bind} = \beta(K - E_{\min})^{2/5}$, $\beta = 6.2 N_b^a \varepsilon R_{eff}^{4/5} S_{eff}^{-2/5}$, and the following condition for capture:

$$E_{\max} < K < E_{\max} + \beta(K - E_{\min})^{2/5} \tag{12}$$

The upper limit to the kinetic energy, K_u, at which capture will occur is determined from the equation

$$K_u = E_{\max} + \beta(K_u - E_{\min})^{2/5} \tag{13}$$

When β is very small, K_u is slightly larger than its lower limit of $E_{\max}$: $K_u' \cong E_{\max} + \beta(E_{\max} - E_{\min})^{2/5}$. For large β (more likely in the cases of practical interest), we neglect both $E_{\max}$ and $E_{\min}$ in comparison to K_u and arrive at the following upper limit for capture, denoted as K_u'':

$$K_u'' \cong \beta^{5/3} \tag{14}$$

3 NUMERICAL CONSIDERATIONS

In this section, we examine the range of parameters that satisfy the conditions of Eq. (14). The number of parameters is large, but we need to focus mostly on those that we can control and those that have a large impact on the radii of the bacteria aerosols that can be captured. We approximate those parameters that are not expected to change by more than a factor of two or three. The first step is to express Eq. (14) in terms of the basic parameters.

For our model, we assume that the scavenger is much larger than the bacteria and that both have approximately the same density, ρ . Eq. (5b) then gives $R_{eff} \cong R_1$. We also obtain $\mu_r = m_1 m_2 /(m_1 + m_2) \cong m_1 = \rho 4\pi R_1^3 / 3$. From our previous studies [1,2], we use a relative velocity, V_{rel} , of about 1 m/sec. Assuming that the bacteria density, ρ , is comparable to that of water ($\rho = 10^3 \, kg/m^3$) and expressing $R_1 = \hat{R} \times 10^{-6}$ in microns give the following expression for the kinetic energy, K_u'' :

$$K_u'' = \frac{\mu_r}{2} V_{rel}^2 = 2.1 \times 10^{-15} \hat{R}^3 \text{ Joules} \tag{15}$$

Assuming the binding sites are separated by a distance $d = 3$ Å, the number of binding sites per unit area, N_b^a , is given by the approximation

$$N_b^a \cong 1/d^2 = 1.1 \times 10^{19} \tag{16}$$

The binding energy per binding center (lattice particle), ε , is highly variable. For cases where the interaction between particles is dominated by electrostatic and van der Waals interactions, it can range from 0.4 kJ/mol to 10 kJ/mol. Since there are 6×10^{23} lattice particles per mol, ε can be written as $\varepsilon = \Delta \times 10^{-20}$ J, where Δ can range from 0.07 to 1.6.

The remaining factor we need to address is the effective modulus of compressibility, S_{eff} . If we assume that the materials are a factor of 2 to 3 more compressible than wood or plastic, we arrive at a value of $S_{eff} \approx 10^{10}$ N/m^2. Eq. (6a) shows that modulus of compressibility, S_{eff} , is controlled by the least compressible of the interacting particles. Being able to design a scavenger with lower compressibility will decrease S_{eff} if that becomes necessary.

Combining the previous factors, we get

$$\beta^{5/3} = 0.62 \Delta^{5/3} \hat{R}_1^{4/3} 10^{-15} \tag{17}$$

Inserting Eqs. (15) and (17) into Eq. (14) gives the maximum radius in microns for which capture can occur. The result is

$$\hat{R}_{1,\max} = 0.5\Delta \tag{18}$$

Using the largest value of $\Delta = 1.6$ appropriate for electrostatic and van der Waals interactions shows that the largest radius for capture will be about 1 µm. This may not be adequate for many applications. On the other hand, if the relative velocity is less than 1 m/sec and/or the effective modulus of compressibility is less than 10^{10} N/m^2, the maximum radius will be greater than a micron.

4 SURFACE CHEMISTRY CONSIDERATIONS

The numerical values obtained in the previous section were based on estimates of different parameters. Even though the results seem to be reasonable, it is clear that applying the model presented in this paper to realistic problems will require a more systematic approach in determining these factors. Molecular simulations of the interaction between the scavenger and bacteria particles offer a cost-effective manner for computing such factors. Although no results based on these simulations are shown in this paper, we briefly touch upon the main issues regarding the simulations and our plans for performing them in the near future.

The nature of the chemical functional groups present on the surface of the dry particulate or aerosol determines the strength of the attractive forces between neutral particles, and this strength can range over several orders of magnitude. Using molecular simulations, we propose to construct a series of model surfaces and calculate the attractive force per unit area as the chemical functional groups are varied through the range of polarity and possible bonding interactions. In an attempt to bracket the limiting behavior for each case, orientations of the groups on the surfaces will be varied to allow for maximum and minimum interactions.

An important question to address before performing molecular simulations is this: What is the chemical functionality on the surface of the biological particles that needs to be considered? Biological particles, such as bacteria and viruses, have complex outer coatings that enable them to attach to cell walls. The following facts regarding the nature of some biological particles are available:

- Through experiments in the aqueous phase (electrophoresis), we know these particles are negatively charged because of acidic sugars called sialic acids. From electrophoresis, it is possible to estimate the number of charged carboxylate groups per unit area.

- In the gas phase, particles will be neutral unless they are processed in a manner to be charged (e.g., using tribocharging or corona discharge techniques).

- In the case of weapons-grade anthrax, the potent airborne is treated with bentonite or silica to dry the surfaces and reduce particle adhesion. This enables the spores to be dispersed finely in air.

Another important question that needs to be addressed during the molecular simulations phase is related to the nature of the long-range and short-range forces. At large separations between the scavenger particles and the biological particles (more than tens of Angstroms), only long-range electrostatic forces between the particles have to be considered. The potential behaves (at first order) as $q_1 q_2 / r$ for net charges, q_i, on each particle and separation distance, r. It is clear that the relative contribution of electrostatic interactions depends on the charges of the interacting particles. Like-charges will lead to repulsive terms that might increase $E_{\max}$ (see Figure 1). Opposite charges could increase the attraction between the scavenger and the biological particles to such an extent that $E_{\max}$ could become zero or negative. In addition, it is quite possible that at least one of the particles is electrically neutral. In these cases, the interaction of higher moments (e.g., dipoles, quadrupoles, and so forth) with charges might be important.

Relevant to the correct simulation of the electrostatics of the system is the assignment of the maximum charge that might be imparted to a particle. Although there are instances where such assignment is not clear, electrophoresis experiments provide a valuable tool to achieve this task. As the particles approach each other, van der Waals interactions become significant. In these cases, the potential is proportional to r_s^{-6}, where r_s is the distance between individual particles on the surface. This step might require appropriate methodologies to obtain interaction parameters for van der Waals potentials based on sound quantum chemical simulations.

Bonding—if it occurs—is very strong. A chemical bond is 1 to 2 orders of magnitude stronger than a hydrogen bond, which is an order of magnitude stronger than a van der Waals interaction. A relatively accurate description of the bonding is critical and must be treated with accurate quantum chemical methods. In the end, a reasonable simulation of the interaction between scavengers and biological particles requires the treatment of the bonding, electrostatics, and van der Waals interactions, given that the energy of the system would most likely be the result of the energetics of a small number of chemical bonds, an intermediate number of electrostatic interactions, and a large number of van der Waals interactions.

5 CONCLUSION

Designing surface chemistry to strengthen the boundary interactions is crucial to maximizing scavenger capability. Weak van der Waals and pair-wise electrostatic interactions may not be sufficient to capture particles with an upper range of kinetic energy. Subsequent models for scavenging airborne bacteria will also include more precise values for the modulus of compressibility, relative velocity, provision for non-head-on collisions, and other-than-spherical shapes.

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