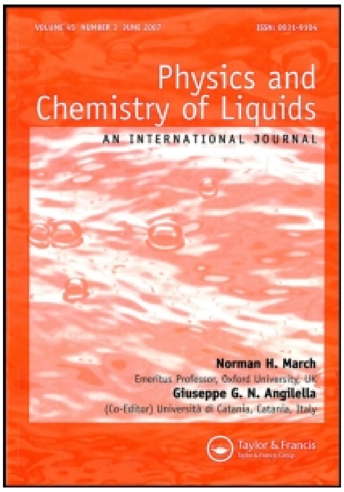

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Entropy Calculations for Charged Spheres and the Entropy of Molten Salts

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We derive an expression for the entropy S of a system of charged hard spheres within the Mean Spherical Approximation (MSA). We study the behaviour of the coulombic contribution as a function of both the charging process and the ionic radii ratio. We find that the latter gives an important ordering contribution to S, which is greatly exaggerated in the MSA. We have also calculated S using the data appropriate for the molten alkali halides. The results compare poorly with the experimental entropies and therefore cast doubts on the MSA as a suitable reference system for molten salts.

1 INTRODUCTION

During the past decade important developments have taken place in our understanding of the thermodynamic and structural properties of molten salts.[1–3]

Progress in the theoretical front has been made possible by computing simulation studies, and the availability of analytic solutions, within the Mean Spherical Approximation (MSA), of a system of charged hard spheres.[5–7] In spite of the known shortcomings of the latter, it is now possible to consider the practicability of using perturbation theories to study the properties of molten salts.

One property which is not directly available from computing simulation studies is the entropy S of the system. During the last few years we have shown that, within the framework of the Gibbs–Bogoliubov variational method, the entropy of simple liquids, where a system of hard spheres (HS) may be thought of as a convenient choice of reference system, is given by

$$S \simeq S_{\mathrm{HS}} \tag{1}$$

and the results thus obtained correlate well with both thermodynamic and structural experimental results.[8–10]

In this work we have attempted a similar analysis for the case of molten salts, in particular molten alkali halides. Although these are binary systems, the charge neutrality condition fixes up the concentration and, consequently, it is the entropy of the system—rather than the entropy of mixing as in other other binary liquids—which is the object of interest.

We are assuming here that a system of charged hard spheres is a suitable reference system for molten salts and, within the MSA, we show that a simple analytic expression for the entropy is obtained. We shall see, however, that unlike the case of simple liquids, the entropy of the reference system, say S_0, is not the only contribution to the entropy of the system, though we argue that it is the dominant term.

The results obtained in this paper confirm this view, but they mirror the shortcomings of the MSA and, hence, tend to correlate better with the experimental results when the ionic radii are of similar size.

In Section 2 we derive the expression for the entropy, which is applied to the molten alkali halides in Section 3. We complete the paper with a discussion of our results.

2 FORMALISM

The starting point in the Gibbs–Bogoliubov approach is the inequality

$$F \leq \tilde{F} \equiv F_0 + \langle \Phi - \Phi_0 \rangle_0 \tag{2}$$

where F and F_0 are, respectively, the Helmholtz free energies of the system and the reference system. We may assume, although it is not necessary for the purposes of this work, that the potential energy of the system is given by the Born–Huggins–Mayer form of the rigid-ion potential[4]

$$\phi_{ij}(r) = Z_i Z_j \frac{e^2}{r} + B_{ij} \exp(-\alpha_{ij} r) - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} \tag{3}$$

i.e., a pairwise interaction which includes a coulombic term, a short-range repulsive term of the Born–Mayer form, and dipole–dipole and dipole-quadrupole attractive van der Waals interactions. For the reference system, we assume the potential to be

$$\phi_{ij}^0(r) = \begin{cases} \infty & r < \sigma_{ij} \\ Z_i Z_j (e^2/r) & r > \sigma_{ij} \end{cases} \tag{4}$$

In both equations, (3) and (4), i and j can be either $+$ or $-$ and, henceforth, we assume the system to be fully ionic, i.e. $|Z_i| = 1$ for all alkali-halides.

Equation (4) is the potential energy of interaction of a system of charged hard-spheres with hard-sphere diameter σ_i, σ_j and such that $\sigma_{+-} = \frac{1}{2}(\sigma_+ + \sigma_-)$. The radial distribution functions for this system, $g_{ij}^0(r)$, depend not only on the relative distance between the ions and on the density n, but also on a parameter—say Λ—which is the ratio between the coulombic and thermal energies of the system.

The second term on the rhs of Eq. (2) is the ensemble average, over the reference system, of the difference between the potential energies of interaction of the system and the reference system, which reads

$$\langle \Phi - \Phi_0 \rangle_0 = \tfrac{1}{2} n \sum_{i,j} x_i x_j \int_{\sigma_{ij}}^{\infty} v_{ij}(r) g_{ij}^0(r) 4\pi r^2 \, \mathrm{d}r \tag{5}$$

where x_i is the concentration of species i, such that $\sum_i x_i = 1$, and we have defined $v_{ij}(r) \equiv \phi_{ij}(r) - \phi_{ij}^0(r)$.

Assuming the hard-sphere diameters to be the variational parameters, these may be chosen by taking $(\partial \tilde{F}/\partial \sigma_i)_{T,V,\sigma_j} = 0$, and we may assume thereafter that $F \simeq \tilde{F}$. In this case the entropy is given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,\sigma_+,\sigma_-} = S_0 - \tfrac{1}{2} n \sum_{i,j} x_i x_j \left[\frac{\partial}{\partial T} \int_{\sigma_{ij}}^{\infty} v_{ij}(r) g_{ij}^0(r) 4\pi r^2 \, \mathrm{d}r\right] \tag{6}$$

The temperature derivative on the second term of the rhs above can go under the integral sign since the only term depending explicitly on the T is $g_{ij}^0(r)$, i.e.

$$\begin{aligned} &- \int_{\sigma_{ij}}^{\infty} v_{ij}(r) \left[\frac{\partial}{\partial T} g_{ij}^0(r)\right] 4\pi r^2 \, \mathrm{d}r \\ &= - \frac{\Lambda}{T} \int_{\sigma_{ij}}^{\infty} v_{ij}(r) \left[\frac{\Lambda}{\partial \Lambda} g_{ij}^0(r)\right] 4\pi r^2 \, \mathrm{d}r \end{aligned} \tag{7}$$

Thus, besides the entropy of the reference system S_0, there is a contribution arising as a result of the temperature dependence of $g_{ij}^0(r)$ and containing the weak, attractive, van der Waals forces. It is generally agreed[3,4] that the long-range character of the coulombic forces, already taken care of in S_0, is the dominant part of the potential and it is therefore sensible to assume that the contribution of S_1 to the entropy of the system will be small compared to S_0.

Since in this work we are only interested in S_0 and have not implemented the variational procedure we shall not make predictions as to the quantitative value of S_1. We shall henceforth drop suffices when referring to the entropy of the reference system.

The analytic solution of a system of charged spheres, within the MSA, for the general case when the hard-sphere diameters are different is due to Blum.[6] As with all approximate theories, different thermodynamic routes lead to different results. We have chosen the internal energy route for two reasons: (i) it is the one which gives better agreement with computing simulation results, and (ii) the expression for the entropy is easily derived.

We start with the thermodynamic relation

$$F = E - TS \tag{8}$$

where F and E denote, respectively, the Helmholtz and the internal energy.

Following Hiroike,[7] we have†

$$\frac{F}{Nk_BT} = \frac{F_{\mathrm{HS}}}{Nk_BT} + \frac{E}{Nk_BT} + \frac{k_BT\Gamma^3}{3\pi n} \tag{9}$$

where F_{HS} is the hard sphere contribution, ΔE the excess energy due to the charges and Γ a generalized Debye inverse screening length, which can be obtained by solving a transcendental equation which we include in the Appendix for completeness. N is the total number of particles in the system such that, in the particular case of the alkali-halides $N_+ = N_- = \frac{1}{2}N$. The second and third terms on the rhs of Eq. (9) are obtained from ΔE via Kirkwood's charging process.

Combining (8) and (9), and bearing in mind that the internal energy is given by $E = \frac{3}{2}Nk_BT + \Delta E$, we have for the entropy

$$S = S_{\mathrm{HS}} + S_C \tag{10}$$

i.e. the entropy of the system of charged hard spheres is just the additive contribution of the hard spheres and the coulombic terms.

For S_{HS} we use the Percus–Yevick compressibility equation of state, which gives[11]

$$S_{\mathrm{HS}} = S_i + S_x + S_{\mathrm{S}} + S_\sigma \tag{11}$$

where the rhs of Eq. (11) is made up by the following contributions:

the ideal gas term:

$$\frac{S_{id}}{Nk_B} = \frac{5}{2} + \ln\left[\frac{1}{n}\left(\frac{mk_BT}{2\pi h^2}\right)^{3/2}\right]; m = m^{x_1}m^{x_2} \tag{12}$$

with m_i the mass of species i;

---

† We have corrected here a misprint which appears in Eq. (11) of Hiroike's paper.

the ideal mixing term

$$\frac{S_x}{Nk_B} = -(x_+ \ln x_+ + x_- \ln x_-) \tag{13}$$

the packing term

$$\frac{S_\eta}{Nk_B} = \ln(1-\eta) + \frac{3}{2}\left[1 - \frac{1}{(1-\eta)^2}\right] \tag{14}$$

where $\eta = \frac{1}{6}\pi n \sum_i x_i \sigma_i^3$;

and the mismatch term

$$\frac{S_\sigma}{Nk_B} = \frac{\pi x_+ x_- n(\sigma_+ - \sigma_-)^2[12(\sigma_+ + \sigma_-) - \pi n(x_+\sigma_+^4 + x_-\sigma_-^4)]}{24(1-\eta)^2} \tag{15}$$

The MSA expression for S_C is given by

$$\frac{S_C}{Nk_B} = -\frac{\Gamma^3}{3\pi n} \tag{16}$$

Note that Eqs. (12) to (16) give the entropy per ion in units of the Boltzmann constant.

Before we proceed to present the numerical results a short discussion of the shortcomings of Eq. (10)—together with Eqs. (11) to (16)—is in order.

We believe that Eq. (10) may be improved in two ways:

i) By using a better approximation than the MSA for the system of charged spheres. Recent analytic results have become available which may be very useful,[12,13] and we are currently trying to find out whether a simple, closed expression, for the entropy may be obtained from the new results. Whatever improvements may be attained, we believe that the additive form of Eq. (10) will be preserved, except that the expressions for S_{HS} and S_C will be different. Moreover we expect that S_C will still be proportional to Γ^3, though its expression may be affected by the improved approximation. In the simpler Debye–Hückel theory this is also the case and this behaviour appears to be the feature of the coulombic contribution to the entropy.

ii) By assuming that the reference system is made up by soft charged spheres. The entropy contribution due to the softness of the repulsive potential is not negligible but is small compared to S_{HS}. This has, in fact, been the conclusion of Kumaravadivel and Evans[14] in considering the contribution of the softness of repulsive potentials to the entropy of liquid metals, and there are no good reasons to believe that it will be different for molten salts.

3 RESULTS

We have used the equations of the preceding section to calculate the entropies of charged hard spheres at thermodynamic states corresponding to the melting points of the alkali halides. In our calculations we have used as input data the experimental densities and temperatures[15] and the ionic radii of Fumi and Tosi.[4] The latter choice is due to the fact that these give a good fitting to the compressibility and partial structure factors of the alkali halides, within the MSA.[16,17]

Before we present these results it is useful to consider how S_C—Eq. (16)—varies with $|Z_i|$ and the ionic radii ratio, which is shown in Figures 1 and 2.

Figure 1 shows how S_C changes as the charges vary from $|Z_i| = 0$ to 1. The main feature here is the degree of "ordering" brought about by the charging process. In these calculations we have assumed that $\sigma_+ = \sigma_- = 3$ Å, $T = 1000$ K and $n = 0.05$ Å^{-3}, which do not differ greatly from molten K Cl.

More important are the changes in S_C as a function of the ratio of the ionic diameters, say σ_+/σ_-, shown in Figure 2. These are large between 0.1

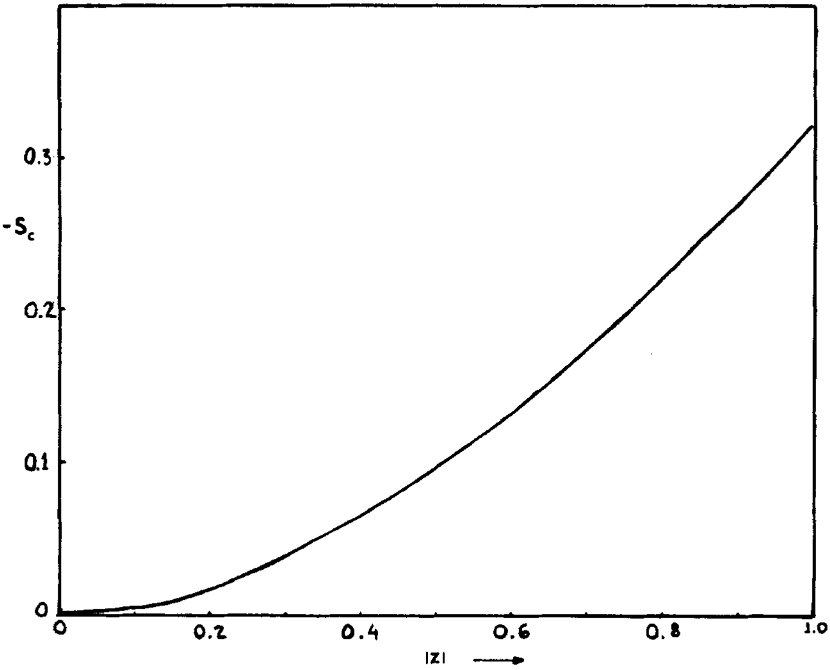

FIGURE 1 Coulombic contribution to the entropy (Eq. 16). Charge variation. Units as in tables. Input data: $\sigma_+ = \sigma = 3.0$ Å; $T = 1000$ K; $n = 0.05$ Å^{-3}.

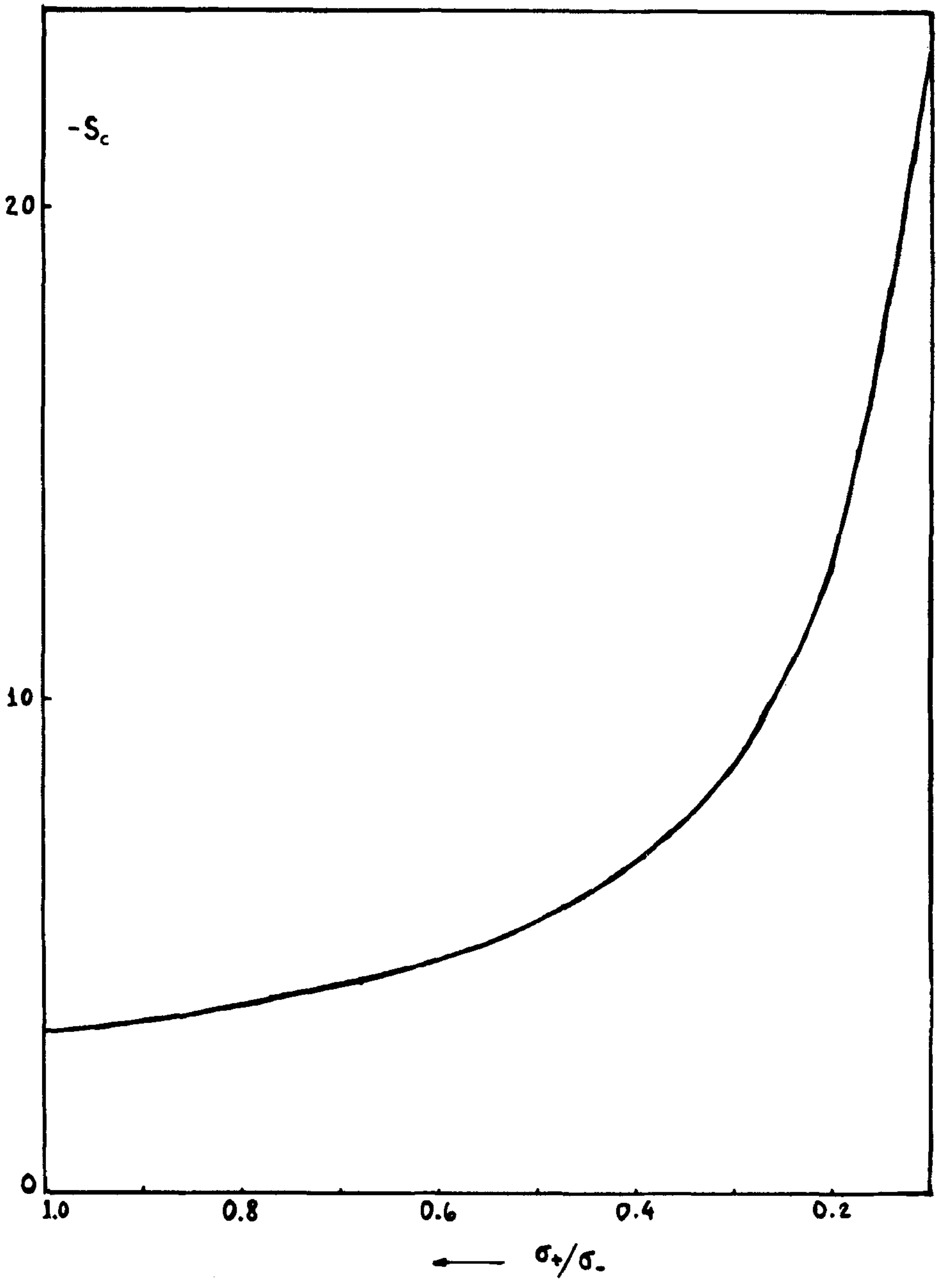

FIGURE 2 Coulombic contribution to the entropy (Eq. 16). Variation of the ionic radii ratio. Units as in tables. Input data: $|Z| = 1.0$; $\sigma_- = 3.0$ Å; $T = 1000$ K; $n = 0.05$ Å^{-3}.

and 0.4 and suggest that the more the ionic diameters differ, the less charge penetration—a measure of the charge fluctuations in the system—will be. This is in line with the recent neutron scattering results of Biggin and Enderby[18] for molten ZnCl which show that the screening of the smaller ions, Z_n^+, by the larger ions, Cl^-, is so complete that the radial distribution functions show no charge penetration at all. Thus, in the light of our results, it follows that the lithium-halide series will show more screening than the other alkali-halides. Recent computing simulation work by Dixon and Gillan[19] on the molten alkali-chloride family do not lend support to the above assertion. There is, of course, slightly less charge penetration in LiCl than the others, but this effect is only just perceptible. The fact is that the MSA exaggerates the effects of ionic size difference, as demonstrated in the recent work of Abernethy *et al.*[20] Consequently we should expect our results to worsen with increasing ionic radii ratio.

We now turn to the entropy calculations for the molten alkali-halides. Table I lists the different contributions to the entropy—Eqs. (12) to (16)—except for the entropy of mixing which has the same value $S_x = 0.693$ for all systems. All values are given as entropy per ion in units of the Boltzmann constant.

TABLE I

Contributions to the entropies of charged hard spheres The temperatures and densities listed in columns 1 and 2 are those given by Lumsden.[15] The Fumi–Tosi diameters—columns 3 and 4—are those listed in Sansgter and Dixon.[4] All values are given as entropy per ion in units of k_B.

Salt	$T(K$	$n/\text{Å}^{-3}$	$\sigma_+/\text{Å}$	$\sigma_-/\text{Å}$	S_{id}	^-S_S	S_σ	^-S_c
LiF	1121	0.0836	1.632	2.358	10.596	2.913	0.162	4.839
NaF	1268	0.0558	2.340	2.358	12.085	2.858	$\simeq 0$	3.568
KF	1131	0.0394	2.926	2.358	12.660	3.074	0.064	3.612
RbF	1048	0.0351	3.174	2.358	13.246	3.408	0.132	3.749
CsF	976	0.0289	3.440	2.358	13.663	3.304	0.196	3.926
LiCl	883	0.0426	1.632	3.170	11.381	3.231	0.466	5.707
NaCl	1073	0.0321	2.340	3.170	12.853	2.819	0.111	3.741
KCl	1043	0.0247	2.926	3.170	13.473	2.710	0.008	3.396
RbCl	995	0.0223	3.174	3.170	14.090	2.779	$\simeq 0$	3.401
CsCl	918	0.0200	3.440	3.170	14.409	2.881	0.009	3.520
LiBr	823	0.0350	1.632	3.432	12.080	3.343	0.563	6.035
NaBr	1020	0.0273	2.340	3.432	13.549	2,890	0.172	3.835
KBr	1007	0.0215	2.926	3.432	14.165	2.732	0.031	3.401
RbBr	965	0.0197	3.174	3.432	14.778	2.783	0.008	3.381
CsBr	909	0.0177	3.440	3.432	15.125	2,827	$\simeq 0$	3.427
LiI	742	0.0279	1.632	3.814	12.497	3,820	0.768	6.548
NaI	933	0.0221	2.340	3,814	13.976	3.092	0.280	4.051
KI	954	0.0177	2.926	3.814	14.627	2.788	0.085	3.449
RbI	920	0.0164	3.174	3.814	15.237	2,813	0.043	3.394
CsI	899	0.0147	3.440	3,814	15.640	2.752	0.013	3.325

TABLE II

Excess entropies of molten alkali-halides The experimental results are taken from the compilation listed in Barin and Knacke.[22] The excess entropy is defined as $\Delta S = S - (S_{id} + S_x)$. All values are given as entropy per ion in units of k_B.

Salt	$-\Delta S$ (this work)	$-\Delta S$ (exptl)
LiF	7.6	3.6
NaF	6.4	3.6
KF	6.6	3.4
RbF	7.0	3.5
CsF	7.0	3.7
LiCl	8.5	3.6
NaCl	6.4	3.3
KCl	6.1	3.4
RbCl	6.2	4.2
CsCl	6.4	3.7
LiBr	8.8	3.7
NaBr	6.6	3.4
KBr	6.1	3.4
RbBr	6.2	4.1
CsBr	6.3	3.8
LiI	9.6	3.8
NaI	6.9	3.4
KI	6.2	3.4
RbI	6.2	4.2
CsI	6.1	3.4

In Table II we compare the experimental results and those obtained in this work for the excess entropy $\Delta S = S - (S_{id} + S_x)$. Since the ideal mixture contribution is model independent, ΔS is, in our view, a stricter test of the approximation used. As in Table I the results quoted are given as the entropy per ion in units of k_B.

Our results show that the MSA constitute a poor reference system for molten salts. Although the trends are right, it is clear that the effects due to charge ordering are over-emphasized, notably when the ionic radii ratio are large.

4 DISCUSSION

Our calculations are based on the assumption that a perturbation theory of the Gibbs-Bogoliubov type is a practical proposition for molten salts, with a system of charged spheres as a reference system. Moreover we have assumed that a rigid ion potential may be construed as a good effective pair potential for such systems. In their seminal computer simulation work on molten salts using a rigid ion potential, Woodcock and Singer[21] have shown that the entropy of molten KCl is reproducible to within 1 %. These authors used a free volume theory expression for the entropy, such that part of the data required is obtained directly from their computer experiment. We have asserted that the contribution to the entropy due to the weak van der Waals forces is small, Indeed, preliminary calculations on molten KCl suggest that it is no more than 0.4 in the units used herein. The contribution due to the soft repulsive potential is unlikely to be larger. Detailed calculations of both contributions are under way and shall be reported on completion.

The main problem, however, is with the MSA. Our calculations lead to the conclusion that we ought to look at the generalised MSA or other related improved approximations and find out whether one of these may become a reasonable reference system for molten salts.

In spite of the preceding remarks, our calculations show some interesting qualitative features which should not be overlooked.

First the ordering effect due to the ionic size difference. Although the consequences of this effect seem to be important, we are not aware of any systematic theoretical study of this problem.

Secondly, our calculations help us to understand why, as a result of charge ordering, the entropy of mixing of liquid binary alloys with ionic tendencies should show a pronounced minima at the stoichiometric composition.

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Appendix

EXPRESSION FOR Γ

Following Hiroike[7] we define

$$\Gamma^2 = \frac{\pi e^2 n}{\varepsilon_0 k_B T} \sum x_i X_i^2 \tag{A1}$$

such that

$$(1 + \Gamma\sigma_i)X_i + \zeta\sigma_i^2 \sum_j n x_j \sigma_j X_j = Z_i \tag{A2}$$

and

$$\zeta = \frac{\pi}{2} \frac{1}{1 - \eta}. \tag{A3}$$

In all our calculations we have taken the dielectric constant ε_0 to be unity. Γ is obtained by solving the transcendental equation (A2)—using (A1) and (A3)—solving for X_i and then replacing these values in (A1) to obtain Γ.

The values for Γ in our work span between 0.8 to 1.6 Å^{-1}.