Abstract: On the basis of binary perfectly inelastic collision theory, the time evolutions of kinetic energy and surface area for a particle agglomerate system, due to Brownian motion, are investigated by using the Taylor series expansion technology. The asymptotic behaviors over a long time period show a significantly negative power function of time. The thermodynamic constraints of this system are then obtained according to the principle of maximum entropy, which establishes a relationship of inequality between the first three particle moments and some physical parameters (i.e., surface tension and temperature). In the thermodynamic equilibrium state, this function provides a new approach for estimating the effect of molecular structure on surface tension of liquid polymers.

Keywords: thermodynamic equilibrium; entropy criterion; Brownian agglomeration; moment method; asymptotic solutions; population balance equation

1. Introduction

Particle agglomeration is a common phenomenon in both nature and industrial applications, such as particle synthesis and soot formation processes. It plays a significant role in these aerosol processes by profoundly affecting the size distribution of a particle system [1], which strongly determines the physical properties of aerosol particles, such as light scattering, toxicity, deposition rate and diffusion. Nowadays with the escalation of fine particle pollution, the agglomeration processes are also widely used in the field of contamination control to improve removal efficiency, especially for the particles whose diameters are less than 2.5 μm [2,3]. The main principle is that through physical or chemical action, particles can coagulate with each other to form particles with larger particle size and then be removed efficiently. An appropriate approach for investigating the time evolution of particle size distribution (PSD) due to agglomeration is typically called the population balance equation (PBE) or the classic Smoluchowski equation (SE), which can be expressed as the following form [4]:

$$\frac{\partial n(v, t)}{\partial t} = \frac{1}{2} \int_0^v \beta(v_1, v - v_1)n(v_1, t)n(v - v_1, t)dv_1 - \int_0^\infty \beta(v_1, v)n(v, t)n(v_1, t)dv_1 \quad (1)$$

where \(n(v, t)\) is the number density function of the particles with volume from \(v\) to \(v + dv\) at time \(t\); \(\beta(v, v_1)\) is the collision frequency function between particles with volume \(v\) and \(v_1\).

Due to the strong non-linear integro-differential structure, the PBE is difficult to solve analytically. By trading off between accuracy and computational cost, three main numerical methods are proposed and developed, including the method of moments (MOM) [5,6], sectional method (SM) [7] and Monte Carlo method (MCM) [8]. It can’t be ignored that the analytical solutions show great merit in computational cost and direct physical insights.
into agglomeration mechanisms. Thus, some researchers focus on the asymptotic or analytical solutions of the moments of PSD by converting the original PBE to a system of ordinary differential equations (ODEs). Due to the complexity of its kernel function and the universality of Brownian motion, the study on the solution of the PBE for Brownian agglomeration is considered to be important but one of the most difficulties. Mainly using the log-normal method of moments (LG-MOM) [6] or the Taylor series expansion method of moments (TEMOM) [9], the asymptotic behavior of moments, due to Brownian coagulation (for spherical particles) and agglomeration (for agglomerates) over the entire particle size regimes [10–13], the analytical solution for Brownian coagulation in the free-molecule and the continuum regime [14], and so on, are obtained. These articles reveal that the geometric standard deviation will reach a constant for a long period of time, namely, the self-preserving size distribution theory [15].

Particle coalescence upon collisions subject to conservation of mass and momentum is called ballistic aggregation, but it is well known that the kinetic energy of this system decreases with time [16]. However, the loss of particle kinetic energy after collisions is rarely taken into account in the framework of PBE. Nowadays, with an assumption of a perfectly inelastic collision process, the rate of change for kinetic energy is correlated with that of particle number density, and the relationship of inequality between particle moments and some physical parameters (i.e., surface tension and temperature) for Brownian coagulation have been firstly proposed by Xie and Yu based on the principle of maximum entropy [17,18]. In this paper, we will extend their efforts to Brownian agglomeration, and the asymptotic behaviors of kinetic energy, surface area and entropy over a long period of time are obtained.

2. Theory and Model

2.1. Brownian Agglomeration

Particle agglomeration due to thermal motion is called Brownian agglomeration. Unlike spherical particles, agglomerates are not rigid structures and can be described as fractal morphology statistically. They are clusters of primary particles, which are ideally considered to be spherical with point contacts and uniform size. Considering the case of monodisperse primary particles, which form power law agglomerates, the Brownian agglomeration kernels $\beta$ are represented as [1]:

$$\beta_{FM} = B_1 (v_i^{-1} + v_j^{-1})^{1/2} \left( v_i^{1/D_f} + v_j^{1/D_f} \right)^2$$

$$\beta_{CR} = B_2 (v_i^{-1/D_f} + v_j^{-1/D_f}) \left( v_i^{1/D_f} + v_j^{-1/D_f} \right)$$

Here, the subscripts $FM$ and $CR$ stand for agglomeration in the free molecular and continuum regimes, respectively, the constants $B_1 = \left( \frac{6k_B T}{\mu \rho_p} \right)^{1/2} \left( \frac{3/4 \pi}{a_p^0} \right)^{1/2} \left( \frac{2 - 6/D_f}{D_f} \right)$, and $B_2 = 2k_B T/3\mu$, with $k_B$ the Boltzmann’s constant; $T$ is the temperature; $\mu$ is the gas viscosity; $\rho_p$ is the particle density; $a_p^0$ is the radius of a primary particle; $v$ is the particle volume; $D_f$ is called the fractal dimension, which can be related to the arrangement of the primary particles within an agglomerate. It should be noted that $D_f < 2$ is not applicable for Equation (2) in physics [1], thus the following discussions are limited to a range of $2 \leq D_f \leq 3$.

2.2. Taylor Series Expansion Method of Moments

With the definition of $k$-th order moment $M_k$,

$$M_k = \int_0^{\infty} v^k n(v) dv$$

Equation (1) can be converted into a system of original differential equations by multiplying both sides with $v^k$ and then integrating over all particle sizes:
where the coefficients \(a\) are:

\[
\begin{align*}
    a_1 &= D_f^4 - 24D_f^3 + 70D_f^2 - 48D_f + 16 \\
    a_2 &= 54D_f^3 - 144D_f^2 + 52D_f^2 + 96D_f - 32 \\
    a_3 &= 73D_f^4 + 168D_f^3 - 122D_f^2 - 48D_f + 16 \\
    b_1 &= 3D_f^4 + 16D_f^3 + 10D_f^2 - 16D_f - 16 \\
    b_2 &= 2D_f^4 - 96D_f^3 - 212D_f^2 + 32D_f + 32 \\
    b_3 &= -133D_f^4 + 80D_f^3 + 202D_f^2 - 16D_f - 16
\end{align*}
\]

2.3. Principle of Maximum Entropy

As a characteristic function composed of internal energy \(U\), total particle volume \(M_1\), and particle number \(M_0\), the rate of change for entropy \(S\) of a disperse system can be expressed as:
\[
\frac{dS}{dt} = \frac{dS}{dM_0} \frac{dM_0}{dt} + \frac{dS}{dU} \frac{dU}{dt} + \frac{dS}{dM_1} \frac{dM_1}{dt}
\] (11)

According to the thermodynamic analysis [18], the rate of change for \( S \) can be arranged and then correlated with that of \( M_0 \), the particle kinetic energy \( k_e \), and the particle specific surface area \( s \):

\[
\frac{dS}{dt} = -k_B \ln(M_0 \lambda_{th}^3) \frac{dM_0}{dt} + \frac{1}{T} \left( \frac{dk_e}{dt} + \gamma \frac{ds}{dt} \right)
\] (12)

in which \( \lambda_{th} \) is the thermal wavelength and \( \gamma \) is the surface tension. Thus, the focal point is to determine \( dk_e/dt \) and \( ds/dt \). With the assumption of simplified physical model according to the binary perfectly inelastic collision theory, the loss of particle kinetic energy after collision for two colliding particles and the whole system are [18]:

\[
\Delta k_e = -\frac{k_B T}{2} \left( 1 - \frac{2\sqrt{v_1 v_2}}{v_1 + v_2} \right) \leq 0 \] (13)

\[
\frac{dk_e}{dt} = -\frac{k_B T}{4} \int_0^\infty \int_0^\infty \left( 1 - \frac{2\sqrt{v_1 v_2}}{v_1 + v_2} \right) \beta(v_1, v_2) n(v_1, t) n(v_2, t) dv_1 dv_2 (14)
\]

Assuming that \( v_1 \) is the larger particle, the relative loss of \( k_e \) increases with a larger ratio of \( v_1 \) to \( v_2 \), which is illustrated in Figure 1. This shows that a wider range of PSD, namely, a larger \( M_C \), would lead to a more rapid reduction in \( k_e \). Substituting Equation (2) into the above equation and then using the Taylor series expansion technology, we can get the rate of change for kinetic energy in the free molecular regime:

\[
\frac{dk_e}{dt} \bigg|_{FM} = k_B T \left( \frac{x_1 M_C^2}{a_1 M_C^2 + a_2 M_C + a_3} + x_2 M_C + x_3 \right) \frac{dM_0}{dt}
\] (15)

in which \( x_1, x_2, x_3 \) are:

\[
x_1 = \left( D_f^4 - 12D_f^3 + 8D_f^2 \right)/2
\]

\[
x_2 = 15D_f^4 + 12D_f^3 - 8D_f^2
\]

\[
x_3 = \left( -31D_f^4 + 12D_f^3 + 8D_f^2 \right)/2
\] (16)

![Figure 1. The relationship between $|\Delta k_e/k_e|$ and $v_1/v_2$.](image)

As the structure of agglomerate is complex, modeling of its surface area is even more difficult, given the scarcity of experimental data. It is also very difficult to numerically determine which part of primary particles are the boundary particles and which part of
the surface of these boundary particles forms the agglomerate surface. For an ideal case that \( k \) primary particles agglomerate with point contacts, its surface area equals \( 4 \pi a_0^2 \), where \( a_0 \) is the radius of primary particle [20]. Obviously, it is more suitable for chain-like structures with \( D_f \rightarrow 1 \) but not compact aggregates with \( D_f \rightarrow 3 \). In a statistical sense, the collision radius of agglomerates composed of \( k \) monomer is [1]:

\[
r = Aa_0 \left( \frac{v}{v_0} \right)^{1/D_f} = Aa_0k^{1/D_f}
\]

where \( A \) is the dimensionless proportionality constant and can be assumed to be in unity to simplify calculations. In this paper, we will use this collision radius to calculate the surface area approximately:

\[
s = 4\pi r^2 = 4\pi k^{2/D_f} a_0^2 = B_3 v^{2/D_f}
\]

in which the constant \( B_3 = 4\pi (3/4\pi)^{2/D_f} a_0^{2-6/D_f} \). Thus, for chain-like structures with \( D_f = 2 \), \( s = 4\pi a_0^2 \) equals to that of an agglomerate without necking and for compact aggregates with \( D_f = 3 \), \( s = (36\pi)^{1/3} v^{2/3} \) equals to that of a spherical particle. Apparently, the agglomerates composed of the same number of primary particles with smaller \( D_f \) would have larger specific surface area and collision radius. Now the total surface area of this system can be expressed as:

\[
s = \int_0^\infty s_n(v,t)dv = B_3 M_{2/D_f}^2
\]

and the rate of change for \( s \) can be written as:

\[
\frac{ds}{dt} = B_3 \frac{dM_{2/D_f}}{dt}
\]

\[
\frac{ds}{sdt} = \frac{dM_{2/D_f}}{M_{2/D_f} dt}
\]

where the fractional moment \( M_{2/D_f} \) is approximated by using Equation (6):

\[
\frac{ds}{sdt} = \frac{dM_{2/D_f}}{M_{2/D_f} dt}
\]

and its derivative with time \( t \) can be achieved:

\[
\frac{dM_{2/D_f}}{dt} = \left( \frac{1 - 2/D_f}{D_f} \right) \frac{M_{1}}{M_{0}^{2/D_f}} \left[ \left( 1/D_f - 1 \right) (2M_C - 2 - D_f) \frac{dM_0}{dt} - \frac{M_2^2 dM_2}{M_0^2 dt} \right]
\]

Combining the first and third equations in Equation (7) gives:

\[
\left. \frac{dM_2}{dt} \right|_{FM} = \frac{2M_1^2 b_1 M_C^2 + b_2 M_C + b_3 dM_0}{M_0^2 a_1 M_C^2 + a_2 M_C + a_3} \frac{dt}{dt}
\]

Then Equation (23) can be rearranged as:

\[
\left. \frac{dM_{2/D_f}}{dt} \right|_{FM} = \left( \frac{1 - 2/D_f}{D_f} \right) \frac{M_{1}}{M_{0}^{2/D_f}} \left[ \left( 1/D_f - 1 \right) (2M_C - 2 - D_f) - \frac{2(b_1 M_C^2 + b_2 M_C + b_3)}{a_1 M_C^2 + a_2 M_C + a_3} \right] \frac{dM_0}{dt}
\]

Substituting the above equation into Equation (21), the rate of change for \( s \) in the free molecular regime has the following form:
\[ \frac{d\bar{s}}{dt} = \frac{(1 - \frac{2}{D_f}) \left[ (1/D_f - 1)(2\bar{M}_C - 2 - D_f) - \frac{2(\eta_1 \eta_2 \eta_3)}{\eta_1 \eta_2 \eta_3 \eta_4} \right]}{D_f + (2/D_f - 1)(M_C - 1)} \]  

Analogously, the rate of change for particle kinetic energy and surface area in the continuum regime can be calculated as:

\[ \frac{dk_C}{dt} = k_B T \frac{q_1 \bar{M}_C^2 + q_2 \bar{M}_C + q_3}{p_1 \bar{M}_C^2 + p_2 \bar{M}_C + p_3} \frac{d\bar{M}}{dt} \]

\[ \frac{d\bar{s}}{dt} = \frac{(1 - \frac{2}{D_f}) \left[ (1/D_f - 1)(2\bar{M}_C - 2 - D_f) + \frac{2}{M_C} \right]}{D_f + (2/D_f - 1)(M_C - 1)} \]

where \( q_1, q_2, q_3 \) are noted as:

\[ q_1 = (-9D_f^4 + 12D_f^2)/16 \]
\[ q_2 = (34D_f^4 - 24D_f^2)/16 \]
\[ q_3 = (-25D_f^4 + 12D_f^2)/16 \]

Finally, the rate of change for \( S \) can be found:

\[ \frac{dS}{dt} = \frac{1}{T} \left( -k_B T \ln(M_0 \lambda^3_{th}) + k_B T C_2 + \frac{\gamma_s}{M_0} C_1 \right) \frac{d\bar{M}}{dt} \]

in which \( C_1, C_2 \) are functions of the dimensionless moment \( M_C \) and fractal dimension \( D_f \):

\[ C_1|_{FM} = \frac{(1 - \frac{2}{D_f}) \left[ (1/D_f - 1)(2\bar{M}_C - 2 - D_f) - \frac{2(\eta_1 \eta_2 \eta_3)}{\eta_1 \eta_2 \eta_3 \eta_4} \right]}{D_f + (2/D_f - 1)(M_C - 1)} \]

\[ C_1|_{CR} = \frac{(1 - \frac{2}{D_f}) \left[ (1/D_f - 1)(2\bar{M}_C - 2 - D_f) + \frac{2}{M_C} \right]}{D_f + (2/D_f - 1)(M_C - 1)} \]

\[ C_2|_{FM} = \frac{\bar{M}_C^2}{\eta_1 \eta_2 \eta_3} + \frac{\bar{M}_C}{\eta_1 \eta_2 \eta_3} \]

\[ C_2|_{CR} = \frac{\bar{M}_C^2}{\eta_1 \eta_2 \eta_3} + \frac{\bar{M}_C}{\eta_1 \eta_2 \eta_3} \]

From the viewpoint of the second law of thermodynamics, the entropy of an isolated system will never decrease: \( dS/dt \geq 0 \). Moreover, the total particle number \( M_0 \) will decrease with time due to agglomeration: \( dM_0/dt < 0 \). Thus, the thermodynamics constraints for Brownian agglomeration at a certain temperature and pressure can be obtained:

\[ \frac{\gamma_s}{k_B T} \leq \frac{M_0 (\ln(M_0 \lambda^3_{th}) - C_2)}{C_1} \]

The equality would hold in the thermodynamic equilibrium state, and the critical time to reach this state can be determined. Moreover, the growth of the mean particle size \( M_1/M_0 \) will tend to a limit depending on the operating temperature and specific surface energy for thermal agglomeration technology.

3. Results

According to the self-preserving size distribution theory, the dimensionless particle moment \( M_C \) will tend to a constant at long time periods, and the asymptotic solutions of
processes based on the TEMOM model can be found [11]. Here, the results are listed in the Appendix A. In the free molecular regime, the asymptotic solution of kinetic energy can be solved by directly integrating Equation (15) with respect to t:

\[ k_e|_{FM} = C_3 + k_b TC_2 M_0 \rightarrow k_b TC_2 [\gamma_1 t]^{-\frac{2D_f}{\pi D_f - 4}} \]  

(36)

where \( C_3 = k_e(t_1) - k_e TC_2(t_1) M_0(t_1) \) is the integral constant, \( t_1 \) is the critical time in which the particle size distribution approaches self-preserving and the definition of \( \gamma_1 \) is shown as Equation (A7). In our previous work [21], a criterion to calculate this critical time has been given based on the asymptotic solution of \( M_0 \) in the continuum regime, which can also be available in the free molecular regime. Now the effect of primary particle size \( a_{p0} \) on \( k_e \) can be obtained, which is as the same as that on \( M_0 \):

\[ k_e|_{FM} \propto a_{p0}^{-\frac{12 - 4D_f}{30D_f - 4}} \]  

(37)

Thus, its relative dissipative rate becomes:

\[ \frac{d (k_e|_{FM})}{d t} = \frac{d M_0}{M_0 dt} = - \frac{2D_f}{3D_f - 4} \frac{1}{t} \]  

(38)

The asymptotic solution of surface area and the effect of primary particle size can be expressed as the following forms after substitution of Equations (A6) and (22) into Equation (19):

\[ s|_{FM} \rightarrow B_3 M_1^{2/D_f} \left[ 1 + \left( \frac{2/D_f - 1}{M_0 \pi / D_f} \right) [\gamma_1 t]^{-\frac{2D_f}{\pi D_f - 4}} \right] \]  

(39)

and its relative dissipative rate becomes:

\[ \frac{d s|_{FM}}{s dt} = \frac{D_f - 2}{D_f} \frac{d M_0}{M_0 dt} = - \frac{2D_f - 4}{3D_f - 4} \frac{1}{t} \]  

(41)

For simplification and without loss of generality, the calculation can be non-dimensionalized through the following relations: \( M_0^* = M_0 / M_{00}, \ M_1^* = M_1 / M_{00}, \ M_2^* = M_0 M_{20} / M_{00}, \ t^* = t B_1 M_0^{(3D_f - 4)/2D_f} M_1^{4(D_f - 2)/2D_f}, \ k_e^* = k_e / (M_0 k_b T), \ s^* = s M_{00}^{2/D_f - 1} M_0^{2D_f / 3} B_3. \) Then the Equation (7) coupling with Equations (15) and (19) can be solved numerically by means of fourth-order Runge–Kutta method with the initial dimensionless conditions set as \( M_0^* = 1, \ M_{10} = 1, \ M_{20} = 4/3, \ k_{e0} = 1/2 \) (the star symbol '*' is omitted thereafter). The numerical and asymptotic solutions of kinetic energy and surface area are shown in Figure 2. According to the principle of equipartition of energy, the agglomerates share the molecular thermal motion of the fluid and have the same initial kinetic energy, thus the dissipative rate of \( k_e \) strongly depends on the collision rate. The evolutions of kinetic energy with time show the larger descent at lower fractal dimension because of the larger collision radius, which result in a more rapid agglomerated rate [22]. Oppositely, the contacting surface between primary particles in an agglomerate with smaller fractal dimension is less than that in an agglomerate with larger fractal dimension, thus the decay of surface area shows the reverse trend in the dual role of the higher specific surface area and more rapid agglomerated rate.
For simplification and without loss of generality, the calculation can be non-dimensionalized through the following relations:

\[ M^*_0 = \frac{M_0}{M_{00}}, \quad M^*_1 = \frac{M_1}{M_{10}}, \quad M^*_2 = \frac{M_C}{M_{20}} \]

\[ t^* = \frac{t B_1 M_{00} (3D_f - 4)}{2D_f M_{10} (4 - D_f)} \]

\[ k^*_{e} = \frac{k_{e0}}{M_{00} k_b T} \]

\[ s^*_{d} = \frac{s_{d0}}{D_f - 1 - M_{20}^2 / D_f} \]

Then the Equation (7) coupling with Equations (15) and (19) can be solved numerically by means of fourth-order Runge–Kutta method with the initial dimensionless conditions set as

\[ M_{00} = 1, \quad M_{10} = 1, \quad M_{20} = 4/3, \quad k_{e0} = 1/2 \]

The numerical and asymptotic solutions of kinetic energy and surface area are shown in Figure 2. According to the principle of equipartition of energy, the agglomerates share the molecular thermal motion of the fluid and have the same initial kinetic energy, thus the dissipative rate of k_e strongly depends on the collision rate. The evolutions of kinetic energy with time show the larger descent at lower fractal dimension because of the larger collision radius, which result in a more rapid agglomerated rate [22]. Oppositely, the contacting surface between primary particles in an agglomerate with smaller fractal dimension is less than that in an agglomerate with larger fractal dimension, thus the decay of surface area shows the reverse trend in the dual role of the higher specific surface area and more rapid agglomerated rate.

\[ \text{(a)} \]

\[ \text{(b)} \]

Figure 2. The decay with time between numerical solutions and asymptotic solutions in the free molecular regime: (a) kinetic energy; (b) surface area.

Analogously, the asymptotic solutions of kinetic energy and surface area, as well as their relative dissipative rates, in the continuum regime can be expressed as:

\[ k_e \bigg|_{CR} \rightarrow k_b T C_2 M_0 = k_b T C_2 g_2^{-1} t^{-1} \]  

\[ \frac{dk_e}{k_e dt} \bigg|_{CR} = \frac{dM_0}{M_0 dt} = -t^{-1} \]

\[ s \bigg|_{CR} \rightarrow B_3 M_1^{2/D_f} \left[ 1 + \frac{(2/D_f - 1)(M_C - 1)}{D_f} \right] g_2 t^{2/D_f - 1} \]

\[ \frac{ds}{s dt} \bigg|_{CR} = \frac{D_f - 2}{D_f} \frac{dM_0}{M_0 dt} = -\frac{D_f - 2}{D_f} t^{-1} \]

where \( g_2 \) is a function of \( D_f \) showed as Equation (A12). The results are showed in Figure 3. These allow us to simplify the rate of change for \( S \) as the asymptotic form in both the free molecular and continuum regime:
\[ \frac{dS}{dt} = \frac{1}{T} \left( -k_B T M_0 \ln(M_0 \lambda_m^3) + k_c + \frac{D_f - 2}{D_f} \gamma_s \right) dM_0/M_0 dt \]  

And the corresponding thermodynamics constraints are:

\[ \frac{\gamma_s}{k_B T} \leq \frac{M_0 (\ln(M_0 \lambda_m^3) - C_2)}{1 - 2/D_f} \]  

Figure 3. The decay with time between numerical solutions and asymptotic solutions in the continuum regime: (a) kinetic energy; (b) surface area.

4. Discussion

The above equation establishes an inequality relationship between moments and some physical parameters, such as temperature and specific surface energy, and the equality holds if and only if the system reaches the thermodynamic equilibrium. Obviously, increasing temperature leads to decreasing particle number density and greater mean volume, which can be useful for dust collection efficiency. It also shows the effect of molecular structure on surface tension. By substituting the expression of surface area into this equation, we can get the following formula in the thermal equilibrium state:
For liquid pure substance, \( M_0 \lambda_{th}^3 \) usually takes the value as \( V_m \) in the free molecular regime and \( M_1 / M_0 = V_m / N_A \), where \( V_m \) is the molar volume and \( N_A \) is the Avogadro constant. A modification coefficient \( \gamma_{\infty} \), which is equal to the value of surface tension at infinite molar volume, should be introduced because the surface tension decreases almost linearly with the increase of temperature. Then a correction function of molar volume can be constructed:

\[
\gamma = \gamma_{\infty} - k_1 \frac{k_0 T}{V_m^{2/3}}
\]

where \( k_1 \) is a function of the temperature and fractal dimension:

\[
k_1 = \frac{\ln(V_m - C_2)}{V_m^{2/D_f - 2/3} B_3 \left(1 - 2/D_f\right)} \frac{N_A^{2/D_f} D_f}{D_f + (2/D_f - 1)(M_C - 1)} k_0 T
\]

The surface tension increases as molar volume increases and tends toward the constant \( \gamma_{\infty} \) at infinite molar volume, and it decreases monotonously with increasing temperature and tends to zero at the critical temperature. Unfortunately, it should be noted that some important factors, i.e., the effect of end groups, cannot be considered. It also can be written as the molecular weight-surface tension relationship with \( V_m = M/\rho \),

\[
\gamma = \gamma_{\infty} - k_2 \frac{k_0 T}{M^{2/3}}
\]

\[
k_2 = \frac{\ln(M/\rho - C_2)}{M^{2/D_f - 2/3} B_3 \left(1 - 2/D_f\right)} \frac{(\rho N_A)^{2/D_f} D_f}{D_f + (2/D_f - 1)(M_C - 1)} k_0 T
\]

where \( M \) is the molecular weight and \( \rho \) is the density. Some research shows that the correlation with molecular weight is better than that with molar volume for alkanes and perfluoro alkanes, but the discrepancy can be ignored for the siloxanes [23]. The effect of fractal dimension on the slope \( k_2 \) is illustrated in Figure 4 for n-alkanes at 0 °C, where \( a_0 = 0.2 \) nm is equal to the radius of methane and \( n \) is the number of carbons. Compared to bulks, the surface tension of molecules with long-chain structure generally increases due to the large contact areas and intermolecular forces, which leads to a small slope \( k_2 \). In the range of 2.7 to 2.8, the result is mostly close to the value \( k_2 = 360 \) of least-squares fitting based on experimental data [24].

Figure 4. The effect of fractal dimension on the slope \( k_2 \) for n-alkanes.
5. Conclusions

On the basis of the theory of maximum entropy and binary perfectly inelastic collision, the thermodynamic constraints of Brownian coagulation for spherical particles are extended to agglomerates, and a relationship of inequality between particle moments and some physical parameters is established using the TEMOM. Meanwhile, the evolutions of kinetic energy and surface area with time are presented, as well as their asymptotic behaviors. While some of our present simplifying assumptions will have to be relaxed, even our present results are of potential interest for a number of applications, for example, the estimation of surface tension of liquid polymers and the enhancement of dust collection efficiency.

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Appendix A. The Asymptotic Solutions of TEMOM Model for Brownian Agglomeration

The self-preserving size distribution theory implies that the dimensionless moment $M_C$ approaches a constant as time advances, thus we have:

$$\frac{dM_C}{dt} = \frac{M_2}{M_1^2} \frac{dM_0}{dt} + \frac{M_0}{M_1^2} \frac{dM_2}{dt} = 0 \quad (A1)$$

Substituting the first and the third equations of Equation (7) into Equation (A1) leads to a third-order algebraic equation of $M_C$ in the free molecular regime:

$$c_1 M_C^3 + c_2 M_C^2 + c_3 M_C + c_4 = 0 \quad (A2)$$

In which $c_1$, $c_2$, $c_3$ and $c_4$ are functions of $D_f$:

$$c_1 = a_1 = D_f^4 - 24D_f^3 + 70D_f^2 - 48D_f + 16$$
$$c_2 = a_2 + 2b_1 = 60D_f^4 - 112D_f^3 + 72D_f^2 + 64D_f - 64$$
$$c_3 = a_3 + 2b_2 = 77D_f^4 - 24D_f^3 - 546D_f^2 + 16D_f + 80$$
$$c_4 = 2b_3 = -266D_f^4 + 160D_f^3 + 404D_f^2 - 32D_f - 32 \quad (A3)$$

and for a given value of $D_f$, the solution of $M_C$, which is also an invariant constant, can be solved as [11]:

$$M_{C1}\big|_{FM} = \frac{1}{6c_1} \left( (d_1 + d_2)^{1/3} - \frac{4d_3}{(d_1 + d_2)^{1/3}} - 2c_2 \right)$$
$$M_{C2}\big|_{FM} = \frac{1}{12c_1} \left( -(d_1 + d_2)^{1/3} + \frac{4d_3}{(d_1 + d_2)^{1/3}} - 4c_2 \right)$$
$$M_{C3}\big|_{FM} = -\frac{c_3 + \sqrt{c_3^2 - 4c_2 c_4}}{2c_2} \quad (A4)$$

where $d_1$, $d_2$ and $d_3$ are:
\[ d_1 = 12c_1 \sqrt[3]{3(27c_1^2c_2^2 - 18c_1c_2c_3c_4 + 4c_1c_3^3 + 4c_2^3c_4 - c_2^2c_3^2)} \]
\[ d_2 = -108c_1^2c_4 + 36c_1c_2c_3 - 8c_2^3 \]
\[ d_3 = 3c_1c_3 - c_2^2 \]

(A5)

Then the asymptotic solution of \( M_0 \) can be obtained:

\[ M_0|_{FM} \rightarrow (g_1 t)^{-\frac{2D_f}{3D_f}} \]  
(A6)

where \( g_1 \) is a function of \( D_f \):

\[ g_1 = \sqrt{2}B_1(3D_f - 4)M_1^{\frac{4-D_f}{2D_f}}(a_1M_C^2 + a_2M_C + a_3) \]  
(A7)

And its relative agglomerate growth rate is:

\[ \frac{dM_0}{M_0dt}|_{FM} \rightarrow -\frac{2D_f}{3D_f - 4} \frac{1}{t} \]  
(A8)

Analogously, the asymptotic solution of \( M_C \) in the continuum regime is:

\[ M_C|_{CR} = 2 \]  
(A9)

And the asymptotic solution of \( M_0 \) and its relative growth rate are:

\[ M_0|_{CR} \rightarrow (g_2 t)^{-1} \]  
(A10)

\[ \frac{dM_0}{M_0dt}|_{CR} \rightarrow -\frac{1}{t} \]  
(A11)

where \( g_2 \) is a function of \( D_f \):

\[ g_2 = \frac{B_2(1 + 3D_f + 8D_f^2)}{4D_f^4} \]  
(A12)

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