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Analysis of Thermocapacitive Effects in Electric Double Layers under a Size Modified Mean Field Theory

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Thermodynamics of the electric double layer (EDL) has received renewed interest for their potential application in low-grade waste heat harvesting and reversible heating/cooling in supercapacitors. We apply a size-modified mean field theory to analytically capture the influence on the pseudo-Seebeck coefficient $S = \partial\varphi_0/\partial T)_\sigma$ of different factors, including the electrode potential φ_0, asymmetry in ion sizes and ion concentration, under a fixed electrode surface charge σ. The pseudo-Seebeck coefficient is predicted to scale as φ_0/T at low electrode potentials, but it reaches limiting values when the electrode potential exceeds crossover values due to the steric effect. The qualitative behavior changes substantially, however, when the temperature dependence of the permittivity is taken into account. The pseudo-Seebeck coefficient S is then predicted to scale linearly with φ_0 even at high electrode potentials, significantly over-predicting the experimental values. This suggests a strong influence of phenomena not captured in the mean field theory, such as deviation of local effective permittivity from the bulk value, thermally facilitated adsorption or desorption of ions on electrode surfaces and weakening of ionic associations with temperature.

Thermodynamics of the electric double layer (EDL) formed at the interface between a solid electrode and an electrolyte has received renewed interest for its relevance to low-grade waste heat harvesting using thermos-capacitive cycles[1] and reversible heating/cooling in supercapacitors[2,3]. A key parameter in characterizing these processes is the pseudo-Seebeck coefficient $S = \partial\varphi_0/\partial T)_\sigma$, which is analogous to the Seebeck coefficient. Here, T is the temperature, φ_0 the electrode potential, and σ the electrode surface charge. The basic picture is that EDL systems at higher temperatures require higher electrode potentials to balance a larger driving force from thermal energy that causes broader distributions of counter ions.

Previous studies reported analytic expressions for the surface potential as a function of the temperature under the mean field theory for symmetric ions. Janssen et al.[4] noted that the pre-factor $k_B T$ in the expression for φ_0 provides its predominant temperature dependence, suggesting nearly temperature-independent S. This, however, is an incomplete picture. The pseudo-Seebeck coefficient S is a function of the temperature and, as we shall show, the quasi-linearly temperature-dependence of φ_0 reported in the previous study, in fact, reflects dominant influence of the temperature-dependence of permittivity rather than the intrinsic thermodynamics of EDL.

In the present work, we use a size-modified mean field theory (SMFT) that extends the Korynshev-Kilic-Bazant-Ajdari mean field theory on a 1D flat surface[5] to further examine the influence on S of the electrode potential, asymmetry in ion sizes, ion concentration and temperature-dependent permittivity. Although their deficiencies are well-known[6], we employ the mean field theory in the hope of capturing analytically at least some qualitative features of the pseudo-Seebeck coefficient across a wide range of applied electrode potentials. This then

47 enables us to make some useful, albeit preliminary, assessments on the relative importance of

48 different phenomena occurring at the electrode-electrolyte interfaces.

49 We first describe derivation of the analytic expressions for S. Past studies[5,7] used the

50 lattice gas model to write the Helmholtz free energy in terms of the number of cations, anions,

51 and available lattice sites and obtained potential-dependent ion concentrations in terms of

52 modified Boltzmann distributions. These ionic concentrations were then used to express the

53 charge density distribution ρ:

$$\rho_{SMFT}(u) = \left(\frac{2ec_0}{\gamma}\right) \frac{\exp(-u) - \exp(u)\left[\frac{\xi\exp(u)+\eta}{\xi+\eta}\right]^{\frac{1}{\xi}-1}}{\exp(-u) + (\xi+\eta)\left[\frac{\xi\exp(u)+\eta}{\xi+\eta}\right]^{\frac{1}{\xi}}} \tag{1}$$

54

55 Here, u is the dimensionless potential ($= e\varphi/k_B T$); γ is the packing parameter ($= 2N_0/N$); ξ is the

56 volume ratio between the anion and cation; η is the porosity ($= 2/\gamma - 1 - \xi$); N is the total number

57 of available lattice sites that can be occupied by cations; N_0 is the number of ions in the bulk; and

58 c_0 is the ion concentration in the bulk.

59 We note that in the limit of high positive electrode potentials, Eq. (1) approaches

$$\rho \longrightarrow -\frac{2ec_0}{\xi\gamma} \tag{2}$$

60

61 In the limit of high negative electrode potentials, Eq. (1) approaches

$$\rho \longrightarrow \frac{2ec_0}{\gamma} \tag{3}$$

62

63 The effect of this asymmetric behavior on S will be discussed later. The corresponding

64 expression for the charge density distribution under the Gouy-Chapman theory is

$$\rho_{GC}(u) = -2ec_0\sinh(u) = -ec_0[\exp(u) - \exp(-u)] \tag{4}$$

65

3

67   Equation (1) was substituted into the Poisson equation, which was solved to yield the

68   expression for the electrode surface charge σ as a function of the dimensionless electrode

69   potential u_0:

$$\sigma(u_0)_{SMFT} = \text{sgn}(u_0)\, ec_0 L_D \sqrt{\frac{8}{\gamma}} \sqrt{\ln\left[\exp(-u_0) + (\xi + \eta)\left[\frac{\xi\exp(u_0)+\eta}{\xi+\eta}\right]^{\frac{1}{\xi}}\right] + \ln\left(\frac{\gamma}{2}\right)} \qquad (5)$$

71   Note that φ represents the electric potential, which varies spatially across the EDL, whereas φ_0

72   represents the electric potential at the electrode. The corresponding expression under the Gouy-

73   Chapman theory is

$$\sigma(u_0)_{GC} = 4ec_0 L_D \sinh\left(\frac{u_0}{2}\right) \qquad (6)$$

75   The pre-factor in Eq. (5) is sometimes referred to as the crossover surface charge density σ^*:

$$\sigma^* = ec_0 L_D \sqrt{\frac{8}{\gamma}} \qquad (7)$$

77   σ^* can be interpreted as the surface charge density where the electrode potential becomes

78   sufficiently large such that the ion concentration reaches the steric limit, causing the GC theory

79   to deviate from the SMFT theory. The Debye length L_D is defined as

$$L_D = \sqrt{\frac{\varepsilon\varepsilon_0 k_B T}{2e^2 c_0}} \qquad (8)$$

81   Equation (5) gives σ as a function of u_0 (= $e\varphi_0/k_B T$). That is, the expression for $\sigma(\varphi_0,T)$

82   given above only implicitly relates φ_0 and T. We obtain the derivative $\partial\varphi_0/\partial T)_\sigma$ using the basic

83   relation from the multi-variable calculus:

4

$$S = \left.\frac{\partial \varphi_0}{\partial T}\right)_\sigma = -\frac{\left.\frac{\partial \sigma}{\partial T}\right)_{\varphi_0}}{\left.\frac{\partial \sigma}{\partial \varphi_0}\right)_T} = \frac{\left.\frac{\partial \sigma}{\partial T}\right)_{\varphi_0}}{C_d} \qquad (9)$$

85 The partial derivative $\left.\frac{\partial \sigma}{\partial \varphi_0}\right)_T$ may be recognized as the differential capacitance C_d. By taking

86 the respective derivatives of Eq. (5) required for Eq. (9) and performing rather tedious algebraic

87 manipulations, we obtain one of the key equations of the present work:

$$\left.\frac{\partial \varphi_0}{\partial T}\right)_{\sigma,SMFT} = \frac{\varphi_0}{T} + \frac{k_B}{e}\left(1 + \frac{T}{\varepsilon}\frac{d\varepsilon}{dT}\right)\frac{B\ln(B\gamma/2)}{D} \qquad (10)$$

89 Here B and D are defined as
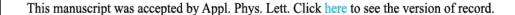
$$B = \exp(-u) + (\xi + \eta)\left[\frac{\xi\exp(u)+\eta}{\xi+\eta}\right]^{\frac{1}{\xi}} \qquad (11)$$

$$D = \exp(-u) - \exp(u)\left[\frac{\xi\exp(u)+\eta}{\xi+\eta}\right]^{\frac{1}{\xi}-1} \qquad (12)$$

92 The corresponding expression under the Gouy-Chapman theory is

$$\left.\frac{\partial \varphi_0}{\partial T}\right)_{\sigma,GC} = \frac{\varphi_0}{T} - \frac{k_B}{2e}\left(1 + \frac{T}{\varepsilon}\frac{d\varepsilon}{dT}\right)\tanh\left(\frac{e\varphi_0}{k_B T}\right) \qquad (13)$$

94 We first consider cases where the temperature dependence of the permittivity can be

95 ignored ($d\varepsilon/dT$). Figure 1 shows the predicted S as a function of the electrode potential φ_0 for

96 some representative values of the relevant parameters. The first terms on the right hand sides of

97 Eqs. (10) and (13) are dominant under low electrode potentials. This can be understood as

98 follows. In the absence of a steric limit on ion concentrations, maintaining the charge

99 distribution ρ is in essence equivalent to keeping the exponent u in the Boltzmann distributions

100 constant (Eq. (4)):

5

$$\frac{\partial}{\partial T}\left(\frac{\varphi}{T}\right) = 0 \quad \rightarrow \quad S = \frac{\partial \varphi}{\partial T} = \frac{\varphi}{T} \qquad (14)$$

This relation is approximate because the Debye length (and hence the spatial extent of the charge density profile) itself is also a function of temperature. Nonetheless, for low electrode potentials, $S = \partial\varphi_0/\partial T)_\sigma$ may be approximated by φ_0/T under both the GC and SMFT theory.

High potential limits of S under the GC theory, however, are very different from those under the SMFT theory. Under the GC theory, S can still well-approximated by φ_0/T. In contrast, under the SMFT theory, S reaches limiting values at high (negative or positive) potentials. This can be understood as follows. Because the charge density is limited by the steric effects, an increase in temperature does not affect the charge density distribution near the electrode surface where the magnitude of the electric potential is larger than crossover values $[\ln(2/\xi\gamma)\ (k_BT/e)$ for positive potentials and $-\ln(2/\gamma)\ (k_BT/e)$ for negative potentials]. An increase in temperature then would only affect the charge density distribution away from the electrode surface where the magnitude of the electric potential is lower. As a result, there is no longer commensurate changes in S.

In the limit of large positive electrode potentials and $\eta \gg \xi$, Eq. (5) can be approximated by ignoring the term $\exp(-u_0)$. The electrode potential can then be expressed as an explicit function of the electrode surface charge:

$$\varphi_0 = -\left(\frac{\xi}{e}\right)k_BT \ln\left[\frac{\eta\gamma\left(\frac{\xi}{\eta}\right)^{\frac{1}{\xi}}}{2}\right] + \frac{\sigma^2\xi\gamma}{4ec_0\varepsilon\varepsilon_0} \qquad (15)$$

In this limit, the electrode potential is a linear function of T. Its derivative S becomes

independent of both the electrode potential and the temperature. It depends only on the ion size

ratio ξ and the packing factor γ:

$$\left.\frac{\partial \varphi}{\partial T}\right)_{\sigma,SMFT,\varphi \to +\infty} \approx -\frac{\xi k_B}{e} \ln \left[\frac{\eta \gamma (\xi/\eta)^{\frac{1}{\xi}}}{2}\right] \qquad (16)$$

Using a similar procedure, we can also find S in the limit of large negative potentials:

$$\left.\frac{\partial \varphi_0}{\partial T}\right)_{\sigma,SMFT,\varphi_0 \to -\infty} \approx \frac{k_B}{e} \ln \left[\frac{\gamma}{2}\right] \qquad (17)$$

These different limiting behaviors under the positive and negative electrode potentials for

electrolytes containing asymmetric ions are expected from the difference between Eqs. (2) and

(3). When anions are smaller than cations ($\xi < 1$), as an example, the maximum allowed density

of anions (at the positive electrode) exceeds that of cations (at the negative electrode). The GC

theory and its predicted linear dependence of S on φ_0 therefore holds to higher values of φ_0 at the

positive electrode interface than at the negative electrode interface. The limiting value of S for

large positive potentials would therefore be larger than that for large negative potentials.

Figure 2 shows the limiting values of S for large positive electrode potential (Eq. (16)) as

a function of the packing parameter γ (i.e. bulk electrolyte ion concentration) for two different

values of ξ. By allowing anions to achieve higher sterically-limited concentrations, the smaller

value of ξ leads to larger values of S_{limit}. For both cases, S_{limit} decreases with increasing packing

parameter γ and hence increasing bulk ion concentration.

So far, our discussion assumed that the permittivity is independent of temperature. In reality,

the permittivity of a solvent, notably water, is itself a function of temperature. Note that our

derivation for S, as expressed in Eq. (10), does account for this temperature-dependence of

permittivity albeit under the mean field approximation of position-independent permittivity.

The term (T/ε) $(d\varepsilon/dT)$ in Eq. (10) can have a magnitude of the order of 1 in some

solvents (e.g., approximately -1.35 for pure water at room temperature) and the temperature

dependence of the permittivity may completely dominate the general behavior of S. In this case,

Eq. (10) may be approximated in the limit of high electrode potentials as:

$$\left.\frac{\partial \varphi_0}{\partial T}\right)_{\sigma,SMFT,|\varphi_0| \to \infty} \approx -\left(\frac{T}{\varepsilon}\frac{d\varepsilon}{dT}\right)\frac{\varphi_0}{T} = -\left(\frac{1}{\varepsilon}\frac{d\varepsilon}{dT}\right)\varphi_0 \qquad (18)$$

That is, the predicted S continues to increase approximately linearly with φ_0 even at high

electrode potentials for non-zero $d\varepsilon/dT$. In fact, the magnitudes of S predicted may significantly

exceed the limiting values calculated from Eq. (16) or Eq. (17) as illustrated in Figure 3.

For typical temperature ranges of practical interest, ε of common solvents varies nearly

linearly with temperature and $d\varepsilon/dT$ can be assumed constant. Equation (18) then predicts S to

be nearly independent of temperature, consistent with the quasi-linear temperature dependence of

φ_0 predicted in the previous study[4]. We would like to emphasize again that this result reflects the

dominant influence of the temperature-dependent permittivity rather than the intrinsic

thermodynamics of EDL captured in the MFT theory.

Experimental values of S reported in the literature from commercial supercapacitors were

approximately 0.5 mV/K at a starting electrode potential of 2.5 V[1]. This is comparable to the

limiting values of 0.1 ~ 0.4 mV/K predicted from Eq. (16) but much smaller than values of the

order of 10 mV/K predicted from Eq. (18) (γ = 0.1~0.5; ξ = 0.1 ~ 1; ε = 50; $d\varepsilon/dT$ = 0.2 K^{-1}).

The electric double layer (EDL) structure is often complicated by multiple factors, such as various conformations of ions, ionic correlations, specific adsorption and electrode morphology. The large discrepancy between the experimentally measured values of S and the prediction from Eq. (10) or Eq. (19) may be explained by one or more of these factors. In fact, some of these factors were suggested as causing the increase in capacitance with increasing temperature despite decreasing solvent permittivity. Such anomaly, observed experimentally but not captured by the current SMFT theory, may also be responsible for the diminished magnitude of S. Recall that the differential capacitance is in the denominator of the expression for S in Eq. (9). Another possibility is that local permittivity is influenced strongly by large local electric fields[8], which then greatly suppresses the temperature dependence of the effective permittivity in the EDL.

As we alluded to, previous studies[9,10] reported that the differential capacitance of EDL capacitors may increase with temperature, in direct contrast to the prediction of traditional models. Some past studies often attributed this positive temperature dependence to the weakening of ionic association at increased temperatures, which leads to more effective screening of the electrode potential. Another study[11] argued instead that decrease in electrolyte viscosity with increasing temperature promotes adsorption of counter ions in electrode pores and is thus responsible for the increase in capacitance. Still other studies, focused on ionic liquids[12], considered competition between two phenomena: 1) overall thickening of the EDL with increasing thermal energy and 2) weakening of specific adsorption of co-ions on an electrode. The latter would enable relatively higher packing of counter-ions and thereby more effective screening of the electrode than otherwise expected. One may then postulate that the reduced

9

182 specific adsorption of co-ions at an increased temperature counteracts a reduction in capacitance

183 accompanying the decrease in permittivity.

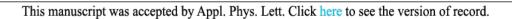184 Related to this discussion are experimental observations[13,14] of thermodiffusion in

185 aqueous suspensions of nano- and micro-scale solid particles. When interpreted using existing

186 theoretical models of the thermodiffusion coefficient, the experimental data suggested that

187 $(T/\varepsilon)(d\varepsilon/dT)$ vary substantially with temperature, changing signs and reaching values as high as

188 +2.44 for aqueous suspensions of polymer particles at room temperature.[14] This value marks a

189 stark departure from the negative value of -1.4 for bulk water, commonly used in previous

190 studies.[13] When averaged over certain temperature windows, the positive contribution of

191 $(T/\varepsilon)(d\varepsilon/dT)$ from one temperature region may then cancel out the negative contribution from

192 another temperature region.

193 The current SMFT theory also does not capture the formation of ordered structures in

194 electrolytes at the electrode interface, such as a multilayer structure described by exponentially

195 decaying sinusoidal oscillations in ion densities perpendicular to the interface, and associated

196 over-screening effects. Unlike the Debye length, the period and magnitude of these oscillations

197 were predicted to decrease with increasing temperature in molecular dynamic simulation of

198 EDLs of a molten salt[15]. At high electrode potentials, however, a previous study using a Landau-

199 Ginzburg-type continuum theory of solvent-free ionic liquids[16] reported that over-screening from

200 short-range correlations is suppressed in favor of steric constraint-induced crowding of counter

201 ions near the electrode.

202 In summary, we apply a size-modified mean field theory to analytically capture the

203 influence of different factors on the pseudo-Seebeck coefficient $S = \partial\varphi_0/\partial T)_\sigma$. We derive

204   analytic expressions of S and show that it scales as φ_0/T at low electrode potentials but reaches

205   limiting values when the electrode potential exceeds crossover values due to the steric effect.

206   The temperature dependence of the permittivity, however, can significantly modify this behavior.

207   For appreciable values of $d\varepsilon/dT$, the parameter S is predicted to scale linearly with φ_0 even at

208   high electrode potentials, significantly over-predicting the experimental values. Our work

209   motivates further experimental and theoretical studies to elucidate the effects of phenomena

210   hitherto not captured under the SMFT theory on the pseudo-Seebeck coefficient.

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212

213   Acknowledgment

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List of Figures

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large negative potential limit

$$\frac{k_B}{e} \ln \left[\frac{\gamma}{2} \right]$$

SMFT

GC theory

$\xi = 0.1$

$\xi = 0.5$

large positive potential limit

$$-\frac{\xi k_B}{e} \ln \left[\frac{\eta \gamma (\xi/\eta)^{\frac{1}{\xi}}}{2} \right]$$

$\gamma = 0.1$

Vertical axis: $S = \partial \varphi_0 / \partial T)_\sigma$ (mV/K)

Horizontal axis: Electrode Potential, φ_0 (V)

SMFT

$\xi = 0.1$

$\xi = 0.5$

$S = \partial \varphi_0 / \partial T)_\sigma$ (mV/K)

Packing Parameter, γ

SMFT

$S = \partial\varphi_0/\partial T)_\sigma$ (mV/K)

$d\varepsilon/dT = -0.2$

$d\varepsilon/dT = -0.1$

$d\varepsilon/dT = 0$

$d\varepsilon/dT = 0.1$

$\xi = 0.25$
$\gamma = 0.25$

Electrode Potential, φ_0 (V)