Fokker-Planck description of particle charging in ionized gases

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We present a Fokker-Planck description of the charging of particles weakly in ionized gases and of the charge fluctuations arising from the statistical nature of this process. Charge fluctuations constitute a Markov process and in the limit of linear charging currents or large particles this process is also Gaussian. The time scale of fluctuations is inversely proportional to the particle size and ion concentration and for small particles it is significantly larger than the particle diffusion time. In this regime Brownian diffusion becomes a mechanism by which charge fluctuations are transported into different regions of the plasma. [S1063-651X(97)12101-8]

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I. INTRODUCTION

Airborne particles routinely accumulate charges by capturing ions and free electrons from their surrounding gas. This situation is encountered in many systems, for example, flames [1], radioactive environments [2], interstellar space [3], plasmas [4–6], or ambient air [7]. The net charge collected depends on the ionic environment. In low-pressure plasmas it can be quite large, 2–10 electrons per nm of particle radius, depending on the electron energy [8]. The high degree of charging is a distinguishing feature of particles in ionized gases and gives rise to interesting as well as unusual behavior. Particle clouds in low-pressure plasmas are observed to hover indefinitely above electrodes [9], to segregate by size near reactor walls [4], and to assemble in stable crystalline structures of macroscopic dimensions [6]. In dealing with the charging of particles, the conventional approach neglects fluctuations and assumes the particle charge to be constant. Nevertheless, fluctuations do occur. On the most fundamental level, the discreteness of the charge produces a fluctuation of magnitude $\pm z_i e$ each time an ion of valence z_i or an electron is captured by the particle. Random fluctuations may grow in magnitude and duration. They may promote agglomeration by lowering the repulsive barrier for particle-particle collisions [10] and enhance particle transport by inducing diffusive motion across magnetic field lines [11,12], thus producing behavior that is not explained by assuming the charge to be constant. Fluctuations have been the subject of theoretical [13–15] and also experimental [7] investigations. However, the scope of these studies has been limited to the prediction of the magnitude of fluctuations in specific charging environments. Moreover, the magnitude alone cannot predict the effect of fluctuations on the behavior of particles in these systems. Clearly, only fluctuations which grow rapidly and dissipate slowly are likely to have a serious impact. Here we formulate a comprehensive theory for the dynamics of charge fluctuations in a way that is independent of the details of the charging currents. Our approach is based on the Fokker-Planck equation and quantifies the statistical properties and lifetime of fluctuations arising from the probabilistic nature of the charging process. We then apply the theory to the charging of particles in glow discharges. Fluctuations of the charge may arise due to other reasons, including trapping and scattering of positive ions in the vicinity of particles [16], oscillation of the charging currents [17], transient conditions [18], or turbulence. Such processes are not considered here.

II. DYNAMICS

We consider a particle surrounded by an atmosphere of electrons and singly charged positive ions, hereafter called charged species. Upon collision with a charged species the particle charge Q undergoes a stepwise change of $\pm e$ with probabilities per unit time given by I_i/e and $-I_e/e$, where I_i, I_e are the ion and electron collection currents, respectively, and e is the electron charge. Assuming that the charging currents depend on the instantaneous charge but not on prior history, the particle charge constitutes a Markov process whose master equation is given by [19]

$$\left.\frac{\partial W}{\partial t}\right|_Q = [I_i W|_{Q-e} - I_e W|_{Q+e} - (I_i - I_e) W|_Q]/e, \tag{1}$$

where $W=W(Q,t)$ is the probability for a particle to carry the charge Q at time t. We treat the particle charge as a continuous variable and linearize the currents in the vicinity of the steady-state charge $\overline{Q}$ defined by the condition $I_i(\overline{Q})+I_e(\overline{Q})=0$. Equation (1) then becomes

$$\frac{\partial W}{\partial (t/\tau_f)} = \frac{\partial (Q-\overline{Q})W}{\partial Q} + \sigma^2 \frac{\partial^2 W}{\partial Q^2}, \tag{2}$$

where τ_f and σ^2 are defined as

$$\tau_f = 1/(-\overline{I'_e} - \overline{I'_i}), \tag{3}$$

$$\sigma^2 = \frac{e}{2}\left(\frac{\overline{I_i} - \overline{I_e}}{-\overline{I'_i} - \overline{I'_e}}\right). \tag{4}$$

Here primes indicate derivatives with respect to Q and overbars indicate calculation at $Q=\overline{Q}$. Equation (2) is a Fokker-Planck equation with a linear convective term and constant diffusivity $D_Q = \sigma^2/\tau_f$. This formulation views the ionization state of the particle as a stochastic variable diffusing in the charge space and opposed by a force produced by the deterministic charging currents. Mathematically, Eq. (2) is identical to the Fokker-Planck equation for diffusion of a particle in a harmonic potential. The time τ_f is the inverse of the characteristic steady-state charging frequency [15,17]. The significance of the parameter σ^2 becomes clear upon solving Eq. (2) for the distribution function W. With initial condition $W(Q,t=0)=\delta(Q-Q^*)$ the solution is [20]

$$W(t,\overline{Q}+x)=\frac{1}{\sigma\sqrt{2\pi(1-e^{-2t/\tau_f})}}\exp\left[-\frac{(x-x^*e^{-t/\tau_f})^2}{2\sigma^2(1-e^{-2t/\tau_f})}\right], \tag{5}$$

where $x=Q-\overline{Q}$ is the charge deviation form the steady-state value. The charge distribution, therefore, is at all times Gaussian and approaches a steady state in which the mean charge is $\overline{Q}$ and variance σ^2. The steady-state values are approached with a time constant τ_f, provided that Q^* is within the linear range of the currents. The dependence of the variance on the charging currents is given in Eq. (4). Alternatively, σ^2 can be written in the form

$$\left(\frac{\sigma}{e}\right)^2=\frac{\tau_f}{2\tau_c}, \tag{6}$$

where $\tau_c=e/(\overline{I_i}-\overline{I_e})$. In this form σ^2 is expressed as the ratio of two characteristic times: τ_f, which we shall show is the fundamental time scale of the fluctuations, and τ_c, which is the mean time for collisions of a particle with charged species.

To obtain the time evolution of the particle charge, the conventional charging equation must be extended to read

$$dQ/dt=I_i+I_e+\Gamma(t), \tag{7}$$

where Q is the instantaneous particle charge and $I_i+I_e=-(Q-\overline{Q})/\tau_f+\cdots$ is the (linearized) net current to the particle. $\Gamma(t)$ is a stochastic forcing function with zero mean and accounts for the fluctuating part of the charge. By averaging Eq. (7) we recover the deterministic equation for the mean particle charge. With the stochastic term included, it is the Langevin equation of the particle charge. If the fluctuations are uncorrelated in time, as was assumed in writing Eq. (1), the forcing function must satisfy the condition [21]

$$\langle\Gamma(t)\Gamma(t+t')\rangle=2\tau_f\sigma^2\delta(t'-t), \tag{8}$$

where $\delta(t)$ is the Dirac delta function and σ^2 is the variance of the fluctuations. Equations (7) and (8) provide the complete Langevin description of the process. Other statistical properties are readily computed. For example, the autocorrelation function of the fluctuations is $\langle Q(t)Q(t+t')\rangle=\exp(-t'/\tau_f)$ [21] and the corresponding power spectrum is a Lorentzian function with characteristic frequency $1/\tau_f$.

To quantify the lifetime of fluctuations we define the growth time $t_g(\delta Q)$ to be the mean time for the transition $Q\to Q+|\delta Q|$ to occur, and the dissipation time $t_d(\delta Q)$ to be the mean time for this fluctuation to revert to the mean. We treat the growth and dissipation of fluctuations as a first-passage problem for a stochastic process described by the linear Fokker-Planck equation [19] and find

$$t_g(\delta Q)=\tau_f\left[\sqrt{\pi/2}\int_0^{|\delta Q|/\sigma}e^{x^2/2}\mathrm{erf}(x/\sqrt{2})\,dx\right], \tag{9}$$

$$t_d(\delta Q)=\tau_f\left[\sqrt{\pi/2}\int_0^{|\delta Q|/\sigma}e^{x^2/2}\mathrm{erfc}(x/\sqrt{2})\,dx\right]. \tag{10}$$

Both times are proportional to the fluctuation time τ_f while the proportionality constant depends only on the magnitude of the fluctuation.

III. RESULTS AND DISCUSSION

We test these predictions by considering collisional charging in the orbit-motion limit with unscreened Coulomb interactions and Maxwellian energy distribution for both ions and electrons. These conditions represent a standard working model for low-pressure discharges [4,8]. For a negatively charged particle the instantaneous charging currents are

$$I_i=+eK_i(1-\phi_i/k_BT_i), \tag{11}$$

$$I_e=-eK_e\exp(-\phi_e/k_BT_e), \tag{12}$$

where the subscripts i and e refer to ions and electrons, respectively, $K_{i,e}=N_{i,e}\pi R_p^2(8k_BT_{i,e}/\pi M_{i,e})^{1/2}$, R_p is the particle radius, k_B is the Boltzmann constant, $M_{i,e}$ is the mass of the charged species, $N_{i,e}$ is their concentration, $T_{i,e}$ is their temperature, and $\phi_{i,e}=\pm eQ/4\pi\epsilon_0R_p$ with $+/-$ for ions and electrons, respectively. With these currents the variance is [22]

$$\sigma^2=C_pk_BT_e\left(1-\frac{1}{1+T_i/T_e+\overline{\phi_e}/k_BT_e}\right), \tag{13}$$

where $C_p=4\pi\epsilon_0R_p$ is the capacitance of the particle (assumed a perfect conductor), and $\overline{\phi_e}=-e\overline{Q}/4\epsilon_0\pi R_p$ is the repulsive barrier for transferring an electron from the plasma onto the surface of a particle carrying the mean charge. The variance of the charge is directly related to the energy of the fluctuations. For a conducting particle we obtain

$$\langle E\rangle=\frac{\langle(Q-\overline{Q})^2\rangle}{8\pi\epsilon_0R_p}=\frac{\sigma^2}{2C_p}. \tag{14}$$

In the limit $(T_e/T_i)(M_i/M_e)\to\infty$ we find $\overline{\phi_e}/k_BT_e\to0$ and from Eq. (14), $\langle E\rangle\to k_BT_e/2$. If we further require thermal equilibrium between ions and electrons ($T_i=T_e=T$), we observe that the energy of the fluctuations assumes the classical equipartition value $k_BT/2$. In this limit particles achieve electrostatic equilibrium with the plasma and the relative abundance of ionization states is given by the Boltzmann factor $\exp(-E/k_BT)$, where $E=(Q-\overline{Q})^2/2C_p$. If electrostatic equilibrium can be assumed *a priori*, as is the case in some colloidal systems [23], one may obtain the distribution of ionization states directly from the Boltzmann factor with no reference to the charging currents. The existence of electrostatic equilibrium has been postulated as a general property of charged particles in ionized gases [24], but this view has been disputed on the grounds that particle charging does not satisfy detailed balance unless desorption of charges is per-

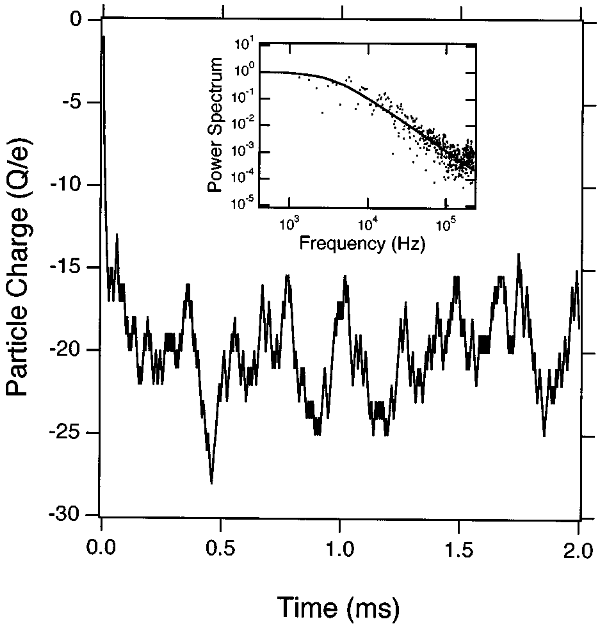

FIG. 1. Monte Carlo simulation of the instantaneous particle charge for $R_p = 10$ nm. The inset graph shows the power spectrum from simulation (dots) and theory (line). The theoretical spectrum is calculated from $P(\nu) = 1/[1 + (2\pi\nu\tau_f)^2]$, where ν is the frequency.

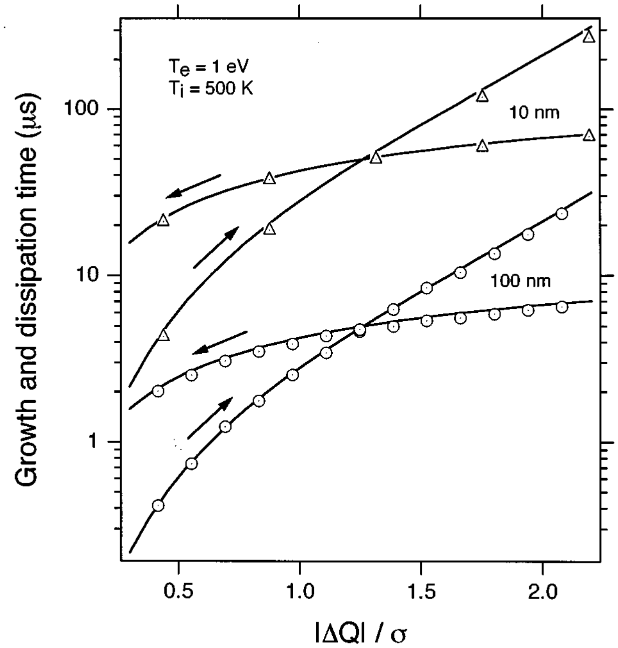

FIG. 2. The characteristic time for growth (right arrow) and dissipation (left arrow) of fluctuations. Symbols are from Monte Carlo simulation; lines are calculations from theory.

mitted [25]. It is evident from our analysis that electrostatic equilibrium is possible (though not true in general), even though the charging of particles is an irreversible process.

With Maxwellian currents the fluctuation time is

$$\tau_f = \left(\frac{4\lambda_i^2}{\overline{v_i} R_p} \right) \frac{1}{1 + T_i/T_e + \overline{\phi_e}/k_B T_e}, \tag{15}$$

where $\lambda_i = (\epsilon_0 k_B T_i / N_i e^2)^{1/2}$ is the Debye length based on ions and $\overline{v_i} = (8 k_B T_i / \pi M_i)^{1/2}$ is the mean ionic speed. The large denominator in Eq. (15) is a weak function of T_e (in glow discharges typically $T_i/T_e \ll 1$, $\overline{\phi_e}/k_B T_e \approx 4$). It follows then that τ_f is a strong function of the ion properties but nearly independent of the electron energy, implying that the time scales of the fluctuations are not sensitive to the assumption of Maxwellian electrons.

To corroborate these results we perform a Monte Carlo simulation in which the particle charge is incremented by $\pm e$ with probability $P_\pm = |I_\pm|/(|I_+| + |I_-|)$. Our calculations are for the bulk of an argon plasma at 0.1 Torr with $T_e = 1$ eV, $T_i = 500$ K, and $N_i = N_e = 10^{10}$ cm^{-3}. These conditions are characteristic of glow discharges in materials processing. Figure 1 shows the instantaneous charge of an initially neutral 10 nm particle as a function of time. The initial transient corresponds to the charge-up time of the particle, which is given by $\tau_0 = 4\lambda_e^2 / R_p \overline{v_e}$, where $\overline{v_e}$ is the mean electron speed [26]. We note that the charge-up time and the fluctuation time are not generally equal. The fluctuation time is the relevant time constant for fluctuations in the linear range of the charging currents, of the order $\pm\sigma$ about the mean. On the other hand, the charging time of an initially neutral particle is primarily determined by the collision time with electrons, τ_0. For the conditions of our simulations, $\tau_0 \approx 0.1\tau_f$. As Fig. 1 demonstrates, the stationary state is approached rapidly but fluctuations are slow by comparison and show correlations which persist over several charging collisions. The inset graph in Fig. 1 shows the power spectrum of the fluctuations. The agreement with the Lorentzian spectrum demonstrates the Gaussian nature of the process. The $1/\nu^2$ decay of the spectrum has been reported previously in simulations of particle charging [14].

The growth and dissipation times for fluctuations of different magnitude are plotted in Fig. 2. Symbols are results from the simulations and correspond to discrete levels of particle ionization. The lines are calculations from Eqs. (9) and (10). Approximately, τ_f corresponds to the point where t_g and t_d are equal. For a particle 100 nm in radius, τ_f is of the order of 5 μs and increases to 50 μs for a 10 nm particle. Both t_g and t_d increase with decreasing size, indicating that small particles resist changes of their ionization state: fluctuations of even a few elementary charges take a long time to grow and even longer to dissipate. Though small in magnitude, such fluctuations represent a large fractional change of the charge because these particles carry few charges (under unscreened Coulomb interactions, the charge-to-radius ratio is independent of the particle charge [22]; for the conditions of our simulations $Q/R_p = -2e/\text{nm}$).

A particle whose charge fluctuates will acquire an additional component of diffusional motion when in the presence of electric or magnetic fields [11,12]. Time scales of the order of 1 to 100 μs are well within the capabilities of dynamic light scattering [27] and we suggest that a suitably designed scattering experiment will observe this motion. In Fig. 3 we compare the fluctuation time to the relaxation time of a particle, τ_p, which is approximately the time for the particle to move by one mean free path against the drag of the fluid. We calculate τ_p from kinetic theory [28] assuming that the drag is solely due to collisions with neutral species.

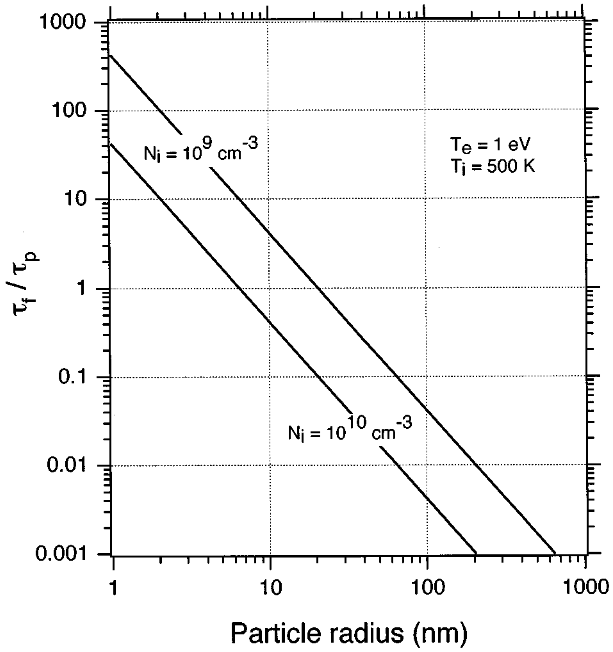

FIG. 3. Comparison between fluctuation and transport time. The particle density is 1 g/cm^3.

The relaxation time is proportional to the radius and so the ratio τ_f/τ_p is inversely proportional to the radius squared. The strong dependence on size produces a sharp distinction between two dynamic regimes. On the one hand, fluctuations on large particles dissipate well within one mean free path, due to the combined effect of rapid fluctuations and small particle mobility. Particles in this regime are equilibrated with their local electrostatic environment and respond rapidly to changes in that environment. Small particles, on the other hand, undergo fluctuations that are slow compared to diffusion, especially in regions of low ionization. Fluctuations persist over several diffusion steps and can be transported away from the regions which produced them. The slow response to environmental changes could be significant for the fate of small particles during transient operation (startup or shutdown) of plasma reactors.

The results presented here are specific to collisional charging in Maxwellian plasmas with orbit-motion limit currents and unscreened Coulomb interactions, but the approach is applicable to any charging model for which the currents are known. There are two major assumptions in the theory. First, charge fluctuations in a particle are assumed uncorrelated to fluctuations in other particles. This requires that interparticle distances be larger than the plasma Debye length λ_D. With $\lambda_D \approx 100$ μm, the particle concentration is restricted to $N_p \ll 1/\lambda_D^3 \approx 2\times 10^6$ cm^{-3}. Second, the charging currents are assumed to be linear functions of the charge in the vicinity of Q. It is fortuitous that the ion current considered in this study is a linear function of the particle charge. For the electron current we write $I_e(Q+\Delta)=I_e(Q)+\beta I_e(Q)\Delta+(\beta^2/2)I_e(Q)\Delta^2+\cdots$, where $\beta=e^2/4\pi\epsilon_0 R_p k_B T_e$ and $\Delta=\pm e,\pm 2e,\ldots$. Thus a criterion for the validity of the theory is $R_p \gg R_p^*$ where $R_p^*=e^2/4\pi\epsilon_0 k_B T_e$. At $T_e=1$ eV we find $R_p^*\approx 1.5$ nm. In light of this condition, conclusions regarding small particles must be evaluated cautiously. As a test we ran a simulation for $R_p=1$ nm and found that, even at this size, the theory performs acceptably and predicts τ_f within 20%.

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