

STATISTICAL THERMODYNAMICS OF CONCENTRATED COLLOIDAL SOLUTIONS

PART 1.—FREE ENERGY OF ELECTRICAL DOUBLE LAYERS

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The so-called electrical free energy F_e of a concentrated colloidal solution is evaluated by applying the familiar Debye-Hückel charging process. A particularly simple expression is obtained for $F_e - E_e$, where E_e is the electrostatic energy of the system. This quantity may usually be equated to $-TS_e$, where S_e is the entropy of the rearrangement of the ions in the formation of the double layers. Expressions for S_e are derived for several types of ion distribution law. The effect of charge distribution inside the colloid particles is also considered.

By varying F_e and the chemical part F_c of the free energy of the system, the equilibrium laws for the charge distribution on the particles are derived. The partial derivatives of F_e with respect to the total number of ions of any given type in the system, and with respect to temperature are given. The method of Verwey and Overbeek for treating the sum $F_e + F_c$ is generalized and extended to concentrated systems.

The formulae obtained enable the free energy for a regular arrangement of rod-like particles, with one ion type in the medium, to be calculated in a simple way; a table is included.

1. INTRODUCTION

In concentrated (aqueous) colloidal solutions the whole of the electrolyte dispersion medium is effectively comprised in the diffuse part of the electric double layers. Thus, though for certain particle configurations there may be "holes" where the electric field is negligible, there is no point in the dispersion medium where the ion concentrations are unaffected by changes in either the charges or mutual configuration of the colloidal particles. This contrasts with a dilute colloidal solution where there is an effectively infinite volume of uncharged electrolyte solution to provide ions for the double layers and whose free energy has been extensively investigated by a number of authors.¹⁻⁸ Recently a number of papers dealing with concentrated sols have appeared, particularly in connection with the study of polyelectrolytes.⁹⁻¹³ However, except for the work of Marcus,¹³ no systematic treatment of the free energy of the double layers has appeared similar to that given by one of the authors for dilute sols.^{4, 5}

The subject-matter of this paper and of later ones will be a unified presentation of the properties of the free energy of a concentrated colloidal system. The electrical part F_e of the Helmholtz free energy of the double layers will be expressed in the form

$$F_e = E_e - TS_e. \quad (1.1)$$

Here E_e is the electrostatic energy of the system and S_e will be expressed in terms of the ionic distributions. The relation (1.1) will be derived for a distribution law more general than the Boltzmann law and under the general condition of dielectric saturation in the double layers. Simple expressions will then be obtained for the changes in F_e due to changes in the number of ions of a given kind either on a particle surface or in the whole system. An extended Gibbs-Helmholtz relation,

including the dependence of the dielectric constants of the dispersion medium and the particle interiors on the temperature, will also be obtained. Finally the method of Verwey and Overbeek³ for treating both F_e and the so-called chemical free energy will be generalized and extended to concentrated sols.

In the work of Marcus¹³ a polyelectrolyte solution is regarded as a single-phase system in which potential distributions originate from the fixed charges on polymers embedded in a homogeneous dispersion medium. The relation (1.1) was derived for the Boltzmann distribution by using an integral of the Poisson equation for the mean potential at a point. This integral applies to a single phase of uniform dielectric constant on the boundary of which the potential and its normal derivative are both zero. This approach could be extended to the multi-phase systems with charged interfaces studied in this paper. However, the methods adopted here, which were developed before the publication of the work of Marcus, are different and follow the general approach originated by Casimir²⁷ and extended further by one of the authors.⁴ The relation (1.1) has appeared previously^{1, 11, 23, 24, 25} though without proof, and was obtained more recently by one of the authors⁵ for dilute sols, though the term entropy was not used to describe S_e .

The present paper deals mainly with the general theory and specific applications will be given in later papers. However, as a brief illustration, we consider a system of rod-like particles arranged parallel to one another in a regular array with only one type of ion present in the dispersion medium. A simple formula for the free energy F_e will be derived from the general theory and a table calculated to show its dependence on the relevant parameters.

2. ASSUMPTIONS AND NOTATION

These are as follows :

(i) P colloidal particles of arbitrary size and shape are immersed in an electrolyte solution. Each particle α ($\alpha = 1, \dots, P$) is of volume v_α is bounded by a surface S_α . The dispersion medium is of volume V and its outer boundary is the surface S_0 .

(ii) There are m types of ion in the colloid system and the number of ions of type i , with charge e_i , per unit volume at a given point is denoted by n_i ($i = 1, \dots, m$). The number N_i of ions of a given type i in the dispersion medium is thus given by

$$N_i = \int_V n_i dv. \quad (2.1)$$

(iii) The surface S_α of a typical particle may become charged by adsorbing ν ions of type 1 per unit area, where ν is a function of position on S_α . Then the charge per unit area is $e_1\nu$ and the number p_α of adsorbed ions on particle α is given by

$$p_\alpha = \int_{S_\alpha} \nu dS. \quad (2.2)$$

The total number p of adsorbed ions is given by

$$p = \sum_{\alpha=1}^P p_\alpha = \int_S \nu dS, \quad (2.3)$$

where S is the whole particle-dispersion medium interface comprising the P surfaces S_α . Alternatively the particle may lose ions of type 1 to the dispersion medium as a result of the dissociation of ionogenic groups present on the surface. In this case, let the number of ions of type 1 desorbed per unit area be $-\nu$. Since the desorbed ions leave an equal and opposite charge behind this convention means that the charge per unit area is again $e_1\nu$ and the same notation can be applied as in adsorption. The numbers p_α ($\alpha = 1, \dots, P$) and p are then, like the function ν , negative

(iv) The colloidal particles are all composed of the same substance so that they can be regarded as forming one phase in contact with the separate phase of the dispersion medium and, as assumed in (iii), all surface charge is due to the same type of ion. The restriction to one type of particle is made for simplicity but the analysis can readily be extended to several different types.^{14, 15} There may, as in the clay minerals,³³ be a charge distribution inside the particles. The number of ions of type i in the interior of a given particle α is denoted by N_i^α and the number in the whole interior phase by N_i^I . Thus

$$N_i^I = \sum_{\alpha=1}^P N_i^\alpha = \sum_{\alpha=1}^P \int_{v_\alpha} n_i dv = \int_{V^I} n_i dv, \quad (2.4)$$

where $V^I = \sum_{\alpha=1}^P v_\alpha$ is the total volume of the particles. (Of course, some ion types may not be present in both phases and therefore N_i or N_i^I may be zero for some i .)

(v) The total number of ions of type i in the system is denoted by N_i° so that (since ions of type 1 only are present on the surfaces)

$$N_1^\circ = N_1 + N_1^I + p; \quad N_i^\circ = N_i + N_i^I \quad (i = 2, \dots, m). \quad (2.5)$$

Since the whole system must be electrically neutral the numbers satisfy the relation

$$\sum_{i=1}^m e_i N_i^\circ = 0. \quad (2.6)$$

(vi) Let ψ be the average value of the electric potential at a point in the system. The ion concentrations at a given point depend on ψ through a distribution law, which in view of recent attempts to modify the usual Boltzmann distribution,¹⁶⁻²⁰ will be introduced in the following generalized form. It is assumed that the ion concentrations can be determined from the chemical potentials, μ_i , of the ions by means of the semi-grand partition function

$$\sum_{n_i} g(n_i) \prod_{i=1}^m \{\phi_i \lambda_i \exp(-e_i \psi / kT)\}^{n_i},$$

where the summation is over all possible values of the n_i . Here $g(n_i)$ is the number of configurations available to numbers n_i of the m ion types in a unit volume. For an ion of type i , ϕ_i is the partition function for interactions with neighbouring solvent molecules and of any internal energy levels while $\lambda_i = \exp(\mu_i / kT)$ is its absolute activity. If, as usual, the equilibrium values of the n_i are taken to be those giving the maximum term of the semi-grand partition function then, introducing the notations,

$$\chi = \ln g, \quad \chi_i = \partial \chi / \partial n_i, \quad \xi_i = -kT \ln \phi_i, \quad (2.7)$$

the ion concentrations are given by the m equations

$$\mu_i = -kT \chi_i(n_j) + \xi_i + e_i \psi. \quad (2.8)$$

The potential ψ is taken as zero at a reference point, whose choice is a matter of convenience, in the dispersion medium. The ion concentrations at this reference point will be denoted by n_i° and, since chemical potentials are uniform, it follows from (2.8) that

$$e_i \psi = kT \{\chi_i(n_j) - \chi_i(n_j^\circ)\}. \quad (2.9)$$

The above is essentially a generalization of Grimley's¹⁷ method of obtaining distribution laws. The relation (2.8) implies that the diffuse layers can be divided into small volumes in each of which there is a statistically significant number of ions and yet the variation of ψ can be ignored. This is probably feasible provided the particles are not too small.

(vii) The Boltzmann distribution is obtained as a particular case for

$$g = 1 / \prod_{i=1}^m n_i!, \quad (2.10)$$

when, using Stirling's formula,

$$\chi(n_i) = - \sum_{i=1}^m (n_i \ln n_i - n_i), \quad \chi_i(n_i) = - \ln n_i. \quad (2.11)$$

Then the general distribution law (2.9) reduces to

$$e_i \psi = - kT \ln (n_i / n_i^\circ). \quad (2.12)$$

Other distributions will be introduced in § 4.

(viii) The functions χ and ξ_i will in general be different in the particle interiors and will there be denoted by the symbols χ^i and ξ_i^i ($i = 1, \dots, m$). The ion concentrations will be given by equations similar to (2.8). When the system is in equilibrium the chemical potential of each ion type i is uniform throughout so that the interior distribution is related to that at the reference point in the dispersion medium by the equations

$$e_i \psi + \Delta \xi_i = kT \{ \chi_i^i(n_i) - \chi_i(n_i^\circ) \} \quad (2.13)$$

where $\Delta \xi_i$ is defined by $\Delta \xi_i = \xi_i^i - \xi_i$. (2.14)

If the distribution inside the particles is of the Boltzmann type, then (2.13) becomes

$$n_i = n_i^\circ \exp(-\Delta \xi_i / kT) \exp(-e_i \psi / kT). \quad (2.15)$$

(ix) Instead of the mean potential ψ at a point, the mean potential of an ion located at this point should really be used in the relevant formulae for the free energy. Loeb²⁹ terms the difference the "perturbation potential" and its omission means the neglect of the so-called mutual Debye-Hückel energy of interaction of the ions. We disagree with Ikeda's⁸ suggestion that this neglect is correct in principle.

(x) Owing to the intense electric fields that may exist in the diffuse layers, dielectric saturation will occur and its effect will be considered. However, corrections due to other effects, such as the fluctuation term in the modified Poisson-Boltzmann equation and short-range forces near the particle surfaces will be ignored.

(xi) The free energy of the electric double layers is determined for a fixed particle configuration, Brownian motion not being considered in the present paper.

(xii) Strictly the function F_e evaluated here is the Helmholtz free energy of charging at constant volume and if compressibilities are taken as zero; this is equal to the Gibbs free energy of charging at constant external pressure.

3. DETERMINATION OF THE FREE ENERGY FORM (1.1)

The free energy F_e of the electric double layers of the colloidal particles is evaluated by the Debye-Hückel process of charging all the ions continuously at a uniform rate. Let λ be the fraction of the final charge present on each ion, ρ the volume charge density at any point in the diffuse layers, either outside or within the particles and σ the charge per unit surface area. Then

$$\rho = \lambda \sum_{i=1}^m e_i n_i = \lambda f, \quad \sigma = \lambda e_1 \nu, \quad (3.1)$$

where we denote the ratio ρ/λ by the symbol f . The free energy is given by

$$F_e = 2 \int_0^1 \frac{d\lambda}{\lambda} E_e^*(\lambda), \quad (3.2)$$

$$\text{where} \quad E_e^*(\lambda) = \frac{1}{2} \int_S \psi \sigma \, dS + \frac{1}{2} \int_{V+V_1} \psi \rho \, dv. \quad (3.3)$$

If there is no dielectric saturation in the diffuse layers, $E_e^*(\lambda)$ is the ordinary electrostatic energy of the ion distribution at stage λ of charging (see Levine ⁶). During the charging process all the following quantities are kept constant: (i) $N_i(i = 1, \dots, m)$; (ii) $N_i^\alpha(i = 1, \dots, m, \alpha = 1, \dots, P)$ and hence $N_i^1(i = 1, \dots, m)$; (iii) the surface ion density function ν .

As mentioned in § 2 (vi) the potential ψ is taken as zero at a reference point in the dispersion medium. From the condition (2.6) of electrical neutrality any quantity constant with regard to position but possibly dependent on λ and ν may be subtracted from ψ without changing E_e^* which is therefore not affected by a change of reference point.

The analysis in this section will not involve the form of the ion distribution laws. As a result of dielectric saturation, the dielectric constants ϵ and ϵ^1 in the diffuse layers of the dispersion medium and the particle interiors respectively will be functions of position and of λ . Then in these two regions (which are assumed to be isotropic) Poisson's equation will be

$$\nabla \cdot (\epsilon \nabla \psi) = -4\pi\rho, \quad \nabla \cdot (\epsilon^1 \nabla \psi) = -4\pi\rho. \quad (3.4)$$

If, as often occurs, there is no charge within the particles the second relation of (3.4) reduces to Laplace's equation. At the particle surfaces ψ is continuous and, in addition,

$$\epsilon(\partial\psi/\partial n_s) - \epsilon^1(\partial\psi/\partial n_s)^1 = 4\pi\sigma, \quad (3.5)$$

where $\partial/\partial n_s$ denotes differentiation in a direction perpendicular to S and inward to V^1 and $(\partial\psi/\partial n_s)^1$ denotes the normal component of the electric intensity just inside the particle.

A boundary condition is also required for the outer surface, S_0 , which will usually consist of the inner surface of the wall of the container and, possibly, an interface with the air. It may be assumed immediately that $(\partial\psi/\partial n_s)^1$ is zero on S_0 , which means that the influence of external electric forces on the system is ignored. When the wall is charged a surface integral over S_0 should be added to E_e . If the wall is uncharged then, at all points on S_0 ,

$$\partial\psi/\partial n_s = 0. \quad (3.6)$$

This simple boundary condition is sufficient from a thermodynamic point of view since any other assumption would make the free energy depend significantly on the shape of the container. For dealing with a concentrated colloidal system of identical particles it will usually be expedient to assume a regular arrangement so that the medium is divisible into P similar sub-volumes on each of whose boundaries (3.6) is satisfied (e.g. in the model treated in § 7).

It is not difficult to derive the form (1.1) from the expression (3.2). If the subscript λ denotes differentiation with respect to λ then

$$\rho/\lambda = f = \rho_\lambda - \lambda f_\lambda; \quad \sigma/\lambda = e_1\nu = \sigma_\lambda, \quad (3.7)$$

where the second relation depends on the fact that ν remains constant during the charging process. If (3.3) is substituted into (3.2) and use is made of (3.7), it is found that

$$F_e = \int_0^1 d\lambda \int_S \psi \sigma_\lambda dS + \int_0^1 d\lambda \int_{V+V^1} \psi \rho_\lambda dv - \int_0^1 d\lambda \int_{V+V^1} \lambda \psi f_\lambda dv. \quad (3.8)$$

It will now be shown that the first two terms on the right-hand side of (3.8) are equal to the electrostatic energy in the fully charged state. The electrostatic field energy in the dispersion medium (for any value of λ) is defined by

$$E_e^D(\lambda) = \frac{1}{4\pi} \int_V dv \int_0^D E dD, \quad (3.9)$$

where E and D are the magnitudes of the electric intensity and dielectric displacement respectively. The electrostatic energy $E_e^1(\lambda)$ in the particle interiors is defined

similarly, and the total electrostatic energy is $E_e(\lambda) = E_e^D(\lambda) + E_e^I(\lambda)$. We shall now obtain the variation $\delta E_e(\lambda)$ for arbitrary variations in ρ , σ and ϵ . This general result includes the variation with temperature which will be considered in § 5. We may regard $\epsilon = \epsilon(E, T)$ as a function of E and T and, since $D = \epsilon(E, T)E$, (3.9) may be written in the form

$$E_e^D(\lambda) = \frac{1}{8\pi} \int_V \epsilon E^2 dv + \frac{1}{8\pi} \int_V dv \int_0^E E^2 \left(\frac{\partial \epsilon}{\partial E} \right)_T dE. \quad (3.10)$$

The general variation of any function $f(E, T)$ of E and T is given by

$$\delta f = (\partial f / \partial E) \delta E + (\partial f / \partial T) \delta T.$$

Hence, it is not difficult to show that

$$\delta E_e^D(\lambda) = \frac{1}{4\pi} \int_V E \delta D dv - \frac{\delta T}{8\pi} \int_V E^2 \left(\frac{\partial \epsilon}{\partial T} \right)_E dv + \frac{\delta T}{8\pi} \int_V dv \int_0^E E^2 \frac{\partial^2 \epsilon}{\partial E \partial T} dE. \quad (3.11)$$

A similar expression may be written down for $\delta E_e^I(\lambda)$. On making use of (3.4)-(3.9) it is known from electrostatic theory (see Stratton, *Electromagnetic Theory*, pp. 107-111) that

$$\frac{1}{4\pi} \int_V E \delta D dv = \int_V \psi \delta \rho dv + \frac{1}{4\pi} \int_S \psi \delta (\epsilon \partial \psi / \partial n_s) dS, \quad (3.12)$$

where the symbol δ applied to a position-dependent scalar denotes a change at a fixed point in space. If E is not large then the dielectric saturation may be neglected and so ϵ is a function of T only. The second term on the right of (3.11) now simplifies to $-(\partial \epsilon / \partial T) E_e^D(\lambda)$ and the third term vanishes. A similar expression to (3.11) can be written down for $\delta E_e^I(\lambda)$ and the relation corresponding to (3.12) obtained. Hence, on simplifying the two integrals over S by the use of (3.5), it is readily found that

$$\delta E_e(\lambda) = \int_{V+V_I} \psi \delta \rho dv + \int_S \psi \delta \sigma dS - (\partial \epsilon / \partial T) E_e^D(\lambda) - (\partial \epsilon^I / \partial T) E_e^I(\lambda), \quad (3.13)$$

where, for simplicity, the dielectric saturation is neglected in the last two terms on the right. During the charging process, the temperature is fixed and therefore the last two terms on the right of (3.13) vanish. If we now divide both sides of (3.13) by $\delta \lambda$, it is seen at once that the first two terms in the expression (3.8) for F_e are simply the integral of $\partial E_e(\lambda) / \partial \lambda$ from $\lambda = 0$ to $\lambda = 1$. Hence, if E_e denotes the electrostatic energy in the fully charged state $\lambda = 1$

$$F_e - E_e = - \int_0^1 d\lambda \int_{V+V_I} \lambda \psi f_\lambda dv. \quad (3.14)$$

It is noteworthy that this result is valid under the condition of dielectric saturation and also for a general form of f .

The right-hand side of (3.14) is the part of the free energy due directly to the rearrangement of ions from the initial uniform volume distribution at $\lambda = 0$ to the distribution at $\lambda = 1$. The use of the form $\rho_\lambda - \lambda f_\lambda$ for ρ / λ can now be given a simple physical interpretation. If we put $f_\lambda = 0$ then the charging process is carried out for a fixed volume distribution of ions and it can be seen from (3.14) that the work done in charging, F_e , becomes identical with the electrostatic energy E_e (see Fowler, *Statistical Mechanics*, 2nd ed., p. 267).

If the change to a non-uniform ion distribution which characterizes the development of the double layer field does not involve any alteration in the occupation of the non-electrostatic energy levels then the whole of the ratio $-(F_e - E_e)/T$ will have the nature of an entropy and may be written as S_e . If this is so then (3.14) is equivalent to (1.1) and

$$S_e = S_e^D + S_e^I, \quad (3.15)$$

where
$$S_e^D = T^{-1} \int_0^1 d\lambda \int_V \lambda \psi f_\lambda dv, \quad (3.16)$$

and
$$S_e^I = T^{-1} \int_0^1 d\lambda \int_{V_I} \lambda \psi f_\lambda dv \quad (3.17)$$

are the entropy contributions from the dispersion medium and the particle interiors respectively. In the cases dealt with in detail here (1.1) applies but a case will be mentioned where it does not.

4. EFFECT OF THE ION DISTRIBUTION IN THE DOUBLE-LAYER FIELD

The conclusions expressed by (3.14)-(3.17) were derived without assuming any particular form of distribution law for the ions. We shall now introduce the general distribution laws derived in § 2 (vi) and examine the corresponding form of $F_e - E_e$. Using (2.9) and (3.1) the expression (3.16) for the entropy becomes

$$\begin{aligned} TS_e^D &= \sum_{i=1}^m c_i \int_0^1 d\lambda \int_V \lambda \psi (\partial n_i / \partial \lambda) dv \\ &= kT \sum_{i=1}^m \int_0^1 d\lambda \int_V \chi_i(n_i) (\partial n_i / \partial \lambda) dv - kT \sum_{i=1}^m \int_0^1 \chi_i(n_i^\circ) d\lambda \int_V \partial n_i / \partial \lambda dv. \end{aligned} \quad (4.1)$$

Now, from (1.2)

$$\int_V \partial n_i / \partial \lambda dv = \partial N_i / \partial \lambda = 0 \quad (i = 1, \dots, m), \quad (4.2)$$

so that the second term of the last expression in (4.1) is zero. If it is assumed that, for a given set of n_i , g is independent of λ then, by inverting the order of integration in the remaining term of (4.1) it follows that

$$S_e^D = k \int_V \{ \chi(n_j) - \chi(\bar{n}_j) \} dv = k \int_V \ln g(n_j) / g(\bar{n}_j) dv, \quad (4.3)$$

where $\bar{n}_j = N_j/V$ which is the uniform concentration of ions of type j at $\lambda = 0$ ($j = 1, \dots, m$). If the distribution is of the Boltzmann type so that (2.11) applies, then, by Stirling's formula,

$$S_e^D = -k \sum_{i=1}^m \int_V n_i \ln (n_i / \bar{n}_i) dv. \quad (4.4)$$

In Marcus' model¹³ of a polyelectrolyte there are no particle surfaces or interior phases and the non-uniform ion distribution is caused by charges on macromolecules which are taken as having fixed positions in the dispersion medium. The fixed charge density in the medium is directly proportional to λ so that it makes no contribution to f_λ or, by (3.16), to S_e . Since Marcus assumes a Boltzmann distribution for the mobile ions the entropy is given by (4.4), if the summation is taken over mobile ion types only. Our results thus include the case treated by Marcus.

We shall now introduce the distribution which, as mentioned in § 2 (vi), has been proposed¹⁶⁻²⁰ to account for the volume effect of the hydrated ion. The total number of water molecules per unit volume is taken as independent of position in the diffuse layer and is denoted by n_0 , while it is assumed that a hydration shell of h water molecules is permanently attached to each ion. If n_0/h is denoted by w and a quasi-crystalline lattice with w sites per unit volume available to the ions is assumed then

$$g = w! / \left\{ u! \prod_{i=1}^m n_i! \right\}, \quad (4.5)$$

where $u = w - \sum_{i=1}^m n_i$ is the number per unit volume of empty sites. The distribution law which could be derived by the substitution of $\ln g$, as given by (4.5), into (2.7) and then, after the application of Stirling's formula, into the general distribution relation (2.9) has been obtained by the authors mentioned¹⁶⁻²⁰ (see, in particular, Grimley¹⁷). No study has, however, been made of the effect on the entropy and free energy of assuming (4.5) instead of the Boltzmann distribution (2.10). The electrical entropy corresponding to (4.5) can be obtained at once on substituting the logarithmic form of (4.5) into (4.3) when

$$S_e^D = -k \int_V \left\{ u \ln (u/\bar{u}) + \sum_{i=1}^m n_i \ln (n_i/\bar{n}_i) \right\} dv, \quad (4.6)$$

where $\bar{u} = w - \sum_{i=1}^m \bar{n}_i$ is the number of vacant sites per unit volume in the uncharged state.

The condition that g (and hence χ) depends on λ only through the n_j 's may be secured by keeping the configurational part of the phase space available to the ions fixed during the charging process and hence determined by the fully charged state $\lambda = 1$. Alternatively, it may be pointed out that the real purpose of varying λ from 0 to 1 is to obtain the difference in free energy between the equilibrium ion distribution in the presence of charged particles and the uniform distribution which would exist if the particle charges were removed and such short-range effects as image terms neglected. It seems physically reasonable to postulate the same form of g for these two distributions.

The configuration function g given by (4.5) will depend on λ only through the numbers n_j if (neglecting solvent density variations) the degree of hydration (and hence h) remains fixed. As the energy of hydration is partly electrostatic this seems to present a difficulty³⁴ but the configurational part of the phase space for the ions can be kept fixed by the following device. It must be remembered that the fictitious coupling parameter λ is only introduced into the Gibbs' phase integral, which leads to (3.2), as a mathematical artifice. It is permissible to introduce another coupling parameter, say λ' , into the electrostatic interactions between ions and the molecules in their hydration shells and to treat λ' as independent of λ . Then λ' may be regarded as having already attained its final value of 1 at the beginning of the process of increasing λ from 0 to 1. The part of the free energy dependent on λ' is thus treated as an additive constant. Essentially this (like the general assumption of dependence of g on λ only through the n_j) means that the free energy of interaction between the ions and neighbouring solvent molecules is independent of particle configuration.

Recently Hückel and Krafft³⁴ who were concerned with strong electrolytes, criticized the distribution given by (4.5) as not strictly derived from statistical mechanics. Their alternative approach, however, is not immediately relevant to colloidal diffuse layers, because of two approximations which do not apply to the latter. These are that ψ is small (less than 25 mV) and that the statistical space charges around two neighbouring ions are additive, which must be modified if one ion is replaced by a colloidal particle (see Loeb²⁹ and Williams³⁵). In addition they neglect certain fluctuation terms which Kirkwood³⁶ has estimated to be comparable with the Gronwall-La Mer correction to the original Debye-Hückel theory of electrolytes. Such terms, however, cannot be ignored in any reliable assessment of equation (4.5).

It is now desirable to consider the contribution to $F_e - E_e$ from the integral over the particle interiors in (3.13). This is obviously zero if there is no charge inside the particle surfaces so that $f = 0$ at all points in V^I . It is also zero if the ions inside the particle surfaces are fixed in position so that ρ is proportional to λ (i.e., $f_\lambda = 0$) at each point in V^I and hence the free energy of charging these

ions is identical with their electrostatic energy. The distribution law (2.13) cannot be applied during the charging process since the number N_i^α of ions of each type in the interior of a given particle is fixed and there may therefore not be equilibrium between the particle interior and the dispersion medium. However, at each value of λ there is equilibrium inside each particle and by using a local reference point for the potential in each particle it is easy to derive, in an exactly similar way to (4.3), the relation

$$S_e^I = k \sum_{\alpha=1}^P \int_{v_\alpha} \{X^I(n_j) - X^I(\bar{n}_j^\alpha)\} dv. \quad (4.7)$$

Here the symbol $\bar{n}_i^\alpha = N_i^\alpha/v_\alpha$ is the uniform concentration of ions of type i inside particle α at $\lambda = 0$.

For emulsions, where the particle interiors are liquid, it is possible to assume a Boltzmann ion distribution giving S_e^I the form of a sum of P expressions like (4.4). Another case for which distributions have been derived by Grimley and Mott¹⁶ and by Grimley¹⁷ is that of crystalline particles whose interior ions have a certain amount of mobility due to Schottky defects or "holes". Slightly generalizing Grimley's¹⁷ treatment it will be assumed that there are q_i sites per unit volume available to ions of type i and that, therefore,

$$g^I = \prod_{i=1}^m [q_i! / \{(q_i - n_i)! n_i!\}]. \quad (4.8)$$

If (4.8) is substituted into the expression (4.7) derived for the entropy then, using Stirling's formula and also assuming for simplicity that all $\bar{n}_i^\alpha = \bar{n}_i^I = N_i^I/V^I$,

$$S_e^I = -k \sum_{i=1}^m \int_{V^I} [n_i \ln (n_i/\bar{n}_i^I) + (q_i - n_i) \ln \{(q_i - n_i)/(q_i - \bar{n}_i^I)\}] dv, \quad (4.9)$$

remembering that both N_i^I ($i = 1, \dots, m$) and q_i ($i = 1, \dots, m$) are kept constant during the charging process.

In addition to unoccupied ordinary sites (Schottky defects) certain interstitial sites can be occupied by ions (Frenkel defects). The interstitial ions were given a configuration number of form (3.5) by Grimley,¹⁷ if the symbol w is now taken to denote the number of interstitial sites per unit volume. The case of crystalline particles with both Schottky and Frenkel defects can be dealt with by the methods of this section but no detailed treatment will be given here. It is interesting to note that if the short-range partition function for an ion of type i in an interstitial site is ϕ_i^u , while that for the same ion in an ordinary site is ϕ_i^I then $F_e - E_e$, as given by (2.12) will include a term

$$-kT \sum_{i=1}^m \ln (\phi_i^u/\phi_i^I) \int_{V^I} \Delta n_i dv.$$

Here Δn_i denotes the number per unit volume of ions of type i which transfer from ordinary to interstitial sites, at a given point in the particle interiors, during the charging process. This represents part of the free energy due to the redistribution of ions between the two types of site in the double layer field and will contribute an energy as well as an entropy term to $F_e - E_e$, thus illustrating the point made at the end of § 2.

Where interior charges are zero, dielectric saturation is neglected and the distribution law is given by (2.12), it is possible to derive from (1.1) a simple alternative expression for F_e . Substituting the expression for $\ln n_i$ given by (2.12) in (4.4) and making use of (3.1) and (3.3) at $\lambda = 1$ we have, after simplification,

$$F_e = e_1 \int_S \psi v dS - E_e + kT \sum_{i=1}^m N_i \ln (n_i^0/\bar{n}_i). \quad (4.10)$$

For dilute sols it is not difficult to show that this reduces to the form given by Levine⁵ eqn. (14).

5. VARIATION OF THE FREE ENERGY F_e

In this section changes in the electrical free energy F_e of the fully charged physical state, due to changes in (i) the surface ion distribution function ν , (ii) the numbers N_i^I of ions of each type in the particle interiors, (iii) the total numbers N_i° in the system and (iv) the absolute temperature T will be considered. The function ν varies with the particle configuration, with T and with $N_i^\circ (i = 1, \dots, m)$ in such a way that, for given values of these it takes a form minimizing the total free energy. This also applies to the numbers N_i^I . Changes of F_e with the configuration of the system (i.e. the shape, size and position of the P particle surfaces, S_α , and the outer boundary S_0) will be considered in a later paper; the configuration will here be held constant.

From (3.15) an increment in F_e can be expressed by

$$\delta F_e = \delta E_e - T\delta S_e - S_e\delta T = \delta E_e - T(\delta S_e^D + \delta S_e^I) - S_e\delta T. \quad (5.1)$$

The increment in the entropy term S_e^D is given, using (4.3), by

$$\delta S_e^D = k \sum_{i=1}^m \left\{ \int_V \chi_i(n_j) \delta n_i dv - \chi_i(\bar{n}_j) \delta N_i \right\}, \quad (5.2)$$

assuming that $\chi(n_j)$ depends on the n_j alone and is thus independent of T . Using the distribution law (2.9), (5.2) is readily expressed in the form

$$T\delta S_e^D = kT \sum_{i=1}^m \{ \chi_i(n_j^\circ) - \chi_i(\bar{n}_j) \} \delta N_i + \int_V \psi \delta \rho dv. \quad (5.3)$$

It will be sufficient to consider the case where the average ion concentrations are the same inside all the particles. Then, using (4.5) and (2.13) an equation similar to (5.3) can be deduced for the increment in S_e^I which is then given by

$$T\delta S_e^I = \sum_{i=1}^m [kT\{\chi_i(n_j^\circ) - \chi_i(\bar{n}_j)\} + \Delta \xi_i] \delta N_i^I + \int_{V_I} \psi \delta \rho dv. \quad (5.4)$$

By (5.1) any variation δF_e can be found directly by adding a term $-S_e\delta T$ to the expressions for δE_e , $-T\delta S_e^D$ and $-T\delta S_e^I$ given by (3.13) (at $\lambda = 1$), (5.3) and (5.4) respectively.

Suppose the distribution ν of surface ions is varied by transferring ions of type 1 from the dispersion medium to the particle surfaces, which will be denoted collectively by S , while N_i° and $N_i^I (i = 1, \dots, m)$ are kept constant. Then noting that $\delta p = -\delta N_1$, it is found that

$$\delta F_e = e_1 \int_S \psi \delta \nu dS + kT \{ \chi_1(n_j^\circ) - \chi_1(\bar{n}_j) \} \delta p, \quad (5.5)$$

where p is the total number of adsorbed ions. If the number of adsorbed ions on one particle α only is varied, if ψ has the uniform value ψ_0 on S_α and if the Boltzmann distribution equation (2.11) applies then, from (5.5)

$$\delta F_e / \delta p_\alpha = e_1 \psi_0 - kT \ln (n_1^\circ / \bar{n}_1). \quad (5.6)$$

The meaning of (5.6) becomes clear if it is remembered that F_e is the change in the free energy of the system during a charging process at the beginning of which electrical potentials are all zero and the concentration of ions of any type i is uniform and equal to \bar{n}_i . Since ν remains constant the corresponding change in the chemical potential of a surface ion is $e_1 \psi_0$ while that of an ion of type 1 at the reference point is $kT \ln (n_1^\circ / \bar{n}_1)$. The two terms in (5.5), which applies to a group of δp ions, have a similar meaning. To the best of our knowledge the existence of the second term in (5.6) for concentrated sols has not hitherto been realized.²⁸ Changes of reference point cause equal and opposite changes in the two terms of (5.5) or (5.6) so that the whole expressions are invariant to such changes. They would not possess this necessary invariant property if the second terms were absent.

If, for a dilute sol (in the sense described in § 1) the reference point is taken in the undisturbed bulk of the medium then n_1° is infinitesimally close to \bar{n}_1 and the second term in (5.5) or (5.6) disappears. Then (5.6) reduces to a result already derived by Levine⁵ and used originally by Derjaguin¹ and Verwey and Overbeek³ to obtain F_e . However, we may expect this second term to be significant for a concentrated colloidal system with a small amount of added electrolyte and highly charged particles.

If the surface distribution is fixed then, from (3.13), (5.1), (5.3) and (5.4), and using (2.5),

$$\delta F_e = - \sum_{i=1}^m kT \{ \chi_i(n_j^\circ) - \chi_i(\bar{n}_j) \} \delta N_i^\circ - \sum_{i=1}^m [kT \{ \chi_i(\bar{n}_j) - \chi_i^I(\bar{n}_j^I) \} + \Delta \xi_i] \delta N_i^I - S_e \delta T - (\delta \epsilon / \epsilon) E_e^D - (\delta \epsilon^I / \epsilon^I) E_e^I. \quad (5.7)$$

The electrical part of the chemical potential of an ion of a type is at once seen to be given by

$$\mu_{ie} = (\partial F_e / \partial N_i^\circ)_V = -kT \{ \chi_i(n_j^\circ) - \chi_i(\bar{n}_j) \}. \quad (5.8)$$

This depends on the choice of reference point because, in considering the removal of one ion from the system, the condition of electrical neutrality is violated. For a group of ions of zero total charge, such as those forming a molecule, the sum of the μ_{ie} can be seen, from (2.9), to be independent of the location of the reference point. Since the dielectric constants are regarded as functions of the temperature alone it can also be seen from (5.7) that

$$\partial F_e / \partial T = -S_e - (E_e^D / \epsilon) d\epsilon / dT - (E_e^I / \epsilon^I) d\epsilon^I / dT. \quad (5.9)$$

This reduces to the familiar Gibbs-Helmholtz equation if ϵ and ϵ^I are independent of T , a result derived by Marcus¹³ and, for dilute sols, by Ikeda.⁸ If g depends directly on the temperature, then, by (4.3), a term

$$-kT \int_V \partial \{ \chi(n_j) - \chi(\bar{n}_j) \} / \partial T dv. \quad (5.10)$$

(where the numbers n_j and \bar{n}_j are kept constant) and, by (4.7), a similar integral over the interiors must be added to $\partial F_e / \partial T$. These integrals are obviously zero for Boltzmann distributions (see § 2 (vii)). The "anomalous" terms in (5.9) occur in the theory of strong electrolytes. They are due to the derivation of the free energy F_e from an integral over the configurations of the ions which is not the complete configurational part of the phase integral for the system (see Halpern²¹ and Bjerrum²²). The reason for correction terms like (5.10), which are probably quite small, is essentially similar.

6. THE TOTAL FREE ENERGY

For thermodynamic equilibrium, the free energy change must be zero for the transfer of a small number of ions of type 1 from the dispersion medium to a particle surface and of a small number of ions of any type from the dispersion medium to a particle interior. The free energy must, however, contain not only F_e but also a "chemical" term which we shall denote by F_c and which may be divided into three parts, so that

$$F_c = F_c^S + F_c^D + F_c^I, \quad (6.1)$$

where the three terms on the right-hand side are the chemical free energies of the ions on the surfaces, in the interiors and in the dispersion medium respectively. Now F_c will include the electrostatic part of the self-energy (solvation energy) of the ions. If we introduce the additional coupling parameter λ' , as explained in § 4, in the expression for this self-energy then F_c is the free energy of one system in the "discharged" state $\lambda = 0$, $\lambda' = 1$. The ion concentrations are uniform

in this state and equal to \bar{n}_i in the dispersion medium, so that F_c^D depends on $N_i (i = 1, \dots, m)$ and V and T only. Thus, from (2.8)

$$\partial F_c^D / \partial N_i = \mu_i(\lambda = 0) = -kTX_i(\bar{n}_j) + \xi_i \quad (i = 1, \dots, m). \quad (6.2)$$

Similarly

$$\partial F_c^I / \partial N_i^\alpha = -kTX_i^\alpha(\bar{n}_j^\alpha) + \xi_i^\alpha \quad (i = 1, \dots, m; \alpha = 1, \dots, P). \quad (6.3)$$

The corresponding part of the chemical potential of an ion on the surface at a given point will be denoted by $\mu_c^S(\nu)$, in general a function of ν .

The transfer of δp ions from the dispersion medium to the surfaces means that N_i changes by $-\delta p$ so that, using (6.2)

$$\delta F_c = \delta F_c^S + \delta F_c^D = \int_S \mu_c^S(\nu) \delta \nu \, dS - \{\xi_1 - kTX_1(\bar{n}_j)\} \delta p. \quad (6.4)$$

For thermodynamic equilibrium, the corresponding change $\delta F_e + \delta F_c$ must be zero, so that, from (5.5) and (6.4)

$$\delta(F_e + F_c) = \int_S \{e_1 \psi + \mu_c^S(\nu)\} \delta \nu \, dS - \{\xi_1 - kTX_1(n_j^\circ)\} \delta p = 0. \quad (6.5)$$

Here the variation $\delta \nu$ in the function ν is arbitrary apart from

$$\int_S \delta \nu \, dS = \delta p. \quad (6.6)$$

It follows that a necessary and sufficient condition for equilibrium is that at the particle surfaces

$$e_1 \psi + \mu_c^S(\nu) = \xi_1 - kTX_1(n_j^\circ). \quad (6.7)$$

In principle, for any arbitrary distribution ν of ions on the particle surfaces, it is possible to determine the potential distribution at the surfaces by solving the Poisson-Boltzmann equation. However, the relation (6.7) will determine the form of ν . If, for example, $\mu_c^S(\nu)$ is a constant, independent of ν , then the surface potential ψ must be uniform, which is the condition introduced by Verwey and Overbeek;³ and then ν can be determined by applying (3.5). Finally, again applying (5.7), (6.2) and (6.3), the condition that the free energy change for transfer of ions of type i from the medium to the interior of a particle be zero proves simply to be (2.14), which confirms the consistency of the theory.

The form for the total free energy obtained by Verwey and Overbeek³ for dilute sols can be generalized in the following way. For simplicity, it is assumed that the interior of the particles contain no charge. Also it is convenient to express ν in the form $p\nu_0$, where ν_0 is the *relative* distribution of surface ions and then to imagine that ν_0 is held fixed when varying p . Then

$$\partial(F_e + F_c)/\partial p = \int_S \nu_0 \{e_1 \psi + \mu_c^S(\nu)\} \, dS - \xi_1 + kTX_1(n_j^\circ). \quad (6.8)$$

Let the value of F_c when $p = 0$ be $F_c(0)$, which is a function of V , T and $N_i^\circ (i = 1, \dots, m)$, but is independent of the configuration or number of particles. Then the total free energy for a given particle configuration is $F_c(0) + \Delta F$,

$$\text{where} \quad \Delta F = \int_0^p \{\partial(F_e + F_c)/\partial p\} \, dp = - \int_{p=0}^{p=p} p \, d\{\partial(F_e + F_c)/\partial p\}, \quad (6.9)$$

integrating by parts and using the fact that (6.5) applies in the final (equilibrium) state. From (6.8) and (6.9) using the facts that ξ_1 and ν_0 are independent of p ,

$$\Delta F = - \int_S \, dS \int_{\nu=0}^{\nu=p} \nu \, d\mu_c^S(\nu) - \int_S \, dS \int_0^p e_1 \nu \, d\psi - kT \int_{p=0}^{p=p} p \, dX_1(n_j^\circ). \quad (6.10)$$

The third term here is a consequence of the fact that in a concentrated colloid the chemical potential of an ion of type 1 varies with the surface charge. If the

system is dilute and if $\mu_c^S(\nu)$ is taken as independent of the surface ion density ν , then only the second term remains and (6.10) reduces to the result derived by Verwey and Overbeek.³ If a "Langmuir isotherm" expression for F_e^S is assumed, then in the case of adsorption

$$\mu_c^S(\nu) = kT \ln \nu/(n - \nu) + K, \quad (6.11)$$

where the constant K depends on temperature and n is the number of sites available per unit area of surface for ions of type 1. If, in addition, the Boltzmann law is introduced, then (6.10) becomes

$$\Delta F = -nkT \int_S dS \ln n/(n - \nu) - \int_S dS \int_0^\nu e_1 \nu d\psi + kT \int_{p=0}^{p=p} p d \ln n_1^\circ. \quad (6.12)$$

In desorption, the first terms on the right of (6.11) and (6.12) become respectively

$$kT \ln (n + \nu)/(-\nu) \quad \text{and} \quad -nkT \int_S dS \ln n/(n + \nu). \quad (6.13)$$

From (5.5) we derive

$$\partial F_e / \partial p = e_1 \int_S \nu_0 \psi dS + kT \ln (\bar{n}_1 / n_1^\circ), \quad (6.14)$$

If this is integrated, then, noting that $F_e = 0$ at $p = 0$, an expression for F is obtained from which, by comparison with the equivalent formula (4.10), it is easily seen that

$$\int_S dS \int_0^\nu e_1 \nu d\psi = E_e - kT \sum_{i=1}^m N_i \ln (n_i^\circ / \bar{n}_i) + kT \int_0^p \ln (\bar{n}_1 / n_1^\circ) dp. \quad (6.15)$$

These results will be applied in the following section.

7. FREE ENERGY OF POLYELECTROLYTE OF ROD-SHAPED PARTICLES

Perhaps the simplest application of the general formula (1.1) is to a system containing long identically charged rod-like particles of circular cross-section which are arranged parallel to one another in a regular array, with each rod equidistant from its nearest neighbours. Ionogenic groups on the surface dissociate so that counterions of charge e_1 dissolve into the dispersion medium where they are the only type of ion present. Solutions of the Poisson-Boltzmann equation (in the absence of dielectric saturation and under simplified boundary conditions) have been derived by Alfrey, Berg and Morawetz³⁰ and by Fuoss, Kalchalsky and Lifson³¹ and we need only quote their results. The potential ψ is assumed to depend only on the perpendicular distance from the axis of the particle, denoted by r , and at the boundary $r = R$ of the electrically neutral cylindrical sub-volume assigned to each particle, $d\psi/dr$ is equated to zero. To give the correct total volume V for the medium R must satisfy the relation

$$V = \pi Pl(R^2 - a^2), \quad (7.1)$$

where $r = a$ is the cylindrical surface of a particle and R is its length. The surface charge density, νe_1 , is uniform and if it is assumed that there is no charge in the interior of the particles, the number of counterions N_1 is

$$N_1 = V\bar{n}_1 = -2\pi Pl a \nu \quad (7.2)$$

since, according to the convention introduced in § 1 (iii), ν is negative in desorption. Finally, the reference point is so chosen that $n_1^\circ = \bar{n}_1$.

The potential distribution is given by

$$\psi(r) = \frac{kT}{e_1} \ln \left\{ \frac{2\eta}{\beta^2} \frac{r^2}{R^2 - a^2} \sinh^2 (\beta \ln Ar) \right\}. \quad (7.3)$$

Here $\eta = -2\pi a v e_1^2 / \epsilon kT$ (which is denoted by λ by the above authors) and A and β are constants of integration determined from the boundary conditions, from which one obtains the relation

$$\eta = (1 - \beta^2) / \{1 + \beta \coth(\beta\gamma)\}, \quad (7.4)$$

where $\gamma = \ln(R/a)$. The quantity β can be real or imaginary. The electrostatic energy E_e has been evaluated by Katchalsky and Lifson,^{31, 28} who obtain the expression

$$E_e = \frac{1}{4} Pl \epsilon \int_0^R (d\psi/dr)^2 r dr = Pl \epsilon (kT/e)^2 u(\eta, \gamma), \quad (7.5)$$

$$\text{where } u(\eta, \gamma) = (1 + \beta^2)\gamma + \ln \left[\frac{(1 - \eta)^2 - \beta^2}{(1 - \beta^2)} \right] + \eta, \quad (7.6)$$

a dimensionless quantity, noting that β is given as a function of η and λ by (7.4). Then these authors, using the Debye-Hückel charging method, obtained F_e by numerical integration of E_e (as given by (2.2)) with respect to λ .

However, it is possible to obtain a simple closed formula for F_e in the above case. Since there is only one ion type present in the medium and $n_1^\circ = \bar{n}_1$ it follows from (4.10) that

$$F_e = 2\pi Pl a e_1 v \psi(a) - E_e. \quad (7.7)$$

A comparable simplification would not be possible if more than one type of ion were present in the medium. The potential at the particle surface may be expressed as

$$\psi(a) = -\frac{kT}{e_1 \eta} y(\eta, \gamma), \quad y(\eta, \gamma) = \eta \ln \left[\frac{\{\exp(2\gamma) - 1\} (1 - \eta)^2 - \beta^2}{2\eta} \right]. \quad (7.8)$$

Hence, substituting (7.6) and (7.8) into (7.7), we obtain

$$F_e = Pl \epsilon (kT/e_1)^2 f(\eta, \gamma), \quad f(\eta, \gamma) = y(\eta, \gamma) - u(\eta, \gamma). \quad (7.9)$$

The entropy may be similarly expressed:

$$-TS_e = F_e - E_e = Pl \epsilon (kT/e_1)^2 \{-Ts(\eta, \gamma)\}, \quad (7.10)$$

$$\text{where } Ts(\eta, \gamma) = 2u(\eta, \gamma) - y(\eta, \gamma). \quad (7.11)$$

Values of y , u , f and $-TS$ for various values of the ion density parameter η , calculated for $\eta = 5, 3.5, 2$ and 1 , are displayed in table 1. Katchalsky and Lifson³² and Katchalsky²⁸ give graphs of f as computed by numerical integration, against η for $\gamma = 2.0$ to 5.0 , at intervals of 0.5 and as far as can be seen from the curves for $\gamma = 3, 4.5$, and 2 , our values of f agree with theirs. For low values of η , f is nearly equal to u , which means that the electrostatic energy E_e makes up nearly the whole electrical free energy F_e . However, at the highest values of η studied, $-TS$ is comparable in magnitude with u .

It is quite simple to obtain the total free energy ΔF , defined by (6.12) and (6.13), where a Langmuir adsorption isotherm is assumed. Noting that $n_1^\circ = \bar{n}_1$, $p = V n_1$, and that we have the case of desorption, it readily follows from (6.12)-(6.15) and (7.2) that

$$\Delta F = 2\pi Pl a k T n \ln \frac{n + v}{n} - E_e - k T V \bar{n}_1. \quad (7.12)$$

If, as for a polyelectrolyte, it is assumed that the ionizable groups on each particle form a linear uniform array at separation b , then $n = 1/2\pi a b$ and we readily verify that (7.12) becomes

$$\Delta F = Pl \epsilon (kT/e_1)^2 [s^{-1} \ln(1 - s\eta) - f(\eta, \gamma) - \eta], \quad (7.13)$$

where $s = \epsilon k T b / e_1^2$. This result will be applied to specific polyelectrolytes in a later paper.

TABLE 1

$\gamma = 5$											
β	0.8	0.6	0.4	0.2	0	0.2i	0.4i	0.6i	0.8i	1.0i	1.2i
η	0.1999	0.3993	0.5937	0.7603	0.8333	0.9216	1.0673	1.4199	1.6020	1.8887	2.2787
γ	0.3318	1.2789	2.7014	4.2061	4.9213	5.8177	7.3460	11.170	13.176	16.362	20.739
u	0.1644	0.6239	1.2901	1.9522	2.2498	2.6063	3.1723	4.382	4.922	5.684	6.593
f	0.1673	0.6550	1.4113	2.2538	2.6715	3.2114	4.1737	6.788	8.254	10.678	14.147
$-Ts$	0.0028	0.0311	0.1212	0.3016	0.4217	0.6051	1.0014	2.406	3.332	4.994	7.554
$\gamma = 3.5$											
β	0.8	0.6	0.4	0.2	0	0.2i	0.4i	0.6i	0.8i	1.0i	1.2i
η	0.1993	0.3955	0.5786	0.7213	0.7778	0.8404	0.9300	1.0851	1.3745	1.6350	2.0952
γ	0.2118	0.7987	1.6272	2.4191	2.7604	3.1545	3.7419	4.8136	6.9369	8.9369	12.594
u	0.1046	0.3878	0.7722	1.1233	1.2696	1.4349	1.6739	2.0884	2.8354	3.4635	4.472
f	0.1071	0.4109	0.8550	1.2958	1.4908	1.7196	2.0680	2.7252	4.1015	5.4733	8.122
$-Ts$	0.0025	0.0231	0.0828	0.1725	0.2212	0.2847	0.3941	0.6368	1.2661	2.0098	3.650
$\gamma = 2$											
β	0.8	0.6	0.4	0	0.3i	0.5i	0.6i	0.7i	0.8i	0.9i	1.0i
η	0.1927	0.3721	0.5242	0.6667	0.7577	0.8462	1.1028	1.3295	1.6792	2.2911	2.8167
γ	0.0940	0.3354	0.6404	0.9977	1.2578	1.8630	2.4232	3.3109	4.8136	7.7125	10.389
u	0.0462	0.1628	0.3060	0.4694	0.5857	0.8483	1.0825	1.4375	2.0011	2.9847	3.804
f	0.0476	0.1726	0.3344	0.5283	0.6721	1.0147	1.3406	1.8734	2.8125	4.7278	6.585
$-Ts$	0.0013	0.0098	0.0284	0.0587	0.0864	0.1664	0.2581	0.4359	0.8114	1.7431	2.781
$\gamma = 1$											
β	0.8	0.6	0.4	0	0.4i	0.6i	0.8i	1.0i	1.2i	1.4i	1.6i
η	0.1633	0.3023	0.4092	0.5000	0.5961	0.7246	0.9229	1.2180	1.6638	2.3843	3.7345
γ	0.0264	0.0885	0.1593	0.2341	0.3274	0.4733	0.7426	1.2310	2.1362	3.9279	8.0299
u	0.0131	0.0435	0.0777	0.1137	0.1580	0.2267	0.3512	0.5712	0.9634	1.6939	3.2111
f	0.0134	0.0450	0.0815	0.1204	0.1693	0.2466	0.3914	0.6597	1.1728	2.2339	4.8188
$-Ts$	0.0002	0.0015	0.0038	0.0067	0.0113	0.0199	0.0402	0.0885	0.2094	0.5400	1.6077

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