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Thermodynamic analysis of Brownian coagulation based on moment method

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ABSTRACT

In this article, the thermodynamic constraints of Brownian coagulation are proposed based on the binary perfectly inelastic collision theory and the principle of maximum entropy. The constraints can be expressed as inequalities with the Taylor series expansion method of moments. The inequalities establish the relationship between the physical parameters (such as temperature and specific surface energy) and the first three integral moments of particles. The inequalities are verified to determine the critical time for Brownian coagulation to reach the thermodynamic equilibrium. The critical time is proportional to the specific surface energy and inversely related to the temperature, which can be used to determine whether the particle size distribution reaches self-preserving form. Moreover, the critical states provide a new approach for detecting the particle specific surface energy with the moment method. The results further explain Brownian coagulation and offer opportunities to improve environmental quality from the viewpoint of thermodynamics.

1. Introduction

The aggregation kinetics of particles suspended in fluid determines the aggregate size distribution. It is of fundamental interest in aerosol science and has vital implications for areas such as powder technology and controlling air pollution [1]. The collision process among coalescing spherical particles due to random motion is called Brownian coagulation. Brownian coagulation is usually predominant in colloidal particles.

The kinetics of Brownian coagulation is described based on either the Smoluchowski approach or the population balance equation (PBE). In terms of continuous variables, the PBE for Brownian coagulation among particles is written as [1]

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

in which $n(v, t)dv$ is the number of particles per unit of spatial volume with a particle volume from v to $v + dv$ at time t, and β is the collision frequency function of Brownian coagulation.

A particle system is unstable with respect to coagulation. Particle collision and coagulation decrease the total number of particles and increase the average particle size. The asymptotic solution of the PBE reveals that the particle size distribution approaches the self-preserving size distribution (SPSD) after long periods [1]. According to the rule of statistical physics [2], Shannon information entropy is interpreted as a state function of a thermodynamic system and is proportional to the total number of particles. Therefore, a reduction in the total number of particles corresponds to a reduction in the information entropy of a particle system, which must be accompanied by a change of system energy in a dissipative system in accordance with the second law of thermodynamics.

In the classical theory of coagulation, coalescence occurs instantaneously after two particles collide and a new sphere forms [3]. In this theory, the time scale of the collision of two particles is far smaller than the time scale of particle number evolution. Furthermore, collided particles such as aerosols in the air and droplets in clouds need very little time to become spherical. Therefore, Brownian coagulation can be considered a perfectly inelastic collision process because kinetic energy is not conserved due to the action of internal friction. Kinetic energy is usually exchanged between the particles' translational motion and the internal degrees of freedom with each collision. In a perfectly inelastic collision, the colliding particles stick together and the maximum amount of kinetic energy of the system is lost. Concurrently, the particle specific

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Nomenclature

B_1	coefficient of collision kernel function in free-molecule regime
B_2	coefficient of collision kernel function in continuum regime
C	the constant
k_e	particle kinetic energy
k_B	Boltzmann constant
k	real number
M_k	k-th order moment
M_C	dimensionless particle moment
M_0	zero-th moment, which is the total particle number density
M_1	first moment
M_2	second moment
m	mass of particle
N_A	Avogadro constant
n	particle number density
S	entropy of particulate system
s	particle specific surface area
T	fluid temperature
T_C	critical temperature
t	time variant
U	internal energy of particle system
u	particle velocity
V	total volume of particles
V_m	molar volume of liquid pure substance
υ	particle volume

Greek letters

β	collision frequency
σ	particle specific surface energy
μ	gas viscosity
ρ_p	particle density
λ_{th}	thermal wavelength
$\hbar$	Planck constant
κ	the ratio coefficient

Abbreviations

CR	continuum regime
FM	free-molecule regime
LHS	left hand side
PBE	population balance equation
RHS	right-hand side
SPSD	self-preserving size distribution
TEMOM	Taylor series expansion method of moments

surface area of the system decreases with an increase in the average particle volume. A reduction in the particle specific surface area corresponds to a reduction in the surface free energy under conditions of constant temperature and pressure [1].

In the present study, the rates of change for particle specific surface area, particle kinetic energy, chemical potential, and entropy are analyzed based on the binary perfectly inelastic collision theory and the moment method for Brownian coagulation from the perspective of the kinematics and dynamics of a dissipative system. Based on the principle of maximum entropy and the second law of thermodynamics, the physical constraints of Brownian coagulation are quantitatively proposed in the form of inequalities, which can be regarded as an adjoint equation of the PBE.

2. Theory

2.1. Binary perfectly inelastic collision theory

Particles are assumed to be spherical. When two particles collide, they coalesce instantaneously to form a third one whose volume is equal to the sum of the original two. This assumption applies to processes in which the collisional time scale of two particles is far smaller than the time scale of the evolution of particle number of the whole system. According to the simplified physical model for the binary perfectly inelastic collision theory, perfectly inelastic collisions must obey the conservation of mass and momentum.

For mass conservation, the mass of combined particles can be written as

$$m = m_1 + m_2 \tag{2}$$

where m is the mass of a particle. If the particle density is homogenous as ρ_p, then

$$\upsilon = \upsilon_1 + \upsilon_2 \tag{3}$$

where υ is the volume of combined particles with volume υ_1 and υ_2. For momentum conservation, it is

$$mu = m_1u_1 + m_2u_2 \tag{4}$$

where u is the velocity of particles due to Brownian motion. The loss of particle kinetic energy after collision can be expressed as

$$\Delta k_e = \frac{1}{2}mu^2 - \left(\frac{1}{2}m_1u_1^2 + \frac{1}{2}m_2u_2^2\right) = -\frac{1}{2}\frac{m_1m_2}{m_1+m_2}(u_1-u_2)^2 \leqslant 0 \tag{5}$$

where k_e represents the kinetic energy. The reduction in particle surface area after collision is

$$\Delta s = (36\pi)^{1/3}\left[(\upsilon_1+\upsilon_2)^{2/3} - \upsilon_1^{2/3} - \upsilon_2^{2/3}\right] \tag{6}$$

where s represents particle specific surface area. By integrating it for all particle sizes, the rate of change for kinetic energy can be expressed as

$$\frac{dk_e}{dt} = \int_0^\infty \int_0^\infty \Delta k_e \beta(\upsilon_1,\upsilon_2) n_1(\upsilon_1) n_2(\upsilon_2) d\upsilon_1 d\upsilon_2 \tag{7}$$

where $\beta(\upsilon_1, \upsilon_2)$ is the coagulation kernel for two particles with volume υ_1 and υ_2. Because the particles share the molecular thermal motion of the fluid at a certain temperature and pressure, the principle of equipartition of energy is assumed to apply to the translational energy of the particles [1]; that is

$$u^2 = \frac{k_BT}{m} \tag{8}$$

in which k_B is the Boltzmann constant, and T is the temperature. Then, the rate of change for particle kinetic energy can be written as

$$\frac{dk_e}{dt} = -\frac{k_BT}{2}\int_0^\infty \int_0^\infty \left(1 - 2\frac{\sqrt{\upsilon_1\upsilon_2}}{\upsilon_1+\upsilon_2}\right)\beta(\upsilon_1,\upsilon_2) n_1(\upsilon_1) n_2(\upsilon_2) d\upsilon_1 d\upsilon_2 \tag{9}$$

and the rate of change for particle specific surface area can be obtained as

$$\frac{ds}{dt} = \int_0^\infty \int_0^\infty \Delta s \beta(\upsilon_1,\upsilon_2) n_1(\upsilon_1) n_2(\upsilon_2) d\upsilon_1 d\upsilon_2 \tag{10}$$