# Analytical tractability and computability of the phase diagram of ionic compounds in strong electric fields

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**Abstract**

## 1 Introduction

## 2 Gibbs ensemble of ions in different phases

In this article, one explains the statistical mechanics of the ions in the isothermal-isobaric ensemble, also known as the Gibbs ensemble, well described in [4, 5]. This ensemble of particles is in a container which is maintained at constant temperature $T$ and pressure $P$, and has fixed number of particles $N$. The partition function for the Gibbs ensemble can be computed from that of the canonical ensemble as follows [4, 5],

$$Z(N,P,T) = \int_{V=0}^{V=\infty} \frac{PdV}{k_B T} e^{-\frac{PV}{k_B T}} Z_c(N,V,T) \tag{1}$$

where $k_B$ is the Boltzmann constant and $Z_c$ the partition function for the canonical ensemble, which in turn can be computed from the Hamiltonian $H(\mathbf{r},\mathbf{p})$ in conservative systems,

$$Z_c(N,V,T) = \frac{1}{h^{3N}C} \int d^{3N}\mathbf{r} \int d^{3N}\mathbf{p} \quad exp\bigg( - \frac{H(\mathbf{r},\mathbf{p})}{k_B T} \bigg) \tag{2}$$

where $h$ is the Planck's constant introduced to ensure non-dimensionalisation of the partition function and $C$ is the over-counting factor. Note that the integration of the position variables happen over the 'available volume' to the particles from the total volume $V$ of the system. After having computed the partition function, one can extract the complete thermodynamics from the Gibbs' free energy,

$$G(N,P,T) = -k_B T log(Z(N,P,T)) \tag{3}$$

and the Helmholtz free energy $F = G - PV$. In the subsequent sections, we will consider the different assumptions for the Hamiltonian of the ionic compound in its different phases in the presence of strong background electric field and compute the Gibbs partition function from this to prove its analytical tractability, i.e. the existence of a closed-form expression in terms of all the variables in our parameter space which eradicates the necessity to compute the partition function by numerical integration techniques such as Monte Carlo stochastic sampling.

## 2.1 Solid state thermodynamics

In this subsection and the next, we assume for simplicity an electric field $E_0$ in the x-direction of the presumed anisotropy (isotropy for the fluid phases) of the arrangement of ions (prove the choice of the electric field here). About the arrangement of ions, the case of a solid salt, with simple cubic unit cell propagating throughout its crystallography, is considered, for example caesium chloride (CsCl). The radius of caesium ions is 174 pm and those of the chloride ions is 181 pm. One can easily show that the lattice constant computed from the radii and the geometry is $a = 419$ pm. For generalisation to similar binary ionic compounds with the anions and cations of same magnitude of charge, I would assume the *charge* to be $q$ (for instance, in the case of CsCl, $q = 1.6 \times 10^{-19}$ C).

Before proceeding further, it is important to enunciate on the assumption of the *strong electric field*. Throughout this article, until and unless stated, the underlying assumption is that the electric field $E_0$ is way larger than the characteristic electrostatic forces of the ions, i.e.

$$E_0 >> \frac{q}{4\pi\epsilon_0 a^2} \tag{4}$$

where $\epsilon_0 = 8.85 \times 10^{-12}\ Fm^{-1}$ is the vacuum permittivity. Plugging in the numbers one obtains $\frac{q}{4\pi\epsilon_0 a^2} = 8.31 \times 10^8\ NC^{-1}$. The software which was written in [2] to simulate and calculate the models discussed now, or otherwise, considered electric fields of the order of $10^{15}$-$10^{20}\ NC^{-1}$. In this regime, we will *not be considering the influence of Coulombic forces* in the Hamiltonian in this case (or even in the fluid case). Also, I am ignoring the oscillatory modes of the crystal lattice therewith.

The Hamiltonian of this system is fairly simple; $H_- = \frac{-qE_0 na}{k_B T}$ for the negative ions and $H_+ = \frac{qE_0 na}{k_B T}$ for the positive ions, $0 \leq n \leq \lfloor N^{\frac{1}{3}} \rfloor - 1$. Thus the canonical partition function (including the correction factors)

$$Z_c(N,V,T) = \frac{N^{\frac{2}{3}}}{\Gamma(\frac{N}{2}+1)^2} \sum_{n=0}^{\lfloor N^{\frac{1}{3}} \rfloor - 1} e^{-\frac{qE_0na}{k_BT}} + e^{\frac{qE_0na}{k_BT}} \tag{5}$$

$$\implies Z_c(N,V,T) = \frac{2N^{\frac{2}{3}}}{\Gamma(\frac{N}{2}+1)^2} \sum_{n=0}^{\lfloor N^{\frac{1}{3}} \rfloor - 1} sinh\left(\frac{qE_0na}{k_BT}\right)$$

$$\implies Z_c(N,V,T) = \frac{N^{\frac{2}{3}}}{\Gamma(\frac{N}{2}+1)^2} \left(\frac{cosh(\frac{qE_0a}{2k_BT}(2N^{\frac{1}{3}}-1)) - cosh(\frac{qE_0a}{2k_BT})}{sinh(\frac{qE_0a}{2k_BT})}\right)$$

As such, there is no explicit dependence of the canonical partition function on the volume; the implicit relationship between $V$ and $N$ is dictated by the symmetric geometry, $V = Na^3$. This simplifies the calculation of the Gibbs partition function,

$$Z(N,P,T) = \int_{V=0}^{V=\infty} \frac{PdV}{k_BT} e^{-\frac{PV}{k_BT}} Z_c(N,V,T)$$

$$\to Z(N,P,T) = \int_{V=0}^{V=\infty} \frac{PdV}{k_BT} e^{-\frac{PV}{k_BT}} \frac{N^{\frac{2}{3}}}{\Gamma(\frac{N}{2}+1)^2} \left(\frac{cosh(\frac{qE_0a}{2k_BT}(2N^{\frac{1}{3}}-1)) - cosh(\frac{qE_0a}{2k_BT})}{sinh(\frac{qE_0a}{2k_BT})}\right)$$

Therefore,

$$Z(N,P,T) = \frac{N^{\frac{2}{3}}}{\Gamma(\frac{N}{2}+1)^2} \left(\frac{cosh(\frac{qE_0a}{2k_BT}(2N^{\frac{1}{3}}-1)) - cosh(\frac{qE_0a}{2k_BT})}{sinh(\frac{qE_0a}{2k_BT})}\right) \tag{6}$$

The independence of the Gibbs' partition function of the pressure is reminiscent of the solid phase is resistant to external pressure. The usual values of this function has enormous exponents so the log-log plots of the same have been plotted (an example being the figure 1) and explored in [2] and is highly recommended for the reader to explore the symbolic computation. As one can see, the computation of the partition function is fairly trivial in the solid phase, which becomes a bit more involved in the case of fluid phases as is described in the next subsection.

## 2.2 Partition function for the molten salts and salt vapours

As mentioned above, the Hamiltonian of the system will not be including the electrostatic forces between the ions in the strong electric field regime. The system of the molten salt (and also the salt vapour), whenever in an isochoric setup, is assumed to be enclosed in a box of size $L \times L \times L$. The energy

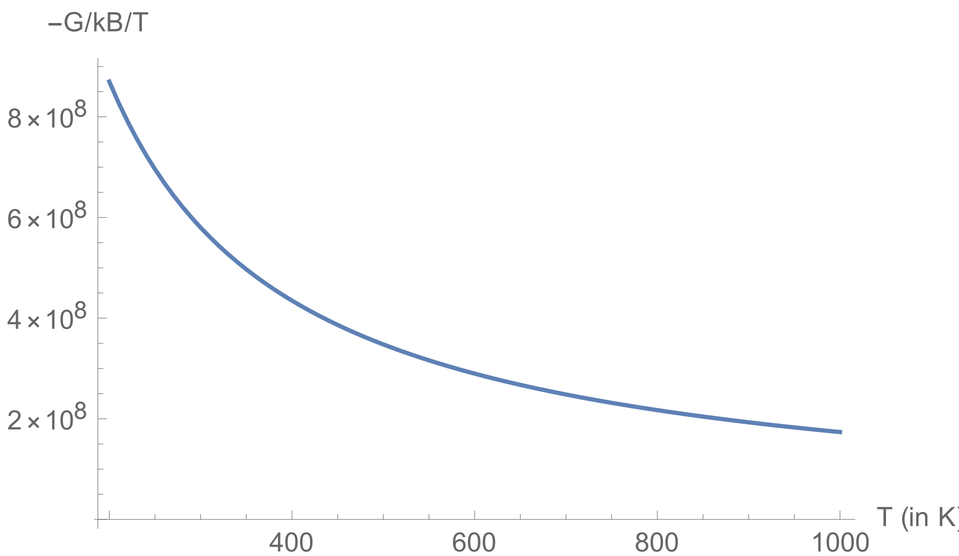


Figure 1: The plot of the non-dimensionalized Gibbs' free energy $\frac{-G}{k_B T}$ against the temperature $T$. Here $N = 5 \times 10^4$, $q = 1.6 \times 10^{-19}$ C, $E_0 = 10^{15}$ $NC^{-1}$ and $a = 419$ pm

for the system (i.e. the Hamiltonian) of the molten salts will be described with the following physical assumption; since there is a translational degree of freedom with a restriction of viscous forces against the ions, the anions rearrange themselves away from the electric field $E_0$, i.e. in the regime $0 \leq x \leq \frac{L}{2}$ and the cations rearrange themselves from the electric field, i.e. in the regime $\frac{L}{2} \leq x \leq L$. The Hamiltonian for the molten salts is given as follows:

$$H = \frac{\mathbf{p} \cdot \mathbf{p}}{2m} - qE_0 x, \forall 0 \leq x \leq \frac{L}{2} \tag{7}$$

and

$$H = \frac{\mathbf{p} \cdot \mathbf{p}}{2m} + qE_0 x, \forall \frac{L}{2} \leq x \leq L \tag{8}$$

where $L = V^{\frac{1}{3}}$. The canonical partition function $Z_{c,-}$ for one single anion,

$$Z_{c,-} = \frac{1}{h^3} \int_{p_x=-\infty}^{\infty} \int_{p_y=-\infty}^{\infty} \int_{p_z=-\infty}^{\infty} \int_V dp_x dp_y dp_z d^3\mathbf{r} \quad e^{-\frac{H(\mathbf{r},\mathbf{p})}{k_B T}}$$

$$= \frac{1}{h^3} \left( \int_{p=-\infty}^{p=\infty} dp \quad e^{-\frac{p^2}{2mk_B T}} \right)^3 L^2 \int_{x=0}^{x=\frac{L}{2}} dx \quad e^{\frac{qE_0 x}{k_B T}}$$

$$\rightarrow Z_{c,-} = \frac{k_B T L^2}{qE_0} \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \left( e^{\frac{qE_0 L}{2k_B T}} - 1 \right)$$

Similarly for the canonical partition function $Z_{c,+}$ for one single cation,

$$Z_{c,+} = \frac{1}{h^3} \int_{p_x=-\infty}^{\infty} \int_{p_y=-\infty}^{\infty} \int_{p_z=-\infty}^{\infty} \int_V dp_x dp_y dp_z d^3\mathbf{r} \quad e^{-\frac{H(\mathbf{r},\mathbf{p})}{k_B T}}$$

$$= \frac{1}{h^3} \left( \int_{p=-\infty}^{p=\infty} dp \quad e^{-\frac{p^2}{2mk_BT}} \right)^3 L^2 \int_{x=\frac{L}{2}}^{x=L} dx \quad e^{\frac{-qE_0 x}{k_B T}}$$

$$\rightarrow Z_{c,+} = \frac{k_B T L^2}{qE_0} \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \left( e^{\frac{-qE_0 L}{2k_B T}} - e^{\frac{-qE_0 L}{k_B T}} \right)$$

From the above simple canonical partition functions, one can extend these to compute the complete canonical partition function.

$$Z_c(N, L, T) = (Z_{c,+})^{\frac{N}{2}} + (Z_{c,-})^{\frac{N}{2}}$$

$$= \left( \frac{k_B T L^2}{qE_0} \right)^{\frac{N}{2}} \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{4}} \left( \left( e^{\frac{-qE_0 L}{2k_B T}} - e^{\frac{-qE_0 L}{k_B T}} \right)^{\frac{N}{2}} + \left( e^{\frac{qE_0 L}{2k_B T}} - 1 \right)^{\frac{N}{2}} \right)$$

Finally I will take into account the over-counting factor $\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)! = \Gamma(\frac{N}{2} + 1)^2$.

$$Z_c(N, L, T) = \frac{L^N}{\Gamma(\frac{N}{2}+1)^2} \left( \frac{k_B T}{qE_0} \right)^{\frac{N}{2}} \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{4}} \left( \left( e^{\frac{-qE_0 L}{2k_B T}} - e^{\frac{-qE_0 L}{k_B T}} \right)^{\frac{N}{2}} + \left( e^{\frac{qE_0 L}{2k_B T}} - 1 \right)^{\frac{N}{2}} \right)$$

We come back to the definition of the Gibbs' partition function $Z(N, P, T) = \int \frac{PdV}{k_B T} \quad Z_c(N, V, T) e^{-\frac{PV}{k_B T}}$. I think it is convenient to resort to the reminiscent algebraic transformation $V = L^3 \rightarrow dV = 3L^2 dL$. Therefore the Gibbs' partition function for the molten salt can be calculated as,

$$Z(N, P, T) = \frac{P}{k_B T} \int_{L=0}^{L=\infty} dL \quad \frac{3L^{N+2}}{\Gamma(\frac{N}{2}+1)^2} e^{\frac{-PL^3}{k_B T}} \left( \frac{k_B T}{qE_0} \right)^{\frac{N}{2}}$$

$$\left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{4}} \left( \left( e^{\frac{-qE_0 L}{2k_B T}} - e^{\frac{-qE_0 L}{k_B T}} \right)^{\frac{N}{2}} + \left( e^{\frac{qE_0 L}{2k_B T}} - 1 \right)^{\frac{N}{2}} \right)$$

$$\rightarrow Z(N, P, T) = \frac{6I_1}{\Gamma\left(\frac{N}{2}+1\right)^2} \left( \frac{k_B T}{qE_0} \right)^{\frac{N}{2}} \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{4}}$$

where $I_1$ is given by the integral,

$$I_1 = \int_{L=0}^{L=\infty} dL \frac{PL^{N+2}}{k_BT} e^{\frac{-PL^3}{k_BT}} cosh\left(\frac{NqE_0L}{k_BT}\right)\left(1 - e^{\frac{-qE_0L}{2k_BT}}\right)^{\frac{N}{2}}$$

This integral comes across as intractable at this stage, which could be proven by Liouville's theorem [2, 6, 7]. There are several attempts towards the solution to this problem made in [2], one of which simplifies this one step further from here using binomial theorem.

$$I_1 = \int_{L=0}^{L=\infty} dL \frac{PL^{N+2}}{k_BT} e^{\frac{-PL^3}{k_BT}} cosh\left(\frac{NqE_0L}{k_BT}\right) \sum_{k=0}^{\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k e^{\frac{-kqE_0L}{2k_BT}}$$

$$\rightarrow I_1 = \sum_{k=0}^{\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k \int_{L=0}^{L=\infty} dL \frac{PL^{N+2}}{k_BT} cosh\left(\frac{NqE_0L}{k_BT}\right) e^{\frac{-PL^3}{k_BT} - \frac{kqE_0L}{2k_BT}}$$

$$\rightarrow I_1 = \left(\frac{k_BT}{P}\right)^{\frac{N}{3}} \sum_{k=0}^{\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k \left(\frac{1}{48}\left(\frac{qE_0}{k_BT}\right)^2 \left(\frac{k_BT}{P}\right)^{\frac{2}{3}} \Gamma\left(\frac{N+5}{3}\right) \left\{(2N+k)^2\right.\right.$$

$$ {}_1F_2\left(\left\{\frac{N+5}{3}\right\}, \left\{\frac{4}{3}, \frac{5}{3}\right\}, \frac{-(qE_0)^3(2N+k)^3}{216(k_BT)^2P}\right) + (2N-k)^2 \quad {}_1F_2\left(\left\{\frac{N+5}{3}\right\}\left\{\frac{4}{3}, \frac{5}{3}\right\}\right.$$

$$\left.\left., \frac{(qE_0)^3(2N-k)^3}{216(k_BT)^2P}\right)\right\} + \frac{1}{12}\frac{qE_0}{k_BT}\left(\frac{k_BT}{P}\right)^{\frac{1}{3}} \Gamma\left(\frac{N+4}{3}\right)\left\{(2N-k) {}_1F_2\left(\left\{\frac{N+4}{3}\right\},\right.\right.$$

$$\left.\left\{\frac{2}{3}, \frac{4}{3}\right\}, \frac{(qE_0)^3(2N-k)^3}{216(k_BT)^2P}\right) - (2N+k) {}_1F_2\left(\left\{\frac{N+4}{3}\right\}, \left\{\frac{2}{3}, \frac{4}{3}\right\}, \frac{-(qE_0)^3(2N+k)^3}{216(k_BT)^2P}\right)\right\}$$

$$+\frac{1}{6}\Gamma\left(\frac{N}{3}+1\right)\left\{\quad {}_1F_2\left(\{\frac{N}{3}+1\}, \{\frac{1}{3}, \frac{2}{3}\}, \frac{(qE_0)^3(2N-k)^3}{216(k_BT)^2P}\right) + \right.$$

$$\left.\left. {}_1F_2\left(\{\frac{N}{3}+1\}, \{\frac{1}{3}, \frac{2}{3}\}, \frac{-(qE_0)^3(2N+k)^3}{216(k_BT)^2P}\right)\right\}\right)$$

Therefore the Gibbs canonical partition function for the molten salts is given by,

$$Z(N,P,T) = \frac{6\Xi}{\Gamma\left(\frac{N}{2}+1\right)^2}\left(\frac{k_BT}{P}\right)^{\frac{N}{3}}\left(\frac{k_BT}{qE_0}\right)^{\frac{N}{2}}\left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{3N}{4}} \tag{9}$$

where $\Xi$ is the following sum, which I would like to call the 'xi-sum',

$$\Xi = \sum_{k=0}^{\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k \left(\frac{1}{48}\left(\frac{qE_0}{k_BT}\right)^2 \left(\frac{k_BT}{P}\right)^{\frac{2}{3}} \Gamma\left(\frac{N+5}{3}\right)\Big\{(2N+k)^2\right.$$

$${}_1F_2\left(\left\{\frac{N+5}{3}\right\}, \left\{\frac{4}{3}, \frac{5}{3}\right\}, \frac{-(qE_0)^3(2N+k)^3}{216(k_BT)^2P}\right) + (2N-k)^2 \quad {}_1F_2\left(\left\{\frac{N+5}{3}\right\}\left\{\frac{4}{3}, \frac{5}{3}\right\}\right.$$

$$\left., \frac{(qE_0)^3(2N-k)^3}{216(k_BT)^2P}\right)\Big\} + \frac{1}{12}\frac{qE_0}{k_BT}\left(\frac{k_BT}{P}\right)^{\frac{1}{3}} \Gamma\left(\frac{N+4}{3}\right)\Big\{(2N-k)\,{}_1F_2\left(\left\{\frac{N+4}{3}\right\},\right.$$

$$\left.\left\{\frac{2}{3}, \frac{4}{3}\right\}, \frac{(qE_0)^3(2N-k)^3}{216(k_BT)^2P}\right) - (2N+k)\,{}_1F_2\left(\left\{\frac{N+4}{3}\right\}, \left\{\frac{2}{3}, \frac{4}{3}\right\}, \frac{-(qE_0)^3(2N+k)^3}{216(k_BT)^2P}\right)\Big\}$$

$$+\frac{1}{6}\Gamma\left(\frac{N}{3}+1\right)\Big\{ \quad {}_1F_2\left(\{\frac{N}{3}+1\}, \{\frac{1}{3}, \frac{2}{3}\}, \frac{(qE_0)^3(2N-k)^3}{216(k_BT)^2P}\right) +$$

$$\left.{}_1F_2\left(\{\frac{N}{3}+1\}, \{\frac{1}{3}, \frac{2}{3}\}, \frac{-(qE_0)^3(2N+k)^3}{216(k_BT)^2P}\right)\Big\}\right)$$

The non-dimensionality of $Z(N, P, T)$ could be slightly tedious and non-trivial. Besides, the above sum is the reduced analytic closed-form expression (cannot be simplified further). In the next section, it will be shown how to compute this sum using a simple Monte Carlo algorithm, and then use the partition function to explore the phase transitions by using the Gibbs' partition function.
For the gases, there is the lowest intensity of resistances to the motion of the molecules. And again, the Coulombic interactions are considered negligible with respect to the electric field. Also, I am considering the assumptions

1. that $\frac{r_a^3}{V}, \frac{r_c^3}{V} << 1$ where $r_a$, $r_c$ are the radii of the anions and cations in the vapour, and $V$ being the volume of the container.

2. that the effects of the induced eddy currents in the plasma and the consequent electromagnetic fields are negligible with respect to the applied electric field $E_0$.

3. that the collision between an anion and a cation is elastic, which is definitely not realistic, but serves as a good theoretical simplification for the model being proposed here.

The Hamiltonian happens to be simple here as well; incorporating assumptions (2) and (3) $H(\mathbf{r}, \mathbf{p}) = \frac{\mathbf{p}\cdot\mathbf{p}}{2m} + qE_0x$ for cations and $H(\mathbf{r}, \mathbf{p}) = \frac{\mathbf{p}\cdot\mathbf{p}}{2m} - qE_0x$ for anions, but *unlike the case of molten salts*, and incorporating the assumption

(1), $\forall x, 0 \leq x \leq L$. Repeating the same exercise as is done for the molten salts, one can compute the canonical partition function for the single cation as,

$$Z_{c,+} = \frac{1}{h^3}\int_{p_x=-\infty}^{p_x=\infty}\int_{p_y=-\infty}^{p_y=\infty}\int_{p_z=-\infty}^{p_z=\infty}\int_{\mathbf{r}\in L\times L\times L} dp_x dp_y dp_z d^3\mathbf{r} e^{-\frac{H(\mathbf{r},\mathbf{p})}{k_BT}}$$

$$Z_{c,+} = \frac{1}{h^3}\Bigg(\int_{p=-\infty}^{p=\infty} dp \quad e^{-\frac{p^2}{2mk_BT}}\Bigg)^3 L^2\int_{x=0}^{x=L} dx \quad e^{\frac{-qE_0x}{k_BT}} = \Bigg(\frac{2\pi mk_BT}{h^2}\Bigg)^{\frac{3}{2}}\frac{k_BTL^2}{qE_0}(1-e^{\frac{-qE_0L}{k_BT}})$$

And similarly, the canonical partition function for the single anion as,

$$Z_{c,-} = \frac{1}{h^3}\Bigg(\int_{p=-\infty}^{p=\infty} dp \quad e^{-\frac{p^2}{2mk_BT}}\Bigg)^3 L^2\int_{x=0}^{x=L} dx \quad e^{\frac{qE_0x}{k_BT}} = \Bigg(\frac{2\pi mk_BT}{h^2}\Bigg)^{\frac{3}{2}}\frac{k_BTL^2}{qE_0}(e^{\frac{qE_0L}{k_BT}}-1)$$

And from these, the overall canonical partition function arrives as,

$$Z_c(N,L,T) = (Z_{c,-})^{\frac{N}{2}} + (Z_{c,+})^{\frac{N}{2}}$$

$$= \Bigg(\frac{2\pi mk_BT}{h^2}\Bigg)^{\frac{3N}{4}}\Bigg(\frac{k_BTL^2}{qE_0}\Bigg)^{\frac{N}{2}}\Bigg\{(1-e^{\frac{-qE_0L}{k_BT}})^{\frac{N}{2}} + (e^{\frac{qE_0L}{k_BT}}-1)^{\frac{N}{2}}\Bigg\}$$

And including the Boltzmann overcounting factor,

$$Z_c(N,L,T) = \frac{1}{\Gamma\Big(\frac{N}{2}+1\Big)^2}\Bigg(\frac{2\pi mk_BT}{h^2}\Bigg)^{\frac{3N}{4}}\Bigg(\frac{k_BTL^2}{qE_0}\Bigg)^{\frac{N}{2}}\Bigg\{(1-e^{\frac{-qE_0L}{k_BT}})^{\frac{N}{2}} + (e^{\frac{qE_0L}{k_BT}}-1)^{\frac{N}{2}}\Bigg\}$$

Trailing along the similar lines of analyses for the molten salt case, the Gibbs' canonical partition function is given by the integral,

$$Z(N,P,T) = \frac{3P}{\Gamma\Big(\frac{N}{2}+1\Big)^2 k_BT}\Bigg(\frac{2\pi mk_BT}{h^2}\Bigg)^{\frac{3N}{4}}$$

$$\Bigg(\frac{k_BT}{qE_0}\Bigg)^{\frac{N}{2}}\int_{L=0}^{L=\infty} dL \quad L^{N+2}e^{\frac{-PL^3}{k_BT}}\Bigg\{(1-e^{\frac{-qE_0L}{k_BT}})^{\frac{N}{2}} + (e^{\frac{qE_0L}{k_BT}}-1)^{\frac{N}{2}}\Bigg\}$$

$$Z(N,P,T) = \frac{3}{\Gamma\Big(\frac{N}{2}+1\Big)^2}\Bigg(\frac{2\pi mk_BT}{h^2}\Bigg)^{\frac{3N}{4}}\Bigg(\frac{k_BT}{qE_0}\Bigg)^{\frac{N}{2}}\Bigg(I_1+I_2\Bigg)$$

where the integrals $I_1$ and $I_2$ are given by,

$$I_1 = \int_{L=0}^{L=\infty} dL \quad \frac{PL^{N+2}}{k_BT}e^{\frac{-PL^3}{k_BT}}\Bigg(1-e^{-\frac{qE_0L}{k_BT}}\Bigg)^{\frac{N}{2}}$$

$$I_2 = \int_{L=0}^{L=\infty} dL \quad \frac{PL^{N+2}}{k_BT} e^{\frac{-PL^3}{k_BT}} \left( e^{\frac{qE_0L}{k_BT}} - 1 \right)^{\frac{N}{2}}$$

I would be simplifying both the integrals using the binomial expansion and then integrating using Risch algorithm [2, 6].

$$I_1 = \int_{L=0}^{L=\infty} dL \quad \frac{PL^{N+2}}{k_BT} e^{\frac{-PL^3}{k_BT}} \left( 1 - e^{-\frac{qE_0L}{k_BT}} \right)^{\frac{N}{2}}$$

$$\rightarrow I_1 = \int_{L=0}^{L=\infty} dL \quad \frac{PL^{N+2}}{k_BT} e^{\frac{-PL^3}{k_BT}} \sum_{k=0}^{k=\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k e^{\frac{-kqE_0L}{k_BT}}$$

$$\rightarrow I_1 = \sum_{k=0}^{k=\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k \int_{L=0}^{L=\infty} dL \quad \frac{PL^{N+2}}{k_BT} e^{\frac{-PL^3}{k_BT} - \frac{kqE_0L}{k_BT}}$$

$$\rightarrow I_1 = \sum_{k=0}^{k=\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k \left[ \frac{1}{3} \left( \frac{k_BT}{P} \right)^{\frac{N}{3}} \Gamma\left( \frac{N}{3} + 1 \right) \quad {}_1F_2\left( \{N/3+1\}, \{1/3, 2/3\}, \frac{-k^3(qE_0)^3}{27(k_BT)^2P} \right) \right.$$

$$- \frac{k}{3} \frac{qE_0}{k_BT} \left( \frac{k_BT}{P} \right)^{\frac{N+1}{3}} \Gamma\left( \frac{N+4}{3} \right) \quad {}_1F_2\left( \{N/3+4/3\}, \{2/3, 4/3\}, \frac{-k^3(qE_0)^3}{27(k_BT)^2P} \right)$$

$$\left. + \frac{k^2}{6} \left( \frac{qE_0}{k_BT} \right)^2 \left( \frac{k_BT}{P} \right)^{\frac{N+2}{3}} \Gamma\left( \frac{N+5}{3} \right) \quad {}_1F_2\left( \{N/3+5/3\}, \{4/3, 5/3\}, \frac{-k^3(qE_0)^3}{27(k_BT)^2P} \right) \right]$$

$$\rightarrow I_1 = \left( \frac{k_BT}{P} \right)^{\frac{N}{3}} \sum_{k=0}^{k=\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k \left[ \frac{1}{3} \Gamma\left( \frac{N}{3} + 1 \right) \quad {}_1F_2\left( \{N/3+1\}, \{1/3, 2/3\}, \frac{-k^3(qE_0)^3}{27(k_BT)^2P} \right) \right.$$

$$- \frac{k}{3} \frac{qE_0}{k_BT} \left( \frac{k_BT}{P} \right)^{\frac{1}{3}} \Gamma\left( \frac{N+4}{3} \right) \quad {}_1F_2\left( \{N/3+4/3\}, \{2/3, 4/3\}, \frac{-k^3(qE_0)^3}{27(k_BT)^2P} \right)$$

$$\left. + \frac{k^2}{6} \left( \frac{qE_0}{k_BT} \right)^2 \left( \frac{k_BT}{P} \right)^{\frac{2}{3}} \Gamma\left( \frac{N+5}{3} \right) \quad {}_1F_2\left( \{N/3+5/3\}, \{4/3, 5/3\}, \frac{-k^3(qE_0)^3}{27(k_BT)^2P} \right) \right]$$

$$I_2 = \int_{L=0}^{L=\infty} dL \quad \frac{PL^{N+2}}{k_BT} e^{-\frac{PL^3}{k_BT}} (e^{\frac{qE_0L}{k_BT}} - 1)^{\frac{N}{2}}$$

$$\rightarrow I_2 = \int_{L=0}^{L=\infty} dL \quad \frac{PL^{N+2}}{k_B T} e^{-\frac{PL^3}{k_B T}} \sum_{k=0}^{k=\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^{\frac{N}{2}-k} e^{\frac{kqE_0 L}{k_B T}}$$

$$\rightarrow I_2 = \sum_{k=0}^{k=\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^{\frac{N}{2}-k} \int_{L=0}^{L=\infty} dL \quad \frac{PL^{N+2}}{k_B T} e^{-\frac{PL^3}{k_B T}+\frac{kqE_0 L}{k_B T}}$$

$$\rightarrow I_2 = \left(\frac{k_B T}{P}\right)^{\frac{N}{3}} \sum_{k=0}^{k=\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^{\frac{N}{2}-k} \left[\frac{1}{3}\Gamma\left(\frac{N}{3}+1\right) \quad {}_1F_2\left(\{N/3+1\},\{1/3,2/3\},\frac{k^3(qE_0)^3}{27(k_B T)^2 P}\right)\right.$$

$$+\frac{k}{3}\frac{qE_0}{k_B T}\left(\frac{k_B T}{P}\right)^{\frac{1}{3}}\Gamma\left(\frac{N+4}{3}\right) \quad {}_1F_2\left(\{N/3+4/3\},\{2/3,4/3\},\frac{k^3(qE_0)^3}{27(k_B T)^2 P}\right)$$

$$\left.+\frac{k^2}{6}\left(\frac{qE_0}{k_B T}\right)^2\left(\frac{k_B T}{P}\right)^{\frac{2}{3}}\Gamma\left(\frac{N+5}{3}\right) \quad {}_1F_2\left(\{N/3+5/3\},\{4/3,5/3\},\frac{k^3(qE_0)^3}{27(k_B T)^2 P}\right)\right]$$

Therefore the canonical partition function for the salt vapours is given by,

$$Z(N,P,T) = \frac{\zeta}{\Gamma\left(\frac{N}{2}+1\right)^2}\left(\frac{k_B T}{P}\right)^{\frac{N}{3}}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{4}}\left(\frac{k_B T}{qE_0}\right)^{\frac{N}{2}} \tag{10}$$

where $\zeta$, which I call as the 'zeta-sum', is given by,

$$\zeta = \sum_{k=0}^{k=\frac{N}{2}} \binom{\frac{N}{2}}{k} (-1)^k \left[\Gamma\left(\frac{N}{3}+1\right) \quad {}_1F_2\left(\{N/3+1\},\{1/3,2/3\},\frac{-k^3(qE_0)^3}{27(k_B T)^2 P}\right)\right.$$

$$-k\frac{qE_0}{k_B T}\left(\frac{k_B T}{P}\right)^{\frac{1}{3}}\Gamma\left(\frac{N+4}{3}\right) \quad {}_1F_2\left(\{N/3+4/3\},\{2/3,4/3\},\frac{-k^3(qE_0)^3}{27(k_B T)^2 P}\right)$$

$$\left.+\frac{k^2}{2}\left(\frac{qE_0}{k_B T}\right)^2\left(\frac{k_B T}{P}\right)^{\frac{2}{3}}\Gamma\left(\frac{N+5}{3}\right) \quad {}_1F_2\left(\{N/3+5/3\},\{4/3,5/3\},\frac{-k^3(qE_0)^3}{27(k_B T)^2 P}\right)\right]$$

$$+\binom{\frac{N}{2}}{k}(-1)^{\frac{N}{2}-k}\left[\Gamma\left(\frac{N}{3}+1\right) \quad {}_1F_2\left(\{N/3+1\},\{1/3,2/3\},\frac{k^3(qE_0)^3}{27(k_B T)^2 P}\right)\right.$$

$$+k\frac{qE_0}{k_B T}\left(\frac{k_B T}{P}\right)^{\frac{1}{3}}\Gamma\left(\frac{N+4}{3}\right) \quad {}_1F_2\left(\{N/3+4/3\},\{2/3,4/3\},\frac{k^3(qE_0)^3}{27(k_B T)^2 P}\right)$$

$$+\frac{k^2}{2}\left(\frac{qE_0}{k_BT}\right)^2\left(\frac{k_BT}{P}\right)^{\frac{2}{3}}\Gamma\left(\frac{N+5}{3}\right)\quad {}_1F_2\left(\{N/3+5/3\},\{4/3,5/3\},\frac{k^3(qE_0)^3}{27(k_BT)^2P}\right)\Bigg]$$

Again, this sum cannot be further reduced to a simpler analytical expression. So this sum needs to be computed, and as has been mentioned as a footnote to the case of molten salts, a simple naive Monte Carlo algorithm has been suggested below with results based on the numerical simulation and its feasibility.

# 3 Monte Carlo methods to compute the partition function and phase transitions

As is illustrated in equations 9 and 10, the summations (the xi sum for molten salts and the zeta sum for ionic vapours) required to compute the partition function for the molten salt and the ionic vapour cases do not have a reduced closed-form expression from there on, so one requires to compute it by hand. For $N$ particles, there are $\frac{N}{2}+1$ terms for both the equations 9 and 10. Direct computation of this sum for a system involving macroscopic number of particles ($N \sim 10^{23}$ particles, much similar to the Avogadro's constant) becomes computationally expensive (or rather galactic). This motivates one to adopt a quick approximate algorithm such as the Monte Carlo methods [8]; this adopts choosing terms randomly (by obeying a specific probability distribution) from all the summands in the partition function and including them if they contribute to a large fraction of the final answer. It's good to try with the case of molten salts and assuming the terms being chosen from a uniform distribution; such an attempt in Wolfram Language has been illustrated in figure 2 [2]. The risk with this idea is the error with respect to the original answer; the reason is clearly visible in the plot shown in figure 3, because upon choosing the terms which are equally likely, the ones with the lower $k$ might be ignored abruptly before the while loop of the algorithm in figure 2. The variation of the  The quick remedy is an empirical probability distribution that favours the larger terms more than the smaller ones: a function $f(x)$ defined as,

$$f(x) = \begin{cases} \frac{3}{N} - \frac{4x}{N^2} & 0 \le x \le \frac{N}{2} \\ 0 & x < 0 \lor x > \frac{N}{2} \end{cases} \tag{11}$$

And using $f(x)$, the modified algorithm looks like the Wolfram code segment shown in figure 4. This modification improves the correctness of the algorithm as shown in the figure 5 (the metric of correctness being the percentage of the sum computed by the modified algorithm of the actual total sum) and also the time complexity as shown in the figure 6. After being convinced of the performance of this algorithm, one can now compute the xi sum of the partition function and plot the Gibbs free energy for the molten salt case [2].

```
In[111]:= Block[
  {sum, temp, addtemp, err = 0.01, storebox, k, q = 1.6*10^(-19), L = 10^(-3), E0 = 10^12, kB = 1.38*10^(-23), n = 50, T = 800, P = 10^5},
  sum = 0;
  storebox = {};
  While[True,
   k = RandomInteger[{0, n/2}];
   If[MemberQ[storebox, k],
    Continue[],
    AppendTo[storebox, k];
   ];
   temp = 1/48 (q E0/kB/T)^2 (kB T/P)^(2/3) Gamma[(n + 5)/3]
     ((2 n + k)^2 HypergeometricPFQ[{(n + 5)/3}, {4/3, 5/3}, -(q E0)^3 (2 n + k)^3/216/(kB T)^2/P] +
       (2 n - k)^2 HypergeometricPFQ[{(n + 5)/3}, {4/3, 5/3}, (q E0)^3 (2 n - k)^3/216/(kB T)^2/P]);
   temp = temp + 1/12 (q E0/kB/T) (kB T/P)^(1/3) Gamma[(n + 4)/3]
      (-(2 n + k) HypergeometricPFQ[{(n + 4)/3}, {2/3, 4/3}, -(q E0)^3 (2 n + k)^3/216/(kB T)^2/P] +
        (2 n - k) HypergeometricPFQ[{(n + 4)/3}, {2/3, 4/3}, (q E0)^3 (2 n - k)^3/216/(kB T)^2/P]);
   temp =
    temp + 1/6 Gamma[(n + 3)/3] (HypergeometricPFQ[{(n + 3)/3}, {1/3, 2/3}, -(q E0)^3 (2 n + k)^3/216/(kB T)^2/P] +
        HypergeometricPFQ[{(n + 3)/3}, {1/3, 2/3}, (q E0)^3 (2 n - k)^3/216/(kB T)^2/P]);
   addtemp = Binomial[n/2, k] (-1)^k temp;
   If[Abs[addtemp]/Abs[sum + 0.01] < err,
    Break[],
    sum = sum + addtemp;
   ]
  ];
  Print[Log[Abs[sum]]]; (* You got to return this to the function you want to fit it in .... *)
 ]

2.201384147924690004080037×10^9
```

Figure 2: The Wolfram code fragment that compute the xi sum for the molten salts assuming uniform distribution $U[0, \frac{N}{2}]$.

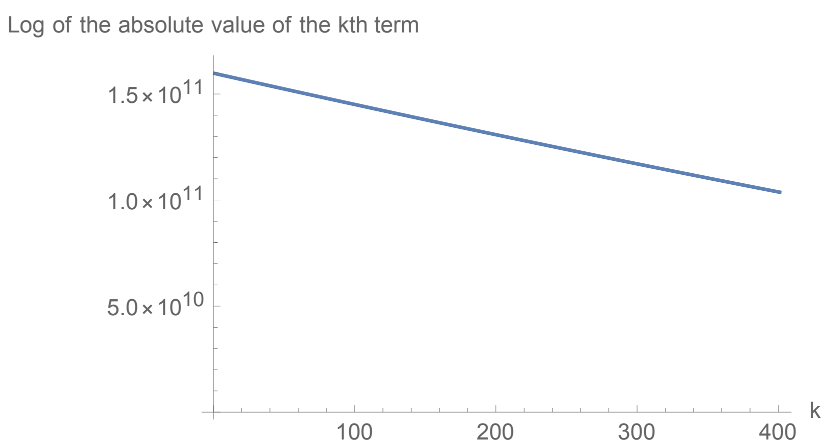


Figure 3: The variation of log of the absolute value of the terms of the xi sum. Here $n = 800$, $q = 1.6 \times 10^{-19}$ C, $E_0 = 10^{12} NC^{-1}$, $T = 800K$, $P = 1$ atm. The probability distribution is designed accordingly.

```
Block[
 {sum, temp, addtemp, err = 0.01, storebox, k, q = 1.6*10^(-19), L = 10^(-3), E0 = 10^12, kB = 1.38*10^(-23), n = 50,
  T = 800, P = 10^5, x},
 sum = 0;
 storebox = {};
 While[True,
  k = RandomVariate[ProbabilityDistribution[3/n - 4 x/n^2, {x, 0, n/2, 1}]];
  If[MemberQ[storebox, k],
   Continue[],
   AppendTo[storebox, k];
  ];
  temp = 1/48 (q E0/kB/T)^2 (kB T/P)^(2/3) Gamma[(n + 5)/3]
    ((2 n + k)^2 HypergeometricPFQ[{(n + 5)/3}, {4/3, 5/3}, -(q E0)^3 (2 n + k)^3/216/(kB T)^2/P] +
      (2 n - k)^2 HypergeometricPFQ[{(n + 5)/3}, {4/3, 5/3}, (q E0)^3 (2 n - k)^3/216/(kB T)^2/P]);
  temp = temp + 1/12 (q E0/kB/T) (kB T/P)^(1/3) Gamma[(n + 4)/3]
     (-(2 n + k) HypergeometricPFQ[{(n + 4)/3}, {2/3, 4/3}, -(q E0)^3 (2 n + k)^3/216/(kB T)^2/P] +
       (2 n - k) HypergeometricPFQ[{(n + 4)/3}, {2/3, 4/3}, (q E0)^3 (2 n - k)^3/216/(kB T)^2/P]);
  temp =
   temp + 1/6 Gamma[(n + 3)/3] (HypergeometricPFQ[{(n + 3)/3}, {1/3, 2/3}, -(q E0)^3 (2 n + k)^3/216/(kB T)^2/P] +
       HypergeometricPFQ[{(n + 3)/3}, {1/3, 2/3}, (q E0)^3 (2 n - k)^3/216/(kB T)^2/P]);
  addtemp = Binomial[n/2, k] (-1)^k temp;
  If[Abs[addtemp]/Abs[sum + 0.01] < err,
   Break[],
   sum = sum + addtemp;
  ]
 ];
 Print[Log[Abs[sum]]]; (* You got to return this to the function you want to fit it in .... *)
]
2.42021082749357622998515 3×10^9
```

Figure 4: The Wolfram code fragment that compute the xi sum for the molten salts assuming the probability distribution function $f(x)$.

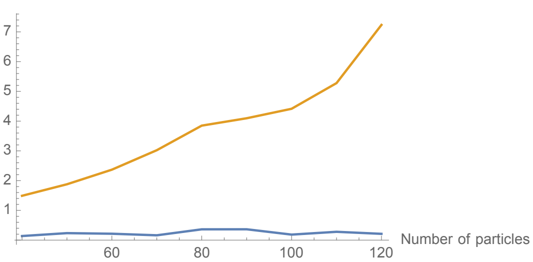


Figure 5: The time complexity of the modified algorithm against that to compute the complete sum and its variation with the number of particles $N$. The time measured is in seconds as plotted along the y-axis.

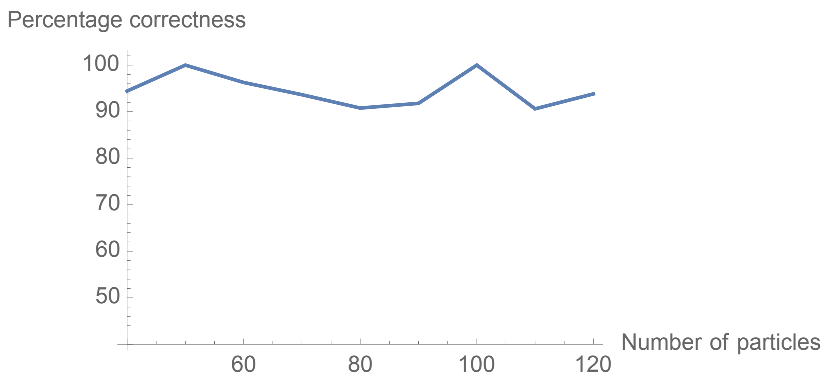


Figure 6: The percentage of the sum computed by the modified algorithm of the actual total sum for a small number of particles.

# 4 Conclusion

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