

## 6.5: Coulomb Systems - Plasmas and the Electron Gas

### Electrostatic Potential

Coulomb systems are particularly interesting in statistical mechanics because of their long-ranged forces, which result in the phenomenon of *screening*. Long-ranged forces wreak havoc with the Mayer cluster expansion, since the Mayer function is no longer integrable. Thus, the virial expansion fails, and new techniques need to be applied to reveal the physics of plasmas.

The potential energy of a Coulomb system is

$$U = \frac{1}{2} \int d^d \mathbf{r} \int d^d \mathbf{r}' \rho(\mathbf{r}) u(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') , \quad (6.5.1)$$

where  $\rho(\mathbf{r})$  is the charge density and  $u(\mathbf{r})$ , which has the dimensions of (energy)/(charge)<sup>2</sup>, satisfies

$$\nabla^2 u(\mathbf{r} - \mathbf{r}') = -4\pi \delta(\mathbf{r} - \mathbf{r}') . \quad (6.5.2)$$

Thus,

$$u(\mathbf{r}) = \begin{cases} -2\pi |x - x'| & , d = 1 \\ -2 \ln |\mathbf{r} - \mathbf{r}'| & , d = 2 \\ |\mathbf{r} - \mathbf{r}'|^{-1} & , d = 3 . \end{cases} \quad (6.5.3)$$

For discrete particles, the charge density  $\rho(\mathbf{r})$  is given by

$$\rho(\mathbf{r}) = \sum_i q_i \delta(\mathbf{r} - \mathbf{x}_i) , \quad (6.5.4)$$

where  $q_i$  is the charge of the  $i^{\text{th}}$  particle. We will assume two types of charges:  $q = \pm e$ , with  $e > 0$ . The electric potential is

$$\phi(\mathbf{r}) = \int d^d \mathbf{r}' u(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') = \sum_i q_i u(\mathbf{r} - \mathbf{x}_i) . \quad (6.5.5)$$

This satisfies the Poisson equation,

$$\nabla^2 \phi(\mathbf{r}) = -4\pi \rho(\mathbf{r}) . \quad (6.5.6)$$

The total potential energy can be written as

$$U = \frac{1}{2} \int d^d \mathbf{r} \phi(\mathbf{r}) \rho(\mathbf{r}) = \frac{1}{2} \sum_i q_i \phi(\mathbf{x}_i) . \quad (6.5.7)$$

### Debye-Hückel theory

We now write the grand partition function:

$$\Xi(T, V, \mu_+, \mu_-) = \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} \frac{1}{N_+!} e^{\beta \mu_+ N_+} \lambda_+^{-N_+ d} \cdot \frac{1}{N_-!} e^{\beta \mu_- N_-} \lambda_-^{-N_- d} \\ \cdot \int d^d \mathbf{r}_1 \cdots \int d^d \mathbf{r}_{N_+ + N_-} e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_{N_+ + N_-})} .$$

We now adopt a *mean field* approach, known as *Debye-Hückel theory*, writing

$$\rho(\mathbf{r}) = \rho^{av}(\mathbf{r}) + \delta \rho(\mathbf{r}) \\ \phi(\mathbf{r}) = \phi^{av}(\mathbf{r}) + \delta \phi(\mathbf{r}) .$$

We then have

$$\begin{aligned}
 U &= \frac{1}{2} \int d^d r [\rho^{av}(\mathbf{r}) + \delta\rho(\mathbf{r})] \cdot [\phi^{av}(\mathbf{r}) + \delta\phi(\mathbf{r})] \\
 &\quad \equiv U_0 \\
 &= \underbrace{-\frac{1}{2} \int d^d r \rho^{av}(\mathbf{r}) \phi^{av}(\mathbf{r})}_{\equiv U_0} + \underbrace{\int d^d r \phi^{av}(\mathbf{r}) \rho(\mathbf{r}) + \frac{1}{2} \int d^d r \delta\rho(\mathbf{r}) \delta\phi(\mathbf{r})}_{\text{ignore fluctuation term}} .
 \end{aligned}$$

We apply the mean field approximation in each region of space, which leads to

$$\begin{aligned}
 \Omega(T, V, \mu_+, \mu_-) &= -k_B T \lambda_+^{-d} z_+ \int d^d r \exp\left(-\frac{e \phi^{av}(\mathbf{r})}{k_B T}\right) \\
 &\quad - k_B T \lambda_-^{-d} z_- \int d^d r \exp\left(+\frac{e \phi^{av}(\mathbf{r})}{k_B T}\right) ,
 \end{aligned}$$

where

$$\lambda_{\pm} = \left( \frac{2\pi\hbar^2}{m_{\pm} k_B T} \right) , \quad z_{\pm} = \exp\left(\frac{\mu_{\pm}}{k_B T}\right) . \quad (6.5.8)$$

The charge density is therefore

$$\rho(\mathbf{r}) = \frac{\delta\Omega}{\delta\phi^{av}(\mathbf{r})} = e \lambda_+^{-d} z_+ \exp\left(-\frac{e \phi(\mathbf{r})}{k_B T}\right) - e \lambda_-^{-d} z_- \exp\left(+\frac{e \phi(\mathbf{r})}{k_B T}\right) , \quad (6.5.9)$$

where we have now dropped the superscript on  $\phi^{av}(\mathbf{r})$  for convenience. At  $r \rightarrow \infty$ , we assume charge neutrality and  $\phi(\infty) = 0$ . Thus

$$\lambda_+^{-d} z_+ = n_+(\infty) = \lambda_-^{-d} z_- = n_-(\infty) \equiv n_{\infty} , \quad (6.5.10)$$

where  $n_{\infty}$  is the ionic density of either species at infinity. Therefore,

$$\rho(\mathbf{r}) = -2e n_{\infty} \sinh\left(\frac{e \phi(\mathbf{r})}{k_B T}\right) . \quad (6.5.11)$$

We now invoke Poisson's equation,

$$\nabla^2 \phi = 8\pi e n_{\infty} \sinh(\beta e \phi) - 4\pi \rho_{ext} , \quad (6.5.12)$$

where  $\rho_{ext}$  is an externally imposed charge density.

If  $e\phi \ll k_B T$ , we can expand the sinh function and obtain

$$\nabla^2 \phi = \kappa_D^2 \phi - 4\pi \rho_{ext} , \quad (6.5.13)$$

where

$$\kappa_D = \left( \frac{8\pi n_{\infty} e^2}{k_B T} \right)^{1/2} , \quad \lambda_D = \left( \frac{k_B T}{8\pi n_{\infty} e^2} \right)^{1/2} . \quad (6.5.14)$$

The quantity  $\lambda_D$  is known as the *Debye screening length*. Consider, for example, a point charge  $Q$  located at the origin. We then solve Poisson's equation in the weak field limit,

$$\nabla^2 \phi = \kappa_D^2 \phi - 4\pi Q \delta(\mathbf{r}) . \quad (6.5.15)$$

Fourier transforming, we obtain

$$-\mathbf{q}^2 \hat{\phi}(\mathbf{q}) = \kappa_D^2 \hat{\phi}(\mathbf{q}) - 4\pi Q \quad \implies \quad \hat{\phi}(\mathbf{q}) = \frac{4\pi Q}{\mathbf{q}^2 + \kappa_D^2} . \quad (6.5.16)$$

Transforming back to real space, we obtain, in three dimensions, the Yukawa potential,

$$\phi(\mathbf{r}) = \int \frac{d^3 q}{(2\pi)^3} \frac{4\pi Q e^{i\mathbf{q}\cdot\mathbf{r}}}{\mathbf{q}^2 + \kappa_D^2} = \frac{Q}{r} \cdot e^{-\kappa_D r} . \quad (6.5.17)$$

This solution must break down sufficiently close to  $r = 0$ , since the assumption  $e\phi(r) \ll k_B T$  is no longer valid there. However, for larger  $r$ , the Yukawa form is increasingly accurate.

For another example, consider an electrolyte held between two conducting plates, one at potential  $\phi(x=0) = 0$  and the other at potential  $\phi(x=L) = V$ , where  $\hat{\mathbf{x}}$  is normal to the plane of the plates. Again assuming a weak field  $e\phi \ll k_B T$ , we solve  $\nabla^2 \phi = \kappa_D^2 \phi$  and obtain

$$\phi(x) = A e^{\kappa_D x} + B e^{-\kappa_D x} . \quad (6.5.18)$$

We fix the constants  $A$  and  $B$  by invoking the boundary conditions, which results in

$$\phi(x) = V \cdot \frac{\sinh(\kappa_D x)}{\sinh(\kappa_D L)} . \quad (6.5.19)$$

Debye-Hückel theory is valid provided  $n_\infty \lambda_D^3 \gg 1$ , so that the statistical assumption of many charges in a screening volume is justified.

### The Electron Gas: Thomas-Fermi Screening

Assuming  $k_B T \ll \varepsilon_F$ , thermal fluctuations are unimportant and we may assume  $T = 0$ . In the same spirit as the Debye-Hückel approach, we assume a slowly varying mean electrostatic potential  $\phi(\mathbf{r})$ . Locally, we can write

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} - e\phi(\mathbf{r}) . \quad (6.5.20)$$

Thus, the Fermi wavevector  $k_F$  is spatially varying, according to the relation

$$k_F(\mathbf{r}) = \left[ \frac{2m}{\hbar^2} (\varepsilon_F + e\phi(\mathbf{r})) \right]^{1/2} . \quad (6.5.21)$$

The local electron number density is

$$n(\mathbf{r}) = \frac{k_F^3(\mathbf{r})}{3\pi^2} = n_\infty \left( 1 + \frac{e\phi(\mathbf{r})}{\varepsilon_F} \right)^{3/2} . \quad (6.5.22)$$

In the presence of a uniform compensating positive background charge  $\rho_+ = en_\infty$ , Poisson's equation takes the form

$$\nabla^2 \phi = 4\pi e n_\infty \cdot \left[ \left( 1 + \frac{e\phi(\mathbf{r})}{\varepsilon_F} \right)^{3/2} - 1 \right] - 4\pi \rho_{ext}(\mathbf{r}) . \quad (6.5.23)$$

If  $e\phi \ll \varepsilon_F$ , we may expand in powers of the ratio, obtaining

$$\nabla^2 \phi = \frac{6\pi n_\infty e^2}{\varepsilon_F} \phi \equiv \kappa_{TF}^2 \phi - 4\pi \rho_{ext}(\mathbf{r}) . \quad (6.5.24)$$

Here,  $\kappa_{TF}$  is the *Thomas-Fermi wavevector*,

$$\kappa_{TF} = \left( \frac{6\pi n_\infty e^2}{\varepsilon_F} \right)^{1/2} . \quad (6.5.25)$$

Thomas-Fermi theory is valid provided  $n_\infty \lambda_{TF}^3 \gg 1$ , where  $\lambda_{TF} = \kappa_{TF}^{-1}$ , so that the statistical assumption of many electrons in a screening volume is justified.

One important application of Thomas-Fermi screening is to the theory of metals. In a metal, the outer, valence electrons of each atom are stripped away from the positively charged ionic core and enter into itinerant, plane-wave-like states. These states disperse with some  $\varepsilon(\mathbf{k})$  function (that is periodic in the Brillouin zone, under  $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{G}$ , where  $\mathbf{G}$  is a reciprocal lattice vector), and at  $T = 0$  this *energy band* is filled up to the Fermi level  $\varepsilon_F$ , as Fermi statistics dictates. (In some cases, there may be several bands at the Fermi level, as we saw in the case of yttrium.) The set of ionic cores then acts as a neutralizing positive background. In a perfect crystal, the ionic cores are distributed periodically, and the positive background is approximately uniform. A charged impurity in a metal, such as a zinc atom in a copper matrix, has a different nuclear charge and a different valency than the host. The charge of the ionic core, when valence electrons are stripped away, differs from that of the host ions, and therefore the impurity acts

as a *local charge impurity*. For example, copper has an electronic configuration of  $[Ar] 3d^{10} 4s^1$ . The  $4s$  electron forms an energy band which contains the Fermi surface. Zinc has a configuration of  $[Ar] 3d^{10} 4s^2$ , and in a Cu matrix the Zn gives up its two  $4s$  electrons into the  $4s$  conduction band, leaving behind a charge  $+2$  ionic core. The Cu cores have charge  $+1$  since each copper atom contributed only one  $4s$  electron to the conduction band. The conduction band electrons neutralize the uniform positive background of the Cu ion cores. What is left is an extra  $Q = +e$  nuclear charge at the Zn site, and one extra  $4s$  conduction band electron. The  $Q = +e$  impurity is, however, *screened* by the electrons, and at distances greater than an atomic radius the potential that a given electron sees due to the Zn core is of the Yukawa form,

$$\phi(\mathbf{r}) = \frac{Q}{r} \cdot e^{-\kappa_{TF} r} . \quad (6.5.26)$$

We should take care, however, that the dispersion  $\varepsilon(\mathbf{k})$  for the conduction band in a metal is not necessarily of the free electron form  $\varepsilon(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m$ . To linear order in the potential, however, the change in the local electronic density is

$$\delta n(\mathbf{r}) = e \phi(\mathbf{r}) g(\varepsilon_F) , \quad (6.5.27)$$

where  $g(\varepsilon_F)$  is the density of states at the Fermi energy. Thus, in a metal, we should write

$$\begin{aligned} \nabla^2 \phi &= (-4\pi)(-e \delta n) \\ &= 4\pi e^2 g(\varepsilon_F) \phi = \kappa_{TF}^2 \phi , \end{aligned}$$

where

$$\kappa_{TF} = \sqrt{4\pi e^2 g(\varepsilon_F)} . \quad (6.5.28)$$

The value of  $g(\varepsilon_F)$  will depend on the form of the dispersion. For ballistic bands with an effective mass  $m^*$ , the formula in Equation 6.5.24 still applies.

### The Thomas-Fermi atom

Consider an ion formed of a nucleus of charge  $+Ze$  and an electron cloud of charge  $-Ne$ . The net ionic charge is then  $(Z - N)e$ . Since we will be interested in atomic scales, we can no longer assume a weak field limit and we must retain the full nonlinear screening theory, for which

$$\nabla^2 \phi(\mathbf{r}) = 4\pi e \cdot \frac{(2m)^{3/2}}{3\pi^2 \hbar^3} \left( \varepsilon_F + e\phi(\mathbf{r}) \right)^{3/2} - 4\pi Ze \delta(\mathbf{r}) . \quad (6.5.29)$$

We assume an isotropic solution. It is then convenient to define

$$\varepsilon_F + e\phi(\mathbf{r}) = \frac{Ze^2}{r} \cdot \chi(r/r_0) , \quad (6.5.30)$$

where  $r_0$  is yet to be determined. As  $r \rightarrow 0$  we expect  $\chi \rightarrow 1$  since the nuclear charge is then unscreened. We then have

$$\nabla^2 \left\{ \frac{Ze^2}{r} \cdot \chi(r/r_0) \right\} = \frac{1}{r_0^2} \frac{Ze^2}{r} \chi''(r/r_0) , \quad (6.5.31)$$

thus we arrive at the **Thomas-Fermi equation**,

$$\chi''(t) = \frac{1}{\sqrt{t}} \chi^{3/2}(t) , \quad (6.5.32)$$

with  $r = t r_0$ , provided we take

$$r_0 = \frac{\hbar^2}{2me^2} \left( \frac{3\pi}{4\sqrt{Z}} \right)^{2/3} = 0.885 Z^{-1/3} a_B , \quad (6.5.33)$$

where  $a_B = \frac{\hbar^2}{me^2} = 0.529 \text{ \AA}$  is the Bohr radius. The TF equation is subject to the following boundary conditions:

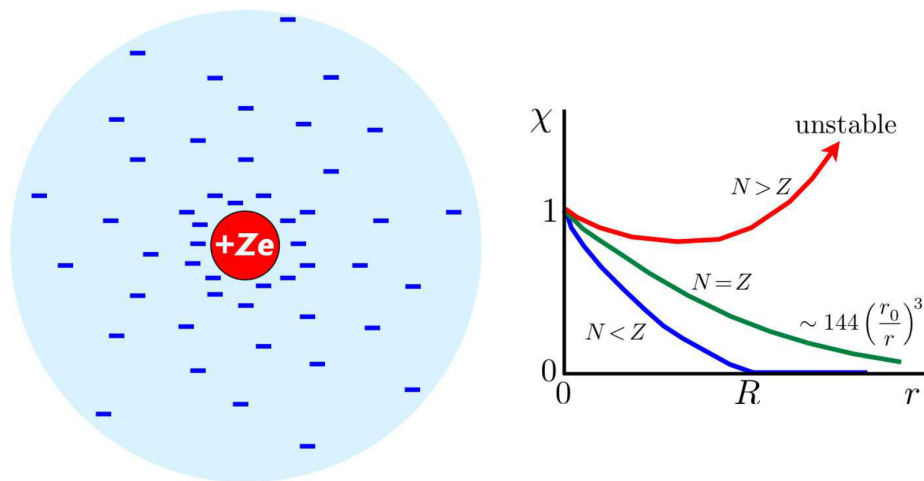


Figure 6.5.1: The Thomas-Fermi atom consists of a nuclear charge  $+Ze$  surrounded by  $N$  electrons distributed in a cloud. The electric potential  $\phi(\mathbf{r})$  felt by any electron at position  $\mathbf{r}$  is screened by the electrons within this radius, resulting in a self-consistent potential  $\phi(\mathbf{r}) = \phi_0 + (Ze^2/r) \chi(r/r_0)$ .

- At short distances, the nucleus is unscreened,

$$\chi(0) = 1. \quad (6.5.34)$$

- For positive ions, with  $N < Z$ , there is perfect screening at the ionic boundary  $R = t^* r_0$ , where  $\chi(t^*) = 0$ . This requires

$$\mathbf{E} = -\nabla\phi = \left[ -\frac{Ze^2}{R^2} \chi(R/r_0) + \frac{Ze^2}{Rr_0} \chi'(R/r_0) \right] \hat{\mathbf{r}} = \frac{(Z-N)e}{R^2} \hat{\mathbf{r}}. \quad (6.5.35)$$

This requires

$$-t^* \chi'(t^*) = 1 - \frac{N}{Z}. \quad (6.5.36)$$

For an atom, with  $N = Z$ , the asymptotic solution to the TF equation is a power law, and by inspection is found to be  $\chi(t) \sim C t^{-3}$ , where  $C$  is a constant. The constant follows from the TF equation, which yields  $12C = C^{3/2}$ , hence  $C = 144$ . Thus, a neutral TF atom has a density with a power law tail, with  $\rho \sim r^{-6}$ . TF ions with  $N > Z$  are unstable.

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