Chapter 6

Pseudo Atoms and the Quantum Ornstein Zernike Relations

6.1 Introduction: Two Component Electron-Ion Mixtures

As noted in the last chapter, at a near fundamental level, liquid metals are complex binary fluids consisting of ions in a sea of conduction electrons. The ions can usually be treated classically while the electrons are typically degenerate and must be treated quantum-mechanically. The traditional theoretical description of liquid metals simplifies this picture by defining effective potentials (pair and higher) between the ions; in the statistical physics of the ions the electron liquid enters only indirectly through the density dependence of these potentials[1]. The development of *ab-initio* simulation techniques based on a Density Functional Theory (DFT) treatment of the electrons[2] bypasses effective potentials and is capable of treating liquid metals (and other materials) as fundamental mixtures of ions and electrons.

However, because of computational constraints, these simulation techniques are limited to relatively small system sizes and as such have difficulty describing first-order phase transitions such as freezing[3]. Concurrent to the development of the electronic DFT, semi-analytic theories based on approximations to the classical *free-energy* density functional of liquids described by pair potentials have successfully given quantitative theories of *inhomogeneous* liquids, including various first order phase transitions[4]. To date these classical theories have been largely limited to *state-independent* potentials while in systems like liquid metals, where the effective potentials are *state-dependent* (i.e. they depend on a thermodynamic variable) the properties of a first order phase transition clearly depend on the potentials, but these in turn depend on the state of the system through the average density. Thus a treatment of liquid metals based on approximations to the *free-energy* functional of a fully coupled quantum-classical electron-ion system, without the shortcomings of effective potentials in classical DFT (nor the problems of finite system size in electron DFT simulations) would be highly desirable.

A first attempt in this direction by Xu, Hansen and Chandler[6] developed a free-energy functional approach to the melting of an ion-electron plasma; in the binary mixture of (classical) ions and (quantum) conduction electrons, the ions freeze while the electrons remain in itinerant states. Xu *et. al.* used a heuristic approximation to the electron-ion correlation function of the system they studied (essentially monatomic hydrogen at extremely high density) and found large variations in melting predictions depending on which electron-ion theory they used. Although these calculations were outside any known experimental regime, they provided a proof of principle that such theories could be successfully constructed and they clearly demonstrated that the liquid state two-body electron-ion direct correlation function is crucial to quantitative accuracy. A successful development of these techniques depends critically on accurate liquid state correlation functions.

Thus the first step of this ambitious general program entails gaining a more coherent understanding of correlation functions in the full electron-ion mixture. This is the focus of the present chapter.

6.2 Hamiltonian and Free-Energy of a Two Component Electron-Ion Mixture

The Hamiltonian for a non-relativistic two-component mixture of N_I ions of valence $Z = Z$ and N_e electrons interacting through potentials $v_{\alpha\beta}(\vec{r}, \vec{r}')$ is given, for the charge-neutral case $N_e = ZN_I$, by:

$$\hat{H} = \sum_{\alpha=I,e} \left\{ \hat{T}_\alpha + \frac{1}{2} \sum_{\beta=I,e} \int_V d\vec{r} \int_V d\vec{r}' v^{(2)}_{\alpha\beta}(\vec{r} - \vec{r}') \hat{n}_{\alpha\beta}(\vec{r}, \vec{r}') \right\}. \tag{6.1}$$

The two-particle density operator is given by:

$$\hat{n}_{\alpha\beta}(\vec{r}, \vec{r}') = \hat{n}^{(1)}_\alpha(\vec{r}) \hat{n}^{(1)}_\beta(\vec{r}') - \delta_{\alpha\beta} \delta(\vec{r} - \vec{r}') \hat{n}^{(1)}_\alpha(\vec{r}), \tag{6.2}$$

a trace over electron and ion coordinates relates this to the pair-correlation or radial distribution functions:

$$\langle \hat{n}_{\alpha\beta}(\vec{r}, \vec{r}') \rangle = \left\langle \hat{n}^{(1)}_\alpha(\vec{r}) \right\rangle \left\langle \hat{n}^{(1)}_\beta(\vec{r'}) \right\rangle g_{\alpha\beta}(\vec{r}, \vec{r}'). \tag{6.3}$$

The long-range nature Coulombic of the potentials requires special attention. First, we rewrite the potentials in terms of a Coulombic part, $\phi_c(\vec{r}, \vec{r}') = e^2/|\vec{r} - \vec{r}'|$, and an excess part $\delta v_{\alpha\beta}(\vec{r}, \vec{r}')$:

$$\begin{aligned} v_{II}(\vec{r}, \vec{r}') &= Z^2 \phi_c(\vec{r}, \vec{r}') + \delta v_{II}(\vec{r}, \vec{r}') && (6.4)\\ v_{eI}(\vec{r}, \vec{r}') &= -Z \phi_c(\vec{r}, \vec{r}') + \delta v_{eI}(\vec{r}, \vec{r}') && (6.5)\\ v_{ee}(\vec{r}, \vec{r}') &= \phi_c(\vec{r}, \vec{r}') + \delta v_{ee}(\vec{r}, \vec{r}'), && (6.6) \end{aligned}$$

where $\delta v_{ee}(\vec{r}, \vec{r}') = 0$. Second, we follow Appendix A of reference [5] and introduce the average densities $n^0_I = N_I/V$ and $n^0_e = ZN_I/V$ as well as two continuous background charge densities of opposite sign, ($+en^0_e$) and (-Zen^0_I), which allow (6.1) to be recast into the form:

$$\begin{aligned}
\hat{H} &= \hat{T}_I + \frac{1}{2}\int_V d\vec{r}\int_V d\vec{r}'\phi_c(\vec{r},\vec{r}')\left\{Z^2\hat{n}_{II}(\vec{r},\vec{r}') - 2Zn_I(\vec{r})n_e + n_e^2\right\} && (6.7)\\
&+ \hat{T}_e + \frac{1}{2}\int_V d\vec{r}\int_V d\vec{r}'\phi_c(\vec{r},\vec{r}')\left\{\hat{n}_{ee}(\vec{r},\vec{r}') - 2n_e(\vec{r})n_e + n_e^2\right\} && (6.8)\\
&- \int_V d\vec{r}\int_V d\vec{r}' Z\phi_c(\vec{r},\vec{r}')\left\{(Z\hat{n}_I(\vec{r}) - n_e)(\hat{n}_e(\vec{r'}) - n_e)\right\}, && (6.9)\\
&+ \delta\hat{H}, && (6.10)
\end{aligned}$$

where $\delta\hat{H}$ denotes the excess part due to deviations from Coulomb's law:

$$\begin{aligned}
\delta\hat{H} &= \frac{1}{2}\int_V d\vec{r}\int_V d\vec{r}'\delta V_{II}(\vec{r},\vec{r}')\hat{n}_{II}(\vec{r},\vec{r}') && (6.11)\\
&+ \int_V d\vec{r}\int_V d\vec{r}'\delta V_{eI}(\vec{r},\vec{r}')\hat{n}_{eI}(\vec{r},\vec{r}'). && (6.12)
\end{aligned}$$

The ion-ion term (6.11) is typically small[1], but the electron-ion term (6.12) may not be small at all, and has physical significance[1]. Nevertheless, none of the terms in (6.11-6.12) are long-ranged, and so they are expected to be finite. Thus (6.7-6.9) represents the same problem as equation (6.1), but now with rigid backgrounds to ensure charge neutrality. Fluctuations are therefore defined w.r.t these backgrounds. A trace over electron and ion coordinates[2] gives, by virtue of equations (6.1) and (6.3), the energy in terms of integrals over the pair-correlation functions:

$$E_{tot} = \mathrm{Trace}_{\{eI\}}\left[\hat{H}\right] = \left\langle \hat{H}\right\rangle = <\hat{T}_I> + <\hat{T}_e>$$

[1] The ion-ion interaction can be well approximated by a Coulomb potential $v_{II}(|\vec{r}-\vec{r}'|) = Z^2/|\vec{r}-\vec{r}'|$ for simple metals. For transition metals with resonant states, the ion is no-longer completely independent of the electron gas and the simple Coulomb form, or even the concept of an ion independent of the electron gas, no longer holds. On the other hand, Gauss' theorem guarantees that the ions do obey a Coulomb interaction law as long as they do not approach close enough for their core-electrons to overlap.

[2] Again, some care as to ensure the proper electro-neutrality conditions must be taken, see for example appendix A of [5].

$$+ \quad \frac{1}{2}\int_V d\vec{r} \int_V d\vec{r}' n_I(\vec{r}) n_I(\vec{r}') v_{II}(\vec{r}-\vec{r}') g_{II}(\vec{r},\vec{r}') \tag{6.13}$$

$$- \quad \int_V d\vec{r} \int_V d\vec{r}' n_I(\vec{r}) n_e(\vec{r}') v_{eI}(\vec{r}-\vec{r}') g_{eI}(\vec{r},\vec{r}') \tag{6.14}$$

$$+ \quad \frac{1}{2}\int_V d\vec{r} \int_V d\vec{r} n_e(\vec{r}) n_e(\vec{r}') v_{ee}(\vec{r}-\vec{r}') g_{ee}(\vec{r},\vec{r}') \tag{6.15}$$

Similarly the free-energy is given by:

$$F = -k_B T \ln \mathrm{Trace}_{\{eI\}} \left[e^{-\beta \hat{H}} \right]. \tag{6.16}$$

If an adiabatic approximation is made between ions and electrons, this trace simplifies further. The free-energy and can be split up into the ideal (F^0) parts which are independent of interactions, and the excess (F^{ex}) parts which stem from interactions:

$$F = F_I^0 + F_e^0 + F_{II}^{ex} + F_{eI}^{ex} + F_{ee}^{ex}. \tag{6.17}$$

As discussed in Appendix C, the Hohenberg-Kohn-Mermin theorem states that a given *set* of external potentials $\{v_I^{(1)}(\vec{r}), v_e^{(1)}(\vec{r})\}$ there exist a unique *set* of one-particle densities $\{n_I(\vec{r}), n_e(\vec{r})\}$. The free energy (6.17) is a unique functional of the one-body external potentials or equivalently of the equilibrium one-particle densities.

6.3 Derivation of the Quantum Ornstein Zernike Relations

We define the direct correlation functions[3] of an arbitrary two-component mixture in the usual way as functional derivatives of the excess free energy (6.17):

$$\frac{-1}{\beta}C_{ij}(r,r') = \left.\frac{\delta^2 F^{ex}}{\delta n_i(r)\delta n_j(r')}\right|_{\{n_i(r)n_j(r')\}\to\{n_i,n_j\}} \tag{6.18}$$

By manipulating generating functionals for correlation function hierarchies, the direct-correlation functions can be related to the response-functions[5, 7], resulting for a two-component quantum system in a relationship between two 2-by-2 matrices:

$$\frac{1}{\beta}C_{ij} = (\chi_{ij})^{-1} - (\chi^0_{ij})^{-1}, \tag{6.19}$$

which we shall call the **Quantum Ornstein Zernike (QOZ)** relations.

By inverting the QOZ 2 by 2 matrix we find the following relations between matrix components:

$$\begin{aligned}
\chi_{11}(q) &= \chi^0_{11}(q)\left(1+\chi^0_{22}(q)C_{22}(q)/\beta\right)/D(q) && (6.20)\\
\chi_{12}(q) &= -\chi^0_{11}(q)\chi^0_{22}(q)\left(C_{12}(q)/\beta\right)/D(q) && (6.21)\\
\chi_{22}(q) &= \chi^0_{22}(q)\left(1+\chi^0_{11}(q)C_{11}(q)/\beta\right)/D(q) && (6.22)\\
D(q) &= \left(1+\chi^0_{11}(q)C_{11}(q)/\beta\right)\left(1+\chi^0_{22}(q)C_{22}(q)/\beta\right) \\
&\quad -\chi^0_{11}(q)\chi^0_{22}(q)C_{12}(q)C_{21}(q)/\beta^2. && (6.23)
\end{aligned}$$

Note that these are *exact relations* for a two component quantum system. The QOZ relations appear to have been first derived by Chihara[8]. Later Ichimaru *et.*

[3] This is actually the definition of $C(r)/\beta$, a notation that stems from the classical context. At zero-temperature only, this ratio is well defined and given by the relation 6.18, $C(r)$ itself is not.

al. derived similar equations from a two-component linear response formulation[9]. The two formulations are equivalent if the definitions of the direct correlation functions (6.19) are linked in the usual way to the local field factors:

$$\frac{C_{ij}(q)}{\beta} = -V_{ij}(q)(1 - G_{ij}(q)), \tag{6.24}$$

For classical species, the fluctuation- dissipation theorem relates the response functions to density-density correlation functions:

$$\lim_{\hbar \to 0} \chi_{ij}(q, 0) = -\beta (n_i n_j)^{1/2} S_{ij}(q). \tag{6.25}$$

In the limit that both species are classical, the QOZ relations reduce to the usual relations between structure factors[10]. For a mixture of classical ions (I=1) and quantum electrons (e=2), equation (6.25) holds for $\chi_{II}(q)$ and $\chi_{eI}(q)$. From the definitions:

$$S_{II}(q) = 1 + n_I^0 \int d\vec{r} e^{-i\vec{q}\cdot\vec{r}} [g_{II}(r) - 1] \tag{6.26}$$

$$S_{eI}(q) = (n_I^0 n_e^0)^{1/2} \int d\vec{r} e^{-i\vec{q}\cdot\vec{r}} [g_{eI}(r) - 1] \tag{6.27}$$

real-space versions of the QOZ relations can be derived.

6.4 Exact Expressions for the Pseudo-Atom Density

By combining the two QOZ relations (6.20) and (6.21) together with the fluctuation dissipation theorem above, the relation between $S_{eI}(q)$ and $S_{II}(q)$ becomes:

$$S_{eI}(q) = \left(\frac{\chi^0_{ee}(q)}{1 - \chi^0_{ee}(q) C_{ee}(q)/\beta}\right) \frac{C_{eI}(q)}{-\beta} \frac{S_{II}(q)}{(n_I/n_e)^{1/2}}. \tag{6.28}$$

As was done in chapter 5, we write this in terms of a **pseudo atom** by rewriting equation (6.28) as:

$$S_{eI}(q) = \frac{n(q)}{\sqrt{Z}} S_{II}(q), \tag{6.29}$$

from which the pseudo-atom density is defined as:

$$n(q) \equiv \left(\frac{\chi^0_{ee}(q)}{1 - \chi^0_{ee}(q) C_{ee}(q)/\beta}\right) \frac{C_{eI}(q)}{-\beta}. \tag{6.30}$$

If the pseudo-atom density is rewritten as:

$$n(q) = \chi'_{ee}(q) \frac{C_{eI}(q)}{-\beta}, \tag{6.31}$$

then the relation (6.24) between the local-field factors $G_{ee}(q)$ and the direct correlation function $C_{ee}(q)$ allows us to rewrite the new function $\chi'_{ee}(q)$ in the suggestive form:

$$\chi'_{ee}(q) = \frac{\chi^0_{ee}(q)}{1 + \chi^0_{ee}(q) v_{ee}(q)(1 - G_{ee}(q))}. \tag{6.32}$$

If $G_{ee}(q)$ is taken to be independent of ionic correlations (but, through charge neutrality, not of the average density n^0_I) then $\chi'_{ee}(q)$ becomes the well known response function $\chi^{jell}_{ee}(q)$ for jellium[4]. Given a local field factor, equation (6.31) implies that

[4] This can also be seen by taking the appropriate limit of the QOZ relation (6.23).

the electron-ion direct correlation function is directly related to the pseudo-atom density: finding one implies finding the other.

The lowest order approximation for the electron-ion correlation function (low density):

$$C_{eI}(q) = -\beta V_{eI}(q) \tag{6.33}$$

coupled with the jellium approximation for $\chi'_{ee}(q)$ results in the usual linear response pseudo-atom density $n_1(q)$ explored in chapters 4 and 5, i.e.:

$$n_1(q) = \rho_1(q) = \chi^{jell}_{ee}(q) V_{eI}(q), \tag{6.34}$$

which is independent of ionic configuration. Clearly the full pseudo-atom density (6.31) is a functional not only of all orders of electron response, but of ionic-configurations as well, since its correlation function ingredients are coupled together by the QOZ relations.

6.5 Effective One-Component Correlation Functions

By equating $S_{II}(q)$ to an effective one-component liquid structure factor:

$$S_{II}(q) = S(q) = \frac{1}{(1 - n_I^0 C(q))} \tag{6.35}$$

one finds (using the QOZ relation (6.20)) an effective one-component direct correlation function of the form:

$$C(q) = -C_{II}(q) + \alpha(q), \tag{6.36}$$

where $\alpha(q)$ is given by:

$$\alpha(q) = \chi'_{ee}(q)\,(-C_{eI}(q)/\beta)^2 = \frac{(n(q))^2}{\chi'_{ee}(q)} \tag{6.37}$$

The nodal function $\Gamma_{II}(q)$ is given by:

$$\Gamma_{II}(q) = h_{II}(q) - C_{II}(q), \tag{6.38}$$

while the Ornstein-Zernike equation of a one-component system gives:

$$\Gamma(q) = h(q) - C(q), \tag{6.39}$$

Requiring the ion-correlations to be equal in the two-component and effective one-component formulations, (i.e. $h_{II}(q) = h(q)$, where $h(r)$ is related to the pair-correlation function by: $g(r) = h(r) + 1$), together with equation (6.36) relates the two nodal functions:

$$\Gamma(q) = \Gamma_{II}(q) - \alpha(q), \tag{6.40}$$

6.6 Effective Potentials from the Quantum-Percus Identity

The the physics of inhomogeneous and homogeneous classical fluids can be linked by a powerful observation due to Percus[11] who showed that if one particle is fixed at the origin and allowed to interact with the other particles its potential plays the role of an external potential, inducing an *inhomogeneous* one-particle density $n_e(r)$ which in turn is directly related to the two-body correlation function of the *homogeneous* fluid. The quantum-classical generalization of the Percus-identity entails fixing one ion at the origin in the full ion-electron system[5]. The surrounding one-body electron density leads to the electron-ion pair correlation function, and the surrounding one-body ion-density leads to the ion-ion pair correlation For the electron density the Percus-identity gives:

$$g_{eI}(0,r) = \frac{n_e(r|I)}{n_e^0}. \tag{6.41}$$

If in addition a Kohn-Sham type approach is employed, reducing the problem to a non-interacting system Euler equation, the pair correlation becomes:

$$g_{eI} = \frac{n_e^0(r|V_{eI}^{MF})}{n_e^0}, \tag{6.42}$$

where V_{eI}^{MF}, the potential of mean-force for the non-interacting electrons, is given by:

$$\beta V_{eI}^{MF}(r) = V_{eI}(r) - \Gamma_{eI}(r) - B_{eI}(r). \tag{6.43}$$

[5] Some care must be taken in adding the requisite number of electrons - i.e. use canonical ensemble and add a fixed ion and Z itinerant electrons. The difference in the Percus-identity between canonical and grand-canonical ensembles disappears in the thermodynamic limit.

and $\Gamma_{eI}(r)$ and $B_{eI}(r)$ are two-component generalizations of the nodal and bridge functions respectively. Similarly for the ions, the Percus identity gives:

$$g_{II}(r) = \frac{n_I(r|I)}{n_I^0} = exp(-\beta V_{II}^{MF}(r)), \tag{6.44}$$

To obtain effective one-component system equations, we require the ion-ion pair correlations to be equal ($h(r) = h_{II}(r)$) which implies that the potentials of mean force are also equal:

$$\begin{aligned} V^{MF}(q) &= V_{II}(q) - \Gamma_{II}(q)/\beta - B_{II}(q)/\beta & (6.45) \\ V_{eff}^{MF}(q) &= V_{eff}(q) - \Gamma(q)/\beta - B(q)/\beta & (6.46) \end{aligned}$$

so that the new one-component effective ion-ion interaction can be identified with

$$V_{eff}(q) = V_{II}(q) - \alpha(q) + (B(q) - B_{II}(q)). \tag{6.47}$$

This pair-potential *exactly* reproduces all pair correlations, and though its definition includes the effect of three-body and higher order potentials. It does not necessarily exactly reproduce higher order correlations though. Another approach would be to start from:

$$C_{II}(q) = -\beta V_{II}(q) + \tilde{C}_{II}(q) \tag{6.48}$$

which together with equation (6.36) results in the following expression for the effective one-component direct correlation function:

$$\begin{aligned} C(q) &= -\beta V_{eff}(q) + \tilde{C}(q) \\ &= -\beta V_{II}(q) + \alpha(q) + \tilde{C}_{II}(q) & (6.49) \end{aligned}$$

so that the effective one-component ion-ion pair interaction can also be identified with:

$$V_{eff}(q) = V_{II}(q) - \alpha(q) + \left(\tilde{C}(q) - \tilde{C}_{II}(q)\right) \tag{6.50}$$

An interesting corollary emerges from the combination of equations (6.47) and (6.50); namely

$$B(q) - B_{II}(q) = \tilde{C}(q) - \tilde{C}_{II}(q). \tag{6.51}$$

If the bridge-functions, or equivalently, the unknown (interaction) parts of the direct correlation functions were equal to each other, this would result in a particularly simple expression for the effective pair potential:

$$V_{eff}(q) = V_{II}(q) - \chi'_{ee}(q)\left(\frac{C_{eI}(q)}{-\beta}\right)^2 \tag{6.52}$$

If in addition to the approximation $B(q) = B_{II}(q)$, $\chi'_{ee}(q)$ is approximated by a jellium form and the classical low density expansion $C_{eI}(q) \sim -\beta v_{eI}(q)$ (see eq(6.33)) is used, this potential reduces to the popular linear response form:

$$V_{eff}(q) = V_{II}(q) + \chi^{jell}_{ee}(q) v_{ei}(q) v_{ei}(-q). \tag{6.53}$$

Clearly improvements in the theory of the pseudo-atom density will lead to improvements in the effective ion-ion potentials; the two are intimately connected.

6.7 Bridge Functions

The one-component ion-ion bridge function is given by the terms beyond second order in the functional Taylor expansion of the direct correlation function $C(r)$:

$$B(r) = \sum_n^{\infty} \frac{(n_I^0)^n}{n!} \int dr_1 ....dr_n C^{(n+1)}(r; r_1...r_n) h^{(2)}(r_1)...h^{(2)}(r_n) \tag{6.54}$$

For the two-component case the generalization is:

$$B_{II}(r) = \sum_n^{\infty} \frac{1}{n!} \sum_{l_1=I}^{l_1=e} ... \sum_{l_n=I}^{l_n=e} \left(n_{l_1}^0 ... n_{l_n}^0\right) \int dr_1 ....dr_n C_{I,l_1...l_n}^{(n+1)}(r; r_1...r_n) h_{Il_1}^{(2)}(r_1)...h_{Il_n}^{(2)}(r_n) \tag{6.55}$$

Together with the definition of the effective one-component two-body direct correlation function (6.36), it would be tempting to write the the one-component bridge-function as:

$$\begin{aligned} B(r) \quad = \quad & \sum_n^{\infty} \frac{(n^I)^n}{n!} \int dr_1 ....dr_n \left[C_{II}^{(n+1)}(r; r_1...r_n) + \right. \\ & \left. \frac{\delta^{n-1}}{\delta n_I(r_1)..\delta n_I(r_n)} \alpha(r, r_1; r_2..r_n) \right] h_{II}^{(2)}(r_1)...h_{II}^{(2)}(r_n). \end{aligned} \tag{6.56}$$

But this is not quite right. Just because there is a relationship between the *functions* $C(q)$ and $C_{II}(q)$, the homogeneous limits of some functional derivatives, it cannot be concluded that there is also a relationship between the *functionals* and higher order derivatives! However, it may be a reasonable (though uncontrolled) approximation.

6.8 The Quantum Hypernetted Chain Equation (QHNC) à la Chihara.

An important approach to the correlation functions of electron-ion mixtures are the integral equation methods pioneered by Chihara[12] who makes the following approximations in his Quantum Hypernetted Chain (QHNC) equations:

1. The effective electron-ion potential $V_{eI}^{MF}(r)$ in equation (6.43) is approximated by neglecting the electron-ion bridge-function $B_{ei}(q)$.
2. The resultant (one-body) Kohn-Sham equations (in LDA approximation) are solved, resulting in $g_{eI}(q)$.
3. A jellium approximation for $C_{ee}(q)$ is made , (Chihara uses the Geldart-Taylor LFC, which is not consistent with using LDA for $g_{eI}(r)$!).
4. By feeding $g_{eI}(q)$ and $C_{ee}(q)$ into the coupled **QOZ** relations ion-ion correlations are obtained.
5. The above procedure is iterated to self-consistency.

Chihara's approach is an interesting one, but it needs to be more clearly connected to other theories of liquid metals, especially to assess the validity of using a one-center equation for the electronic structure. One improvement may be using liquid-theory approaches to approximate $B_{ei}(q)$ which takes into account ion-correlations beyond the one-center approximation. Chihara also neglects the difference between two-component and one-component bridge functions to obtain equation (6.52) for ion-ion pair potentials. Nevertheless he obtains accurate structure factors with this potential. Perhaps this stems from the small difference between $-C_{eI}(q)$ and $-\beta V_{eI}(q)$, or else because mixing local field factors cancels the errors.

6.9 Making Contact with Linear Response Function Formalism

For a two-component electron-ion system, with a fixed configuration of ions, the electrons can be traced out by the Hellman-Feynman coupling constant method:

$$F_{eI} = \int_0^1 d\lambda < \frac{dH_{eI}}{d\lambda} >_\lambda \tag{6.57}$$

In this case:

$$< \frac{dH_{eI}}{d\lambda} >_\lambda = \frac{1}{\Omega} \sum_{k \neq 0} V_{eI}(k) \hat{n}_I(k) < \hat{n}_e(-k) >_\lambda \tag{6.58}$$

By expanding the average over electron coordinates $<>_\lambda$ in powers of the potential:

$$\begin{aligned} < \hat{n}_e(k) >_\lambda &= \lambda \chi_e(k) V_{eI}(k) \hat{n}_I(k) \\ &+ \lambda^2 \sum_{q1} \sum_{q2} \chi^{(2)}(k, q1, q2) V_{eI}(q1) \hat{\rho}_I(q1) V_{eI}(q2) \hat{\rho}_I(q2) + ... \\ &\equiv \rho^\lambda(-k; [\hat{n}_I]) \hat{n}_I(k) \end{aligned} \tag{6.59}$$

we can define $\rho^\lambda(-k; [\hat{n}_I])$, the "static pseudo-atom density", i.e. the pseudo-atom density for a fixed external configuration of ions, which in turn can be expanded as:

$$\rho^\lambda(k; [\hat{n}_I]) = \lambda \rho_1(k) + \lambda^2 \rho_2(k; [\hat{n}_I]) + ... \lambda^p \rho_p(k; [\hat{n}_I]). \tag{6.60}$$

Note that to first order (linear response), the static pseudo-atom density is independent of ionic configuration. However, at higher orders the actual ionic configuration comes into play. In the Born-Oppenheimer approximation, the coupling constant integration can be trivially carried out for each configuration in (6.59) and obtains:

$$F_{ei} = \frac{1}{\Omega} \sum_{k \neq 0} V_{eI}(k) \hat{n}_I(k) \left\{ \sum (\frac{1}{2} \rho_1(-k) + \frac{1}{3} \rho_2(-k; [\hat{n}_I]) + ... \frac{1}{n} \rho_p(-k; [\hat{n}_I]) \right\} \hat{n}_I(-k) \tag{6.61}$$

So that the "static pseudo-atom density" $\rho^\lambda(k;[\hat{n}_I])$ is really an operator $\hat{\rho}$ that acts on the ionic coordinates, and all of our manipulations so far have been on the level of ionic operators. If we now perform the ionic ensemble average we obtain:

$$\begin{aligned} < U_{eI} > &= < F_{eI} >_I = \\ &= \Big\langle \frac{1}{\Omega} \sum_{k \neq 0} V_{eI}(k) \hat{n}_I(k) \hat{n}_I(-k) \\ &\times \Big\{ \sum (\frac{1}{2}\rho_1(k) + \frac{1}{3}\rho_2(k;[\hat{n}_I]) + ... \frac{1}{n}\rho_p(k;[\hat{n}_I]) \Big\} \Big\rangle_I \\ &\equiv \frac{1}{2}\frac{1}{\Omega} \sum_{k \neq 0} V_{eI}(k) N n(k) S(k) \end{aligned} \tag{6.62}$$

which defines the **pseudo-atom density** $n(k)$.

One result of this definition is that the exact electron-ion energy in terms of the pseudo-atom densities is given (to all orders in the potential expansion) by:

$$\frac{< U_{eI} >}{N} = \frac{1}{2\Omega} \sum_{\mathbf{q} \neq 0} V_{eI}(q) n(q) S_{II}(q) = \frac{\sqrt{Z}}{2\Omega} \sum_{\mathbf{q} \neq 0} V_{eI}(q) S_{eI}(q) \tag{6.63}$$

which is just the q-space manifestation of equation (6.14)

$$< U_{eI} > \sim (n_e n_I)^{1/2} \int g_{eI}(r) V_{eI}(r) d\vec{r}, \tag{6.64}$$

(the pure structure independent volume-contributions coming from $q = 0$ are not included above), as discussed in chapter 5.

By writing out the energy in the linear response formalism to second order in the potential, and then equating terms proportional to powers of λ, we find the leading order correction to the pseudo-atom density (i.e. the beyond linear response correction). For example: The third order electron-ion energy is:

$$\begin{aligned} \frac{< U_{eI}^{(3)} >}{N} &= \frac{1}{3\Omega} \sum_{\vec{k} \neq 0} V_{eI}(k) \sum_{\vec{q}} \chi^{(2)}(k, q, |\vec{k} + \vec{q}|) V_{eI}(q) V_{eI}(|\vec{k} + \vec{q}|) \\ &\times \frac{1}{N} < \hat{n}_I(\vec{k}) \hat{n}_I(\vec{q}) \hat{n}_I(|\vec{k} + \vec{q}|) > . \end{aligned} \tag{6.65}$$

The ionic average above is simply the 3-body structure factor:

$$S^{(3)}(\vec{k},\vec{q}) = \frac{1}{N} < \hat{n}_I(\vec{k})\hat{n}_I(\vec{q})\hat{n}_I(|\vec{k}+\vec{q}|) >= S(k)S(q)S(|\vec{k}+\vec{q}|)[1+n_I^2 C^{(3)}(\vec{k},\vec{q})], \tag{6.66}$$

so that (6.65) can be rewritten as:

$$\begin{aligned} \frac{< U_{eI}^{(3)} >}{N} &= \frac{1}{2\Omega}\sum_{\vec{k}\neq 0} V_{eI}(k)S(k)\frac{2}{3}\sum_{q}\chi^{(2)}(k,q,|\vec{k}+\vec{q}|)V_{eI}(q)V_{eI}(|\vec{k}+\vec{q}|) \\ &\times \; S(q)S(|\vec{k}+\vec{q}|)[1+n_I^2 C^{(3)}(\vec{k},\vec{q})] \end{aligned} \tag{6.67}$$

Comparing this with (6.63) gives the second order pseudo-atom density as:

$$n_2(q) = \frac{2}{3}\sum_{\vec{q}}\chi^{(2)}(k,q,|\vec{k}+\vec{q}|)V_{eI}(q)V_{eI}(|\vec{k}+\vec{q}|)S(q)S(|\vec{k}+\vec{q}|)[1+n_I^2 C^{(3)}(\vec{k},\vec{q})] \tag{6.68}$$

This is somewhat different from the second order object $\rho_2(q)$, the non-linear response function we studied in chapter 4, since it includes 3-body ionic correlations and now obviously depends on structure! In essence this is not surprising, as we expect ionic-correlations to play a role in beyond-linear response terms of the pseudo-atom density. For example the 2nd order response of chapter 4:

$$\rho_2(k) = \sum_{\vec{q}}\chi^{(2)}(k,q,|\vec{k}+\vec{q}|)V_{eI}(q)V_{eI}(|\vec{k}+\vec{q}|) \tag{6.69}$$

only contributes to the 2rd order part of an effective ion-ion pair potential[13]. In an effective one-component system, the pseudo-atom density is part of the effective pair potential, which in turn determines the ionic-correlations; beyond linear response it becomes a self-consistent object.

To go to the first level beyond the linear response to calculate requires two ingredients: (1) second order electron response, which was discussed in chapter 4, and (2) the three-body structure factor $S^{(3)}(\vec{k},\vec{q})$. To find it one needs $C^{(3)}(\vec{k},\vec{q})$, the 3-body direct correlation function, to several approximation schemes exist in the literature[15], although many uncertainties persist. The simplest approximation is the convolution approximation[14] which entails setting the the third-order direct correlation function to zero:

$$C^{(3)}(\vec{k}, \vec{q}) = 0, \tag{6.70}$$

a related but stronger condition than that imposed by HNC approximationm namely:

$$\int d\vec{k} d\vec{q} C^{(3)}(\vec{k}, \vec{q}) = 0. \tag{6.71}$$

HNC is known to perform well for systems with long-range potentials, and we expect the convolution approximation to work best under similar conditions.

6.10 Conclusions

Clearly a better understanding of pseudo-atom densities is paramount to a more coherent theoretical description of coupled inhomogeneous electron-ion systems in general and liquid metals in particular. The content of this chapter was but a small step in that direction: the main results are exact expressions for effective ion-ion potentials (equations 6.47 and 6.50) and an exact expression for the second order pseudo-atom (equation 6.68), but much remains to be explored. For example, ab-initio simulations with new, faster Car-Parrinello[2] codes like VASP[16] would give ab-initio pseudo-atoms which in turn would result in better pair-potentials. While we saw in chapter 4 that the 2nd order electron response captures most of the non-linear electron response, it remains to be seen how well the second-order pseudo-atom captures the full non-linear pseudo-atom when various approximations for the triplet liquid structure are used. Nevertheless, we conclude that techniques from liquid theory can be successfully combined with ideas from electron response theory, leading to new insight into electron-ion mixtures.

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