

ELECTRIC DIFFUSION OF MONO AND POLYDISPERSE POLARIZABLE PARTICLES IN AN ELECTRIC FIELD

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(Received December 31, 1991)

Abstract Thermodynamic analysis of nonuniform dispersion of electrically polarizable particles in electric fields is presented. Extensive and intensive energy formulations are used to derive forces that generate electric diffusion and the corresponding diffusion coefficients. Results obtained for monodisperse systems are extended to polydisperse particle mixtures, and transformation of diffusion coefficient from the fluid to the dispersion frame of reference is provided. Finally, differential diffusion of polydisperse particles can constitute the basis for their separation in electric fields.

INTRODUCTION

Interactions between polarizable matter and fields that polarize them are known to involve stresses and body forces. Literature provides data for field-matter interactions in the context of continuum theories [1 - 5]. Less is known in cases where the polarizable matter is in dispersed state where additional degrees of freedom associated with concentration and distribution parameters are involved.

Concentration and distribution parameters such as size, density, shape and polarizability affect local field intensities and energy densities, as well as particle-particle interactions. This is likely to be reflected in changes of chemical potential, or else pressure gradients, and hence in diffusion forces that may arise therefrom.

Field-induced changes in chemical potential and variable diffusion properties of dispersed particles can be used to control separation of selected parts of the particle population. Potential fields of application include chemical, biochemical and biomedical processes. In this paper field-induced diffusion of polarizable and charged particles is considered and related diffusion coefficients are derived using thermodynamics of electromagnetic fields.

THEORY: THERMODYNAMICS OF DIFFUSING POLARIZABLE PARTICLES IN POLARIZING FIELDS

Monodisperse Particles

Thermodynamic variables are classified into extensive and intensive categories. Electromagnetic thermodynamic formulation is presented in the following paragraphs.

Equations (1) and (2) are Legendre Transformation [1] of the fundamental energy $U(X_0, \dots, X_t)$, in which $n+1$ extensive variables have been replaced by their corresponding $n+1$ intensive variables,

$$U(\xi_0, \dots, \xi_n, X_{n+1}, \dots, X_t) = U(X_0, \dots, X_t) - \sum_{k=0}^n \xi_k X_k \quad (1)$$

$$dU(\xi_0, \dots, \xi_n, X_{n+1}, \dots, X_t) = -\sum_{k=0}^n X_k d\xi_k + \sum_{k=n+1}^t \xi_k dX_k \quad (2)$$

where t is an integer, $n = 0, 1, \dots, t$, X_k , $k = 0, 1, \dots, t$ are extensive parameters such as entropy (S), volume (V), mole number (N_j , $j = 1, 2 \dots$), magnetic moment I_M , electric moment I_E , electric charge q ; and $\xi_k = \delta U / \delta X_k$ are corresponding intensive parameters such as temperature (T), pressure ($-P$), chemical potential (μ_j , $j = 1, 2 \dots$), magnetic field intensity (H), electric field intensity (E) and electric potential (Ψ).

Let the extensive and intensive formulations [1, 2] of electromagnetic and interfacial terms be defined by equations (3) and (4), respectively,

$$dU(T, P, \mu, \zeta, I_M, I_E, q, A) = -SdT + VdP - Nd\mu - X_\zeta d\zeta + H \cdot dI_M + E \cdot dI_E + \psi dq + \gamma dA \quad (3)$$

$$dU(T, P, \mu, \zeta, H, E, \psi, \gamma) = -SdT + VdP - Nd\mu - X_\zeta d\zeta - I_M \cdot dH - I_E \cdot dE - qd\psi - Ad\gamma \quad (4)$$

where in eq. (3), $n = 3$, $t = 7$, and in eq. (4), $n = t = 7$. $X_0 = S$, $\xi_0 = T$, $X_1 = V$, $\xi_1 = -P$, $X_2 = N$, $\xi_2 = \mu$, $X_3 = X_\zeta$, $\xi_3 = \zeta$, $X_4 = I_M$, $\xi_4 = H$, $X_5 = I_E$, $\xi_5 = E$, $X_6 = q$, $\xi_6 = \psi$, $X_7 = A$, $\xi_7 = \gamma$. X_ζ and ζ pertain to force fields other than electromagnetic that may exist. For example, in a centrifugal field $X_\zeta = m$, $\zeta = -1/2\omega^2 r^2$ where m is the mass, r is the radius of rotation and ω angular velocity. A and γ are interfacial area and interfacial energy per unit area, respectively,

$$I_M = \mu_o VM \quad (5)$$

$$I_E = VP_E \quad (6)$$

where $\mu_o M$ and P_E are magnetic and electric moments (per unit volume - p.u.v.) and μ_o is permeability of free space. q is the electric charge which is given by:

$$q = \int_V q_v dV + \int_S q_s dS \quad (7)$$

where q_v and q_s are volume and surface charge densities. In order to apply eq. (2) for determination of equilibrium conditions, unconstrained parameters that characterize the system must be defined.

Figure 1 shows a diffusion system enclosed by impermeable diathermal walls. The diffusion system comprises monodisperse particles dispersed in a fluid. The system is in a field ζ_e to which its walls are transparent.

Consider a volume element δV , as shown in Fig. 1. Let $X_0 = \delta S$, $\xi_0 = T$, $X_1 = \delta X_\zeta$, $\xi_1 = \zeta$, $X_2 = \delta N$, $\xi_2 = \mu$, $X_3 = \delta V$, $\xi_3 = -P$, $X_4 = \delta A$, $\xi_4 = \gamma$. Using the above definition of variables in eq. (2), setting $n = 2$, imposing a constraint that for an isothermal diffusion system δV and T are constant, and rearranging, gives at equilibrium:

$$-X_\zeta d\zeta - \delta N d\mu + \gamma d(\delta A) = 0 \quad (8)$$

Note that μ and N pertain to the solute. In cases where concentration of the solute is high, due changes in the solvent, must be accounted for.

Simply replacing δN with δV and μ with $-P$, yields

$$-X_\zeta d\zeta + V dP + \gamma d(\delta A) = 0 \quad (9)$$

Equations (8) and (9) show that for a constant δA , a change in ζ can be transformed into an equivalent change in either chemical potential or in the pressure. For $d\zeta = 0$, the same reasoning applies to a relation between A and μ . It can be shown that the chemical potential of the dispersed phase in the absence of external field is given [2] by

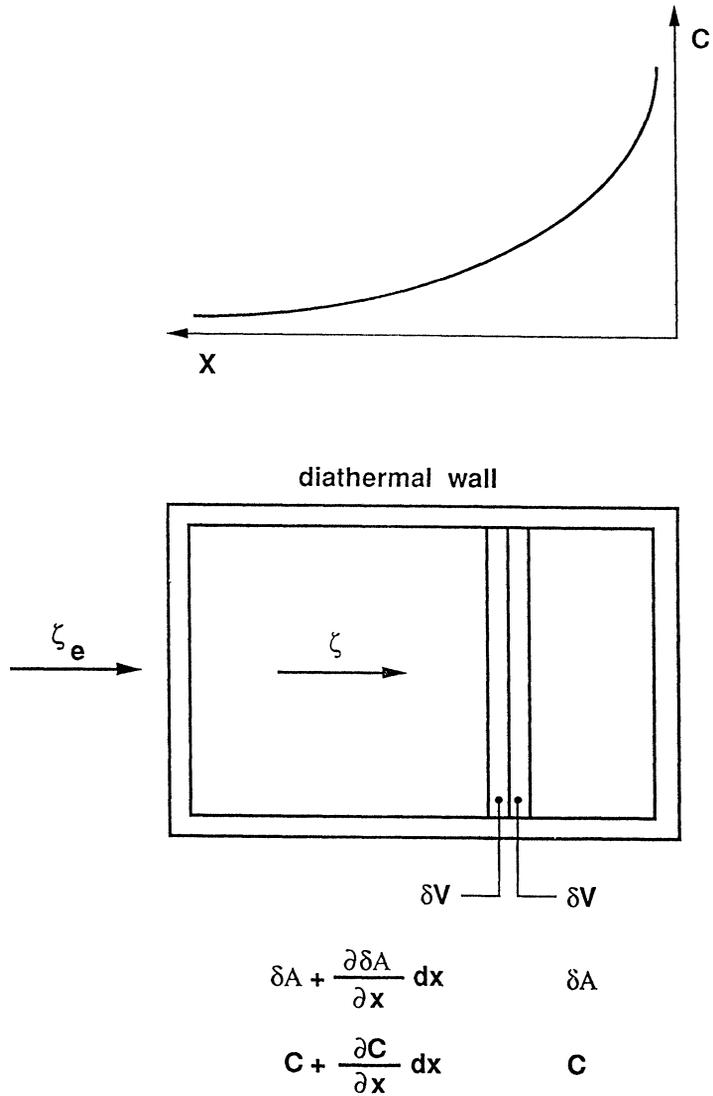


FIGURE 1 Diffusion system enclosed by diathermal impermeable wall in field ζ .

$$\mu = RT(1 + \gamma A_p / k_B T + \ln f_a / \ln C) \ln C \quad (10)$$

where γA_p is interfacial energy per particle having an interfacial area A_p , k_B is the Boltzmann constant and f_a is the activity coefficient that is defined (eq. 11) by the relation between chemical potential μ and activity a of the dispersed phase,

$$\mu = \mu_0 + RT \ln(a/a_0), \quad a = f_a C \quad (11)$$

Note that f_a is a coefficient that stands for deviation of the behaviour of the system from ideality. In such systems, where factors other than concentration affect the energy level of the dispersed phase, the activity a replaces the concentration C as the independent variable in the formulation of the chemical potential.

μ_0 and a_0 are chemical potential and activity at standard state, C is the concentration and R is the gas constant. Note that μ_0 was set to zero in eq. (10). The diffusion driving force F_μ is related to μ by

$$F_\mu = -\nabla\mu \quad (12)$$

The concentration-dependent generalized hydrodynamic drag force per mole of particles, F_h , is given by

$$F_h = -\tilde{N} 3\pi \mu'_\phi d_p U_\phi, \quad \mu'_\phi = \mu_\phi (1+\phi)^{1/3}, \quad \mu_\phi = \mu_f \exp\left(\frac{5}{3} \frac{\phi}{1-\phi}\right) \quad (13)$$

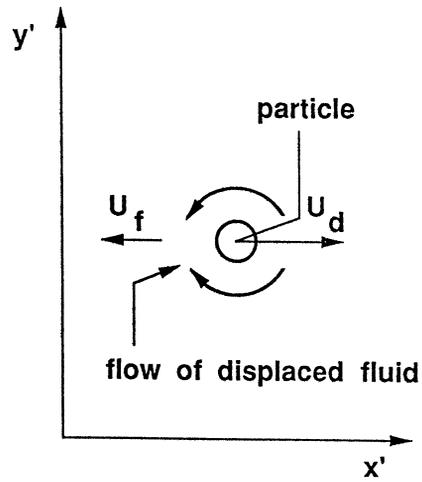
where μ_ϕ is the concentration-dependent effective viscosity of the fluid surrounding the particles and μ'_ϕ is the extended viscosity that incorporates also the interparticle wall hindrance effect.

F_h is derived from the theory of hindered sedimentation of particles [6, 7], \tilde{N} , μ_f , ϕ , d_p and U_ϕ are Avogadro number, fluid viscosity, volume fraction occupied by particles in the dispersion, particle diameter and particle velocity in the fluid frame of reference, respectively,

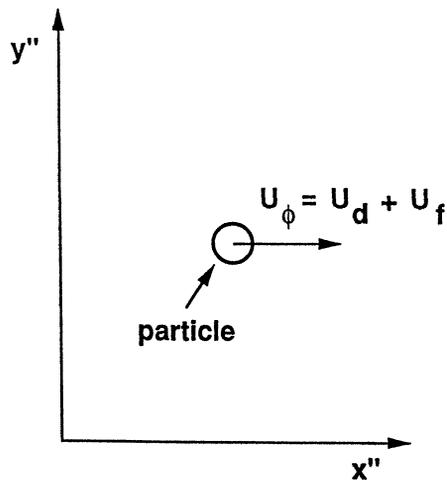
$$U_\phi = U_d + U_f = U_d/(1-\phi), \quad U_f = U_\phi \phi \quad (14)$$

where U_d and U_f are volume-average velocities of particles and of the counterflowing fluid (which is displaced by the particle motion) in the dispersion frame of reference.

The averaging is done over a volume containing a number of particles but which is still small enough to be considered a local average of the dispersion. The dispersion frame of reference is defined with respect to the centre of volume of the dispersion, being independent of the internal distribution of the dispersed phase. The fluid frame of reference represents a Lagrangian system where the observer and hence the system axes move with the fluid.



(a)



(b)

FIGURE 2 Definition of velocities in (a) dispersion and (b) fluid frames of reference.

Figure 2 shows U_ϕ , U_d and U_f in (a) the dispersion and (b) the fluid frame of reference. ϕ is related to the partial molar volume v and to the volume of a single particle V_p by

$$\phi = Cv = C\tilde{N}V_p \quad (15)$$

The molar diffusion flux J is given by

$$J = CU_d = C(1 - \phi)U_\phi = C(1 - C\tilde{N}V_p)U_\phi \quad (16)$$

At steady diffusion

$$F_\mu + F_h = 0 \quad (17)$$

Solving eq. (13) for U_ϕ and using eqs. (10) to (12), (16) and (17) gives

$$J_c = -D_c \nabla C \quad (18)$$

$$D_c = D(1 + \gamma A_p / k_B T + \nabla \ln f_a / \nabla \ln C) f_D(C) \quad (19)$$

$$D = k_B T / (3\pi\mu_f d_p) \quad (20)$$

$$f_D(C) = \frac{1 - C\tilde{N}V_p}{[1 + (C\tilde{N}V_p)^{1/3}] \exp\left(\frac{5}{3} \frac{C\tilde{N}V_p}{1 - C\tilde{N}V_p}\right)} \quad (21)$$

D is the well known [8] Stokes-Einstein diffusion coefficient, and $f_D(C)$ is the hydrodynamic hindrance factor [6, 7].

Consider now diffusion forces that are generated in polarizable dispersions by polarizing fields. Equation (22) gives the value of a physical property η (such as density) characterizing the dispersion (subindex ϕ) in terms of its value in the dispersed (subindex p) and in the fluid (subindex f) phases.

$$\eta_\phi = \phi\eta_p + (1 - \phi)\eta_f \quad (22)$$

Thus, for electric polarization $\eta = P_E$.

P_E varies with the field in the fluid surrounding the particles (see eq. (60) in the sequel). Thus eq. (22) is in accordance with the one given by Landau and Lifshitz [5]. With reference to δV in Fig. 1, let the following differentials denote the electric terms in eqs. (3) and (4).

Extensive formulation (eq. (3)).

$$d(\delta U_{P_E}) = E \cdot d(\delta I_E) = \delta V E \cdot P_E d\phi + \delta V \phi E \cdot dP_E \quad (23)$$

E is the polarizing field existing in the matter, polarization of which is P_E . It is assumed that the polarization of the fluid surrounding the particles can be neglected.

$$d(\delta U_q) = \psi d(\delta q) = \delta V \psi q d\phi + \delta V \phi \psi dq \quad (24)$$

Intensive formulation (eq. (4)).

$$d(\delta U_E) = -\delta V \phi P_E \cdot dE \quad (25)$$

$$d(\delta U_\psi) = -\delta V \phi q d\psi \quad (26)$$

Expressing the differentials as a scalar product of the form $d\nu = \nabla\nu \cdot dr$ where ν denotes a scalar quantity, using the fact that $F_\nu = -\nabla\nu$ (where F_ν is the force associated with ν), and the vector identity $A \cdot dB = \sum A_i \nabla B_i$ where $i = 1, 2, 3$ denotes components such as x, y , and z , and recalling eq. (15), yields:

Extensive formulation:

$$F_{P_E} = -\delta V \tilde{N} V_p E \cdot P_E \nabla C - \mu_o \delta V \tilde{N} V_p C \left(\sum_{i=1}^3 E_i \partial P_{Ei} / \partial C \right) \nabla C \quad (27)$$

$$F_q = -\delta V \tilde{N} V_p \psi q \nabla C - \mu_o \delta V \tilde{N} V_p C \psi (\partial q / \partial C) \nabla C \quad (28)$$

Using electric boundary conditions [3, 4] for an electric field set perpendicular to the dispersion boundary, gives, for the case of intensive formulation:

$$F_E = \delta V \tilde{N} V_p C \sum_{i=1}^3 P_{Ei} \nabla E_{ei} - \delta V \tilde{N}^2 V_p^2 P_E^2 C \nabla C - \delta V \tilde{N}^2 V_p^2 C^2 \left(\sum_{i=1}^3 P_{Ei} \partial P_{Ei} / \partial C \right) \nabla C \quad (29)$$

$$F_\psi = \delta V \tilde{N} V_p C q \nabla \psi - \delta V \tilde{N}^2 V_p^2 q^2 C \nabla C - \delta V \tilde{N}^2 V_p^2 C^2 q (\partial q / \partial C) \nabla C \quad (30)$$

where E_e is the intensity of electric field in absence of dispersion. Equations (27), (28) and (29), (30) disclose factors that affect the electric force acting on the dispersed (and diffusing) particles, namely: energy density per particle, particle concentration, particle-particle interaction (affecting their polarization and charge), concentration gradient and field geometry. Equations (27) to (30)

facilitate definitions of electric diffusion coefficients using force terms that depend on concentration gradients.

Using the same procedure that led to equations (19) to (21), the following electric diffusion coefficients are obtained.

- i. Extensive formulation, polarization and charge unconstrained:
Polarization diffusion coefficient:

1. Polarization energy density per particle

$$D_{PC} = D(V_P E \cdot P_E / k_B T) f_D(C) \quad (31)$$

2. Particle-particle polarization interaction energy

$$D_{PP} = D[V_P C \sum_{i=1}^3 E_i \partial P_{Ei} / \partial C / k_B T] f_D(C) \quad (32)$$

Charge diffusion coefficient:

1. Energy density of charges per particle

$$D_{qC} = D(V_p \psi q / k_B T) f_D(C) \quad (33)$$

2. Particle-particle charge interaction energy

$$D_{qq} = D[V_P C \psi (\partial q / \partial C) / k_B T] f_D(C) \quad (34)$$

- ii. Intensive formulation, field intensity and electric potential unconstrained.
Polarization diffusion coefficient:

1. Concentration effect:

$$D_{EC} = D(v V_P P_E^2 C / k_B T) f_D(C) \quad (35)$$

2. Particle-particle interaction

$$D_{EP} = D[(v V_P C^2 \sum_{i=1}^3 P_{Ei} \partial P_{Ei} / \partial C) / k_B T] f_D(C) \quad (36)$$

Charge diffusion coefficient:

1. Concentration effect:

$$D_{\psi C} = D(v V_P q^2 C / k_B T) f_D(C) \quad (37)$$

2. Particle-particle interaction:

$$D_{\psi q} = D[v V_P C^2 q (\partial q / \partial C) / k_B T] f_D(C) \quad (38)$$

Note that $v = \tilde{N} V_P$, and that the magnetic counterparts of eqs. (31), (32), (35) and (36) are obtained by replacing P_E by M , E by H and multiplying each equation by μ_0 .

Polydisperse Particles

Polydispersity of particles can arise due to various factors such as size, density, shape, polarizability, charge and interfacial energy. Consider polydispersity with respect to polarizability and size where the following categories can be defined.

1. Particles characterized by size distribution and uniform electric moment density
2. Monosize particles characterized by distribution of electric moment density
3. Particles characterized by bivariate size and electric moment density.

As the size is often the cause for polydispersity, the first category is considered in the following.

Let the probability density function of the volume fraction occupied by particles of size d_p be denoted by ϕ' , where $\phi' = \phi'(d_p, r)$ is the function of d_p as well as of the position r along the diffusion path. Given r , ϕ' is defined by

$$\phi' = \frac{1}{\phi} (\partial \phi / \partial d_p) \quad , \quad \int_0^{\infty} \phi' dd_p = 1 \quad (39)$$

$$d\phi = \phi \phi' dd_p \quad (40)$$

$$dC = \frac{6}{\pi \tilde{N}} \frac{\phi \phi'}{d_p^3} dd_p \quad (41)$$

The counterpart of eq. (14) is readily shown to be

$$U_d = U_\phi - U_f = U_\phi - \phi \int_0^\infty U_\phi \phi' dd_p \quad (42)$$

Since $dJ = U_d dC$, combining with eqs. (41) and (42) and integrating gives,

$$J = \frac{6\phi}{\pi\tilde{N}} \int_0^\infty (U_\phi - \phi \int_0^\infty U_\phi \phi' dd_p) \frac{\phi'}{d_p^3} dd_p \quad (43)$$

Eq. (43) shows that the flux J depends on total concentration as well as on the size distribution of the particles. The statistical expectation (or the mean) of the chemical potential μ , which is the equivalent of eq. (10), is given by

$$\bar{\mu} = RT(1 + \gamma \bar{A}_p / k_B T + \overline{\ln f_a / \ln C}) \ln C \quad (44)$$

where the bars denote expectation [9], or weighed mean of the variable. The counterpart of eq. (19) for the case of polydisperse particles is now readily shown to be,

$$D_{C\phi} = D \{ 1 + \gamma \bar{A}_p / k_B T + [\gamma |n(C/C_0) \nabla \bar{A}_p / \nabla \ln C] / k_B T + \nabla \overline{\ln f_a / \nabla \ln C} \} f'_D(C) \quad (45)$$

$$f'_D(C) = 1 / [(1 + (C\tilde{N}V_p)^{1/3}) \exp(\frac{5}{3} \frac{C\tilde{N}\bar{V}_p}{1 - C\tilde{N}\bar{V}_p})] \quad (46)$$

where C_0 is the concentration at the reference state, for example $C_0 = 1$. Eq. (45) shows that if diffusion coefficient of monodisperse particles depends on the energy-related variable (such as A_p) then the diffusion coefficient of polydisperse particles depends, in addition to \bar{A}_p , also on $\nabla \bar{A}_p$.

Note that subindex ϕ in $D_{C\phi}$ denotes that the diffusion coefficient is given in the fluid frame of reference. The transformation of $D_{C\phi}$ to the dispersion frame of reference is discussed in the sequel.

The same arguments apply also to the electric diffusion coefficient (eqs. (31) to (38)). Electric diffusion coefficients for particles in a polydisperse mixture are obtained by replacing (in eqs. (31) to (38)) P_E , V_p and q by \bar{P}_E , \bar{V}_p and \bar{q} , and $f_p(C)$ by $f'_p(C)$.

The additional diffusion coefficients D_{vG} that are functions of the gradient of $\bar{V}_p = \pi_b \bar{d}_p^3$ are given by

$$D_{vG} = D[CU_e (\partial \bar{V}_p / \partial C) / k_B T] f'_D(C) \quad (47)$$

where U_e is either $E \cdot \bar{P}_E$ or $\Psi \bar{q}$, in the case that either polarization, or charge, are involved, respectively.

In the following, we seek the transformation of diffusion coefficient from the fluid to the dispersion frame of reference. The total diffusion flux, at position r , in the fluid frame of reference, is given by

$$\bar{J}_\phi(r) = \int_0^\infty J_\phi(r, d_p) \phi' dd_p = -\bar{D}_\phi(r) \nabla C \quad (48)$$

where given the position r , then $j_\phi(r, d_p)$ is the flux of particles having size d_p , $\nabla C = \nabla C(r)$ is the position-dependent concentration gradient, and $\bar{D}_\phi(r)$ is given by

$$\bar{D}_\phi(r) = \int_0^\infty D_\phi(r, d_p) \phi' dd_p \quad (49)$$

where $D_\phi(r, d_p)$ is the diffusion coefficient of particles having the size d_p , in the fluid frame of reference at position r . Since, by definition,

$$\bar{U}_\phi = \bar{J}_\phi(r) / C = -\bar{D}_\phi(r) \nabla C / C \quad (50)$$

and

$$U_f = \phi \bar{U}_\phi = C \tilde{N} \bar{V}_p \bar{U}_\phi \quad (51)$$

by combining eqs. (50) and (51) we obtain

$$U_f = -\bar{D}_\phi(r) \tilde{N} \bar{V}_p \nabla C \quad (52)$$

hence

$$J_d(r, d_p) = (U_\phi - U_f) C = -(D_\phi(r, d_p) \nabla C - \bar{D}_\phi(r) \tilde{N} \bar{V}_p C \nabla C) \quad (53)$$

where $J_d(r, d_p)$ denotes the diffusion flux at position r of particles having size d_p , in the dispersion frame of reference.

Since $J_d(r, d_p) = -D_d(r, d_p)\nabla C$, where $D_d(r, d_p)$ pertains to the dispersion frame of reference, it follows that

$$D_d(r, d_p) = D_\phi(r, d_p) - \phi \overline{D_\phi(r)} , \quad \phi = C\tilde{N}\tilde{V}_p \quad (54)$$

Equation (54) shows that the diffusion coefficient of particles characterized by size d_p in a polydisperse mixture that is diffusing in the dispersion frame of reference, depends on the product of expectation of diffusion coefficient (in the fluid frame of reference) and on concentration and expectation of particle volume at a given position r .

Eq. (54) can be extended to variables other than size, for example to P_E and q . Let such variables be denoted by η ; hence

$$D_d(r, \eta, d_p) = D_\phi(r, \eta, d_p) - \phi \overline{D_\phi(r)} \quad (55)$$

$$\overline{D_\phi(r)} = \int_0^\infty \int_{-\infty}^\infty D_\phi(r, \eta, d_p) \phi'(\eta, d_p) d\eta dd_p \quad (56)$$

The above analysis can be extended so as to account for effects of pearl chaining. Pearl chaining results in changes in size, shape and polarizability of the dispersed entities. This would require the use of $\eta = P_E$ in eqs. (55) and (56). The treatment of pearl chaining was avoided for the sake of simplicity and is outside the scope of this work. If pearl chaining produces monodisperse chains, then the theory presented here still holds provided that the effective values of size and polarization can be assigned to new elongated particles.

It is of interest to determine when electric and thermal diffusion can be matched. A good measure to this end is provided by eq. (57).

$$V_p P_p \cdot E / k_B T = 1 \quad (57)$$

where other energy terms that contribute to electric diffusion were not included for the sake of simplicity.

Let the dispersion be dilute to the extent that particle- particle interaction can be neglected, and assume spherical particles. Polarization of a sphere is given by

$$P_p = \alpha \frac{\epsilon - 1}{4\pi} E \quad (58)$$

where E is the field inside a particle having dielectric constant ϵ and α is the proportionality constant that depends on system of units used [7]. In the esu system $\alpha = 1$, and in the MKS practical system $\alpha = (36\pi 10^9)^{-1}$. The field inside and outside the sphere are related by

$$E = \frac{3}{2 + \epsilon} E_f \quad (59)$$

where E_f is the field outside, i.e. in the fluid. By combining eqs. (58) and (59) we obtain

$$P_p = \alpha \frac{\epsilon - 1}{4\pi} E \quad (60)$$

Hence eq. (57) takes the following alternative forms:

$$d_p = \left[\frac{8k_B T}{3\alpha E_f^2} \frac{(\epsilon + 2)^2}{\epsilon - 1} \right]^{1/3} \quad (61)$$

$$E_f = \left[\frac{8k_B T}{3\alpha d_p^3} \frac{(\epsilon + 2)^2}{\epsilon - 1} \right]^{1/2} \quad (62)$$

The field of $E_f = 10^6$ V/m, $\epsilon = 2$, at $T = 298$ K and $k_B = 1.38 \times 10^{-23}$ J/K yield $d_p = 270.7$ nm. Larger particles require lower field and for particles that are larger than $1 \mu\text{m}$, $E_f < 1.408 \times 10^6$ V/m ($\epsilon = 2$, $T = 298$ K).

Let us consider the effect of particles on the polarization of the dispersion. If transmission of force between particles and fluid is complete then polarization of a uniform dispersion is given by

$$P_\phi = P_p \phi + (1 - \phi) P_f \quad (63)$$

In the following it is assumed that the effect of fluid polarization P_f can be neglected compared to the one due to particle polarization P_p . Let the external electric field be perpendicular to a boundary of the dispersion. Since the normal component of the electric displacement is continuous across the boundary,

$$\epsilon_0 E_0 = \epsilon_f E_f + \frac{1}{\alpha} \phi P_p = \epsilon_f E_f + \phi \frac{3\epsilon_f}{4\pi} \frac{\epsilon - 1}{2 + \epsilon} E_f \quad (64)$$

where ϵ_0 is the dielectric constant of the medium or space external to the dispersion, ϵ_f is its counterpart in the fluid, and ϵ denotes the ration of dielectric constants of particle to that of the fluid. Hence,

$$E_f = \frac{\epsilon_0}{\epsilon_f + \phi} \frac{3\epsilon_f}{4\pi} \frac{\epsilon-1}{\epsilon+2} E_0 \quad (65)$$

$$P_p = \frac{3\alpha\epsilon_0(\epsilon-1)}{4\pi\epsilon_f(\epsilon+2) + 3\epsilon_f\phi(\epsilon-1)} E_0 \quad (66)$$

and the polarization energy per particle takes the following form:

$$U_{PE} = V_p P_p \cdot E = \frac{36\pi V_p \alpha \epsilon_0^2 (\epsilon-1)}{[4\pi\epsilon_f(\epsilon+2) + 3\epsilon_f\phi(\epsilon-1)]^2} E_0^2 \quad (67)$$

Equation (67) shows that for a given E_0 an increase in ϕ decreases U_p .

CONCLUSIONS

1. Imposition of electric fields on nonuniform dispersions of electrically polarizable or charged particles generates driving forces for electric diffusion.
2. Three types of electric diffusion coefficients can be defined with respect to electric energy density (due to polarization or charge) per particle, particle-particle interaction energies and concentration-related energy. The first two pertain to extensive thermodynamic formulation of the electric energy and the third to the intensive formulation.
3. Electric diffusion coefficients which are comparable to thermal diffusion coefficients can be produced by currently available high-intensity electric fields, in dispersions comprising particles having sizes in the colloidal range, or larger.
4. Electric diffusion coefficients in fluids can be defined as a product of the following three factors: the Stokes- Einstein diffusion coefficient, the ratio of electric to thermal energies and hydrodynamic concentration-dependent hindrance factor.
5. Electric diffusion coefficients of polydisperse particle mixtures can be defined in the fluid frame of reference, using expectations of distributed variables that constitute the electric diffusion coefficients for monodisperse particles. These diffusion coefficients can then be transformed to the dispersion frame of reference by subtracting the product of total volume fraction occupied by the particles and the expectation of the diffusion coefficients.

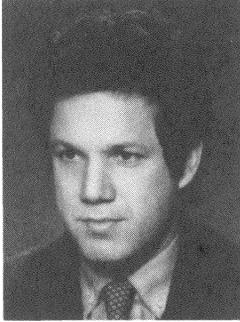
6. Differential electric diffusion can constitute the basis for separation of polydisperse electrically polarizable particles, in uniform, as well as nonuniform electric fields. Simultaneous imposition of additional fields, such as the centrifugal field, can be used to refine the separation process.

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ACKNOWLEDGMENT

This paper was presented at the 23rd Annual Meeting of the IEEE Industry Application Society, Pittsburgh, PA, U.S.A., 1988.



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Keywords: diffusion, electric field, polarization, monodisperse systems, polydisperse systems, electrical separation.