Trajectory calculation of a trapped particle in electrodynamic balance for study of chemical reaction of aerosol particles

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Abstract. Electrodynamic balance (EDB) is a powerful tool for investigating the chemical reactions between a fine particle and gaseous species. But the EDB device alone is inadequate to match the rapid weight change of a fine particle caused by chemical reactions, because it takes a few seconds to set a fine particle at null point. The particle trajectory calculation for the trapped particle added to the EDB is thus a very useful tool for the measurement of the transient response of a particle weight change with no need to adjust the applied DC voltage to set the null point. The purpose of this study is to develop the trajectory calculation method to track the particle oscillation pattern in the EDB and examine the possibility for kinetic studies on the reaction of a single aerosol particle with gaseous species. The results demonstrated the feasibility of applying particle trajectory calculation to realize the research purpose.

1. Introduction

The importance of reactions of a fine particle with gaseous species has been growing in many fields of atmospheric chemistry, combustion, pollution control and material processing during the past decades. The property of the very high surface-to-volume ratios of fine particles is making them readily serve as centres for heterogeneous reactions. Main approaches for heterogeneous reaction of aerosol particles are based on thermo-gravimetric analysis (TGA), drop tube apparatus and fluidized bed reactors. These methods are well developed and provide data over a wide range of experimental conditions. Electrodynamic balance (EDB) is also one of the well established techniques for studying the chemical reactions of a single aerosol particle [1]. EDB is an experimental device for levitating the charged particle in space using electric potential in which DC electric field was used to balance the gravitational force on a charged particle. Hence it is considered to be non-contact type microbalance equipment with great precision for convenience.

The advantages of reaction experiments using EDB device over the conventional approaches of gravimetric measurement using bulk solutions [2] are as follows: 1) the weight change in a particle reactions can be monitored continuously, thus providing unambiguous in situ characterization of them.

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2) The chemical reactions of fine particles can be investigated under well-defined surrounding conditions. 3) A single levitated particle can be investigated over long time periods to have a quantitative understanding of the reaction at an equilibrium state. 4) Supersaturated droplets can be studied since heterogeneous nucleation is suppressed when a droplet is levitated without contacting any foreign surface. 5) The contribution of mass transfer to overall reaction kinetics can be easily estimated and the time scale of mass transfer inside and outside of droplet can be sufficiently short.

However, EDB device is disadvantageous in that it is inadequate for investigation on the relative fast chemical reactions of gaseous species because it takes several seconds to adjust the particle at null point, where the dc field is balanced the gravitational force on a charged particle, by changing the applied DC voltage. Therefore this DC voltage adjustment cannot follow the rapid increase in the particle weight by the chemical reaction (of order few sec).

The AC electric field imposes no net force on a particle when it is stabilized at the null-point, but in the neighbourhood of the null-point, there are the axial components of the AC field which are proportional to the distance from the null-point. Thus, if any particle is positioned away from the null-point, it oscillates by time-dependent forces in the AC field. This oscillation makes it possible to determine the change of the particle weight by following its trajectory.

Maloney et al. [3] generated a step change of DC voltage to obtain the resulting transient response of a particle from an initial steady state using a two dimensional diode array which provides particle position along the EDB centres axis. Then they determined the particle weight by adjusting iteratively to find agreement between measured trajectories and calculated results by a particle dynamic model (PDM), where PDM was a force balance simulation which consisted of electric field forces, gravitational forces, and drag forces acting on a particle. As the gravity is not compensated completely, the resulting oscillatory trajectory is phase lagged with respect to the driving AC field of the EDB, and the phase lag depends only on the drag parameter, particle weight and the AC frequency. Göbel et al. [4] investigated the use of phase lag measurements to size droplets in a four-ring EDB, reporting an uncertainty of less than 6% in the size determination.

Zheng et al. [5] compared four methods for determining the size of particles based on particle oscillation in EDB. The examined methods were: 1) spring point measurements, which corresponds to a sudden large-amplitude oscillation of a levitated particle when the AC electric field is changed to cause the particle to move from a stable to an unstable region based on stability theory for the differential equation of particle motion in EDB. 2) phase lag measurements mentioned above, 3) measurements of the amplitude of the oscillation of an unbalanced particle, and 4) the particle shift from null point as it oscillates due to an unbalance vertical forces. All methods were shown to be in good agreement for spheres (within 3.9%). For non-spherical germanium dioxide particles, the three oscillation methods agreed with the spring point method within 3.4%.

The particle oscillation methods are very useful for a weight measurement of transient response of a particle because adjustment of applied DC voltage for maintaining it at null point in EDB is not necessary. This article describes a development of the gravimetric analysis of the fast heterogeneous reaction of a particle from its oscillation in EDB device. A CCD video camera was used to measure the amplitude of the particle oscillations and numerical calculation of the differential equation of particle motion was performed by adjusting the change of a particle weight to be close agreement with the oscillation patterns of the particle into EDB.

2. Trajectory Calculation Method

The dynamics of the EDB make it possible to determine the particle weight by following particle trajectories. There are two issues that need to be considered when levitated particle is examined. The first is the calculation of an oscillating motion of particle in EDB, and the second concerns the conditions that need to maintain a particle in a stationary state at the null point of the balance [1]. To answer these issues the electric fields inside EDB that affect the particle motions must be determined first and then the differential equation of particle motion must be solved. Assuming that there are no other vertical forces on the particle, a vertical force balance on the levitated particle at null point yields
\[ mg = qE_{DC} \]  

where \( m \) is the particle’s weight (kg), \( g \) is gravitational acceleration (m \( \cdot \) s\(^{-2} \)), \( q \) is charge on the particle (C) and \( E_{DC} \) is the DC electric field required to levitate the particle at null point without oscillation (V \( \cdot \) m\(^{-1} \)). For constant charge \( q \), the voltage required to levitate the particle is proportional to its weight. This is the basis for using the device as an analytical balance for micro particles.

When gravity is not compensated completely by the DC electric field due to the particle weight change, a levitated particle starts to oscillate in the vertical direction. As there is no particle motion in the horizontal direction, it is sufficient to know the vertical component of the equation of particle motion. Therefore the dynamics of an oscillating particle trapped in an EDB is governed by the drag force, gravity force, and electrostatic force. The force balance yields

\[
m \frac{d^2z}{dt^2} = -mg - 3\pi \eta \frac{dp}{d} \frac{dz}{dt} + qE(t,z) 
\]

where \( z \) is the position of the particle with respect to the centre of the balance (m), \( m \) is the weight of single aerosol particle (kg), \( \eta \) is gas viscosity (kg \( \cdot \) (m \( \cdot \) s\(^{-1} \))), \( dp \) is diameter of single aerosol particle (m), and \( E(t,z) \) is vertical electric field strength at the position of a particle (V \( \cdot \) m\(^{-1} \)) [6]. The aerodynamic drag force was defined for sphere in the Stokes’ regime in second term of right side in equation (2). Stokes’ law for a sphere particle is valid up to Reynolds number (\( Re \)) of about 0.1. In our experiments, the \( Re \) reached a maximum value of 0.17 for a brief period but was well within the Stokes’ regime for most of the particle oscillation. Electric field represents the sum of applied AC and DC electric fields (V \( \cdot \) m\(^{-1} \)) as follows:

\[
E(t,z) = E_{AC}(t,z) + E_{DC}(z)
\]

The main problem is the computation of the electric potential distribution inside EDB, which was necessary for the calculations of electric field (\( E_{DC}(z) \) and \( E_{AC}(t,z) \)) strength along the central z-axis. For Cartesian coordinate system, the electric potential is determined from the solution of Laplace equation (4) together with appropriate boundary condition.

\[
\nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0
\]

where \( V \) is electric potential (V) and \( x, y, z \) are Cartesian coordinates (m). The cross section geometry of the double cylindrical tube type EDB used in our experiment was showed in figure 1. This EDB consisted of three stainless cylinders with a coaxial line. An AC high voltage applied to outer cylindrical electrode for stabilization of a particle at centre point (null point) into EDB device, while a DC voltage difference between the inner cylindrical electrodes controls the vertical position of the particle to compensate gravity force on the particle. This vertical z-axis defined the direction of gravity. For cylindrical coordinate with axial symmetry, equation (3) can be easily transform to

\[
\frac{\partial}{\partial r} \left( r \frac{\partial V(r,z)}{\partial r} \right) + r \frac{\partial^2 V(r,z)}{\partial z^2} = 0
\]

where \( r \) is radial coordinate [m]. Boundary conditions of voltage inside EDB were:

\[
\frac{\partial V(0,z)}{\partial r} = 0 \quad \text{(bounded)}
\]
And the potentials are constants over the AC and DC electrode surfaces as shown in figure 2. The boundary value problem can be solved using the Matlab PDE toolbox (The Mathworks Inc.) with finite element method. A contour plot of the equi-potential lines in the EDB as a function of $r$ and $z$ was shown in figure 3, where the origin is at the centre of the balance (null point) and AC peak to peak voltage is 300 V and DC is ±20 V. Grey two rectangles and orange one correspond to the double cylindrical DC electrodes and AC electrode, respectively. It is found that AC potential reached to the centre axis through the gap between the inner cylindrical DC electrodes. In order to calculate the dynamics of a $z$-axis oscillating particle trapped in an EDB, the only electric potential along the centre $z$-axis was necessary.

Figure 1. A cross section of the double cylindrical EDB.

Figure 2. Boundary conditions for electric field calculation inside EDB.

Figure 3. A counter plot of equi-potential lines inside EDB

(-$V_{DC}$: −20V, $V_{DC}$: 20V, $V_{AC}$ pk-pk: 300V).

Figure 4 (a) and (b) show the AC and DC electric potential curves alone the centre $z$-axis respectively, which are extracted from two dimensionally calculated results for potentials of AC peak to peak 300V and DC ±20 V.
As particle trajectory calculation requires a huge number of potential calculations, the approximation equations for a time function \( V_{AC}(t,z) \) and \( V_{DC}(z) \) were derived respectively. A vertical AC electric potential was expressed as Gaussian’s equation (8).

\[
V_{AC}(t,z) = 0.0797 \times V_{AC,pk-pk} \sin(2\pi ft) \cdot \exp\left(-\frac{z^2}{(1.20\times z_{half})^2}\right)
\]

where \( V_{AC,pk-pk} \) is the applied AC peak to peak voltage (V), \( f \) is the frequency of AC voltage (Hz) and \( z_{half} \) is the half value width (m) of the Gaussian distribution curve as shown in figure 4 (a). 0.0797 is a geometric constant which is a function of the specific EDB electrode geometry. The approximation of DC potential curve in figure 4 (b) took the polynomial equation as,

\[
V_{DC}(z) = V_{DC} \times (3.0 \times 10^6 z^3 + 4.25 z^2 - 2.4 \times 10^2 z + 1.42 \times 10^{-5})
\]

where \( V_{DC} \) is the applied DC voltage to electrodes (V) and \( z \) is the distance (m) from null point along with the centre axis of the balance. Therefore the vertical component of electric field is given by the following equation (10).

\[
E(t,z) = E_{AC}(t,z) + E_{DC}(z) = -\nabla(V_{AC}(t,z) + V_{DC}(z)) = \frac{dV_{AC}(t,z)}{dz} + \frac{V_{DC}(z)}{dz}
\]

Figure 5 shows one cycle of the calculated time variation of electric field along z-axis from equation (10). Electric field changes alternately across the null point with time.

Over a small distance from the null point in EDB in figure 4 (b), the DC electric fields can be approximated by

\[
E_{DC} = C_0 \frac{V_{DC}}{Z_0}
\]

where \( C_0 \) is a geometric constant which is a function of the specific EDB electrode geometry. \( C_0 \) for EDB employed in the present study was determined a value of 0.72 by comparing calculated results in figure 4 (b) with equation (11). Numerically, this value is slightly smaller than either that for the flat electrode configuration \( (C_0=1) \) or for the bihyperboloidal system \( (C_0=0.8) \) [1, 7]. In our EDB a higher...
DC voltage must be applied to the electrodes to achieve the same DC field strength as that of bihyperboloidal EDB.

![Figure 5. The calculated time variation of electric field along z-axis.](image)

### 3. Experimental Setup

The coaxial double cylindrical type EDB was used as shown in figure 1. An AC high voltage (Trek: 610C) applied to outer cylindrical electrode for stabilization of a particle at centre point (null point) into EDB device, while a DC voltage difference between the inner cylindrical electrodes controls the vertical position of the particle to compensate gravity force on the particle. The DC voltage was supplied up to 500 V and the typical amplitude of AC field used to drive EDB is about 9-10 kV within the frequency range from 50 Hz to 500 Hz.

The EDB device was placed inside a stainless chamber with equipped with the flexible silicone rubber heaters that can maintain the chamber temperature at about 300 K. A microscope focused on the centre of the EDB was used for visual observation of particle trajectories and their morphologies. Stroboscope was mounted at the opposite side for illuminating the necessary part. A CCD video camera (Sony DCR-TRV70) was equipped with microscope to measure the amplitude of the particle oscillations.

### 4. Comparison of Particle Trajectory Calculations with Experimental Results

Once the calculation method was determined for the electric field, the trajectory of the particle could be easily obtained by solving the ordinary differential equation (2). The calculation procedure was shown in figure 6. First we calculated the electric field in EDB by the given initial condition $V_{AC, pk-pk}$, $V_{DC}$ and frequency. Next we informed the particle initial condition such as mass, charge, particle diameter and the initial position and velocity of the particle and ran the program for solving the equation of motion. Finally the calculated trajectories of a particle were displayed on the computer. The Runge-Kutta algorithm for Matlab and Euler algorithm for LabView (National Instruments) were used to calculate numerical solutions. Because the program using Labview is a real time simulator of particle motion, the Euler method was suitable for iteration calculations in order to determination of particle weight by adjusting the fitting parameter to agree between the calculated particle trajectory and the observed amplitude of oscillating particle. These methods enable us to simulate particle trajectories along z-axis for arbitrary initial particle positions and velocities without any approximation.
The EDB levitation experiments were done for a soda lime-silicate glass particle with a 60 μm diameter (GBL-60, JIS Z 8901) of known density (ρ=2.3 g · cm⁻³). The particle diameter was measured using a high resolution CCD video camera and the particle charge value was determined from equation (1) and the measured value of DC voltage at null point. In order to check the availability of our particle trajectory calculations, the particle oscillation amplitudes were acquired on the video camera for a step change of DC voltage from that at null point. This caused the particle to move to an unbalanced condition where it oscillated with the frequency of the AC electric field. Calculated particle trajectory and oscillating particle photograph, which were obtained by changing from DC 29 V at null point to 19.1 V suddenly, are shown in figure 7. As gravity is not compensated completely by the change of the DC electric field, a levitated particle started to be oscillates in the vertical direction. With increasing distance from the null point, the oscillation amplitude increases linearly due to the $z$ dependence of $E_{AC}(t,z)$. As the Ar ion laser irradiated downward on the transparent particle at null point, two bright glare points can be recognized on top and bottom of the particle. One of them is due to reflected light, the other one is due to refracted light. These points seem to be the bright straight line in the case of oscillating particle as shown on photograph in figure 7 because the particle moves back and forth for several times on one video frame. Therefore the oscillation amplitude could be obtained from distance of this line.

Although the oscillation pattern on photograph agrees with the general trend of the particle trajectory calculation, there are quantitative differences between calculated and experimental results. Oscillation pattern is characterized by two parameter, offset and amplitude. There were some discrepancies of offset and amplitude between calculated results and experimental data. This was considered to be existence of 4 holes drilled through the AC electrodes for optical and observation ports or unreasonable boundary conditions between DC and AC electrodes for the electric potential calculation using Matlab PDE tool.
In order to match the particle trajectory with the particle oscillation amplitude, AC electric potential was modified by introducing a parameter $C_1$ as follows

$$V_{AC}(t, z) = 0.0797C_1 \times V_{AC, pk-pk} \sin(2\pi ft) \cdot \exp\left(-\frac{z^2}{(1.2012z_{half})^2}\right)$$  \hspace{1cm} (12)

Determination of correction factor $C_1$ was performed by the comparison of amplitude on oscillating the glass particles with trajectory calculations by adjusting the AC electric field. The correction factor $C_1$ was obtained as follows and the modified electric field of DC voltage (blue line) was calculated as shown in figure 8.

$$C_1 = |15.28z^{0.5}| + 1$$  \hspace{1cm} (13)
A constant gas flow of nitrogen was provided vertically upwards through the lower DC electrode tube. Therefore it is necessary to take the existence of drag force against the levitated particle into consideration. A vertical force balance on the levitated particle at null point yields

\[ mg = \frac{q C_d V_{DC}}{z_0} + 3 \pi \eta d_p u_g \]  

(14)

The flow velocity \( u_g \) (m \cdot s\(^{-1}\)) of surrounding gas at the null point in EDB was obtained from the DC voltage difference in the presence or absence of nitrogen gas flow (equations (11) and (14)). However, there is some distribution of flow velocity \( u_g \) in space for the oscillating particle and it affects the oscillating particle trajectories. The usual boundary layer theory was adapted for calculation of the velocity distribution equation for circular free jet [8], and it is defined as

\[ u_g (r, z) = \frac{3K'}{8\pi z (1 + \xi^2 / 4)} \]  

(15)

In this equation, \( z \) is a distance from the exit of cylindrical tube which is used as DC electrode (m), \( \nu \) is kinetic viscosity of gas (m\(^2\) \cdot s\(^{-1}\)), \( K' \) is kinetic momentum (m \cdot s\(^{-2}\)) described as

\[ K' = \frac{16(Q / d_0)^2}{3\pi} \]  

(16)

where \( Q \) is total flow rate (m\(^3\) \cdot s\(^{-1}\)) and \( d_0 \) is inner diameter of cylindrical tube (m) and \( \xi(\cdot) \) is defined as

\[ \xi = \frac{r}{4z \nu} \sqrt{\frac{3K'}{\pi}} \]  

(17)

The velocity distribution along the central axis of EDB device can be calculated from

\[ u_g (0, z) = C_2 \frac{2(Q / d_0)^2}{\nu z} \]  

(18)

because of \( \xi = 0 \) at \( r = 0 \). \( C_2 \) is the adjustment parameter in order to agree with measured velocity at null point. Figure 9 represents the velocity distribution when the flow rate was 50 ml \cdot min\(^{-1}\).

Considering the gas flow, the equation (2) of particle motion was rewritten as follows

\[ m \frac{d^2 z}{dt^2} = -mg - 3 \pi \eta d_p \left( \frac{dz}{dt} - u_g (0, z) \right) + qE(t, z) \]  

(19)
null point

\[ mg = qE_{ic} + 3\pi d^3 \nu \]

**Figure 9.** Velocity distribution of flow gas alone the centre z-axis.

Calculation results from equation (19) and photographs of oscillating glass particle are shown in figure 10 in order to verify the validity of trajectory calculation. The calculated result (Green line) with correction for gas flow and electric field was in well agreement with offset and amplitude of the oscillating particle.

**Figure 10.** Comparison between the trajectory calculations with correction for gas flow and/or electric field and the photographs of oscillating glass particle.

In this trajectory calculation, it is important that it takes relaxation time about 0.2 sec (about 20 cycles at 100 Hz) to be stable particle oscillation. This fact indicates that the oscillation amplitude measurement based on commercial video camera could not follow the fast weight change which occurred in less than 0.2 sec. However, our particle trajectory calculations could be used in determination of a weight change of the particle in a few seconds. Then we examined the availability of this trajectory calculation for following the evaporation of a water droplet as an example of the quick weight change of a particle.

The diameter change of a water droplet in a steady state vapour field is given by [9]
\[
\frac{d(d_p)}{dt} = \frac{2ShD_vM}{R \rho_p d_p} \left( \frac{p_\infty}{T_\infty} - \frac{p_d}{T_d} \right)
\]  
(20)

where \(d_p\) is the droplet radius (m), \(D_v\) is the gas phase diffusion coefficient (m\(^2\) \cdot s\(^{-1}\)), \(M\) is the molar mass of water (kg \cdot mol\(^{-1}\)), \(R\) is the gas constant (J \cdot (K \cdot mol\(^{-1}\))), \(\rho_p\) is the density of water (kg \cdot m\(^{-3}\)), \(p_\infty\) is the ambient partial pressure of H\(_2\)O (Pa), \(p_d\) is its equilibrium vapour pressure of H\(_2\)O (Pa), \(T_\infty\) is the ambient temperature (K), \(T_d\) is the droplet temperature (K) and Sherwood number (Sh) is the nondimensional parameters which are expressed as

\[
Sh = 2.0 + 0.6Re^{1/2}Sc^{1/3}
\]

(21)

where Sc is Schmidt number (-) which is defined as the ratio of kinetic viscosity and mass diffusivity.

Assuming that the enthalpy of water evaporation is in balance with the thermal energy conducted to the droplet by the surrounding gas, the droplet temperature may be expressed in the form of

\[
T_\infty - T_d = \frac{L_eD_v(p_d - p_\infty)}{k_gR}
\]

(22)

where \(L_e\) is the specific enthalpy of water evaporation (J \cdot mol\(^{-1}\)) and \(k_g\) is the thermal conductivity of the surrounding gas (W \cdot (m \cdot K)\(^{-1}\)). MATLAB program was developed to solve the coupled system of equations (21) and (22). Simulation of the time-dependent droplet weight calculated for specific experimental conditions in humidity of 0 %, temperature of 303 K and initial droplet diameter of 79\(\mu\)m was plotted with the droplet trajectory calculation accompanying simultaneously with its evaporation, and the plot was shown in figure 11. The time changes of amplitude and offset from null point could follow up the weight decrease over the passage of time in a second except for the transient behaviour in less than 0.1 s.

![Figure 11](image-url)
From the calculation of water droplet evaporation, we found that our trajectory calculation could be useful for following the weight change with the chemical reaction with the order of about 1 sec. Furthermore, gravimetric analysis of chemical reactions does not provide direct identification of the chemical species involved in the reactions. In the case of EDB, it is possible to investigate direct measurement of the chemical species of a levitated particle by an EDB device coupled with a Raman spectroscopy [1].

5. Conclusions
This paper describes the preliminary calculation of the particle trajectories for analysis of the rapid weight change of levitated particle in EDB device. The electric fields in EDB were calculated by MATLAB PDE tool, and an approximate equation of electric field along the central axis of cylindrical electrodes was obtained with time variation. By solving the vertical equation of particle motion, the oscillating particle trajectories could be calculated though some modification of electric field and gas flow. It was found that particle trajectory calculation could follow up the weight change within a few oscillations such as the water droplet evaporation. It demonstrates that trajectory calculation of a particle in EDB is very useful for the kinetic studies on the reaction of a single aerosol particle with gaseous species.

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