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A diagrammatic analysis of the variational perturbation method for classical fluids[†]

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The statistical mechanics of classical fluids can be approached from the particle perspective, where the focus is on the various positions and interactions of the particles, and from the field perspective, where the focus is on the form of the interaction fields generated by the particles. In this work, we combine these two perspectives by examining the variational perturbation method for classical fluids, which has been widely used to describe nonuniform electrolyte systems. Most of this work has been for low orders of the approximation, it has been limited to cases where the electrostatic interactions are weak. We present an exact diagrammatic representation of the method, which greatly facilitates the enumeration and evaluation of higher order corrections to the free energy functional. This framework is able to encapsulate several different approximate theories. Performing a cumulant expansion, leads to the Debye-Hückel and higher order corrections. Including the contribution of chain diagrams leads to a theory closely related to the splitting theory [Hatlo and Lue, *EPL*, 2010, **89**, 25002], which has been shown to be accurate from the weak through to the strong coupling limits. Including all chain and ring diagrams leads to the hypernetted chain approximation; this is a more direct route to the conventional derivation, which also requires a renormalization of the Mayer f -bonds to the total correlation functions. These approximations to the variational perturbation method are applied to the classical one-component plasma in order to assess their relative accuracy and understand their relationship to each other. Strategies for developing improved approximations are discussed.

1 Introduction

Electrostatic interactions play a major role in determining the properties of many important industrial and biological systems, such as governing effective interactions between large, charged particles (e.g., colloidal spheres, proteins, DNA, polyelectrolytes, etc.). Most of our intuition about the influence of these interactions is based on Poisson-Boltzmann (PB) theory. This has been quite successful in rationalizing the effects of electrostatic interactions; however, it is known that this theory is only accurate when the interactions are relatively weak. When the electrostatic interactions become strong, the theory becomes inaccurate, in part due to the fact that it neglects the fluctuations in the electrostatic potential. In addition, PB theory is unable to describe situations when fluctuations play an important role in determining the behavior of a system, such as an electrolyte in the presence of a dielectric discontinuity.

In order to better account for these fluctuations, theoretical approaches have been developed that explicitly describe the

statistics of the charged particles in the system. These particle-based approaches include integral equation theories¹, such as the hypernetted-chain (HNC) approximation and the mean spherical approximation (MSA)². These theories have been successfully used to describe nonuniform electrolyte systems even in the presence of dielectric discontinuities^{3,4}. However, these methods are computationally difficult to apply, especially in more complicated geometries and for particles with distributed charges.

Another perspective that has been taken to model charged systems is to focus on the electrostatic potential generated by the particles rather than the particles themselves. The focus of the theory shifts from the charged particles and their configurations to the electrostatic potential generated by the particles and the fluctuations of the potential. These approaches were initially developed for classical systems by Stratonovich⁵ and Hubbard⁶, and have subsequently been taken forward by several other authors⁷⁻¹¹. These lead naturally to the mean field approximation, however, many approaches can be used to systematically add fluctuation corrections to the mean field approximation, such as the loop expansion, and improve the results. This field theory approach to electrolyte systems has been taken by many authors¹²⁻¹⁸.

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Another successful approach to approximating these field theories is the variational perturbation method¹⁹. This theory naturally incorporates the zero-frequency dispersion interactions resulting from the presence of dielectric inhomogeneities. In the absence of ions, the theory reduces to the Lifshitz theory. In the presence of ions, it describes the coupling between electrostatics and dispersion, such as the screening of the dispersion interactions due to electrolyte motion. This approximation scheme has been applied to determine the behavior of electrolyte systems near dielectric interfaces^{20,21} and nanopores²², and offers a relatively simple method to integrate the electrostatic interactions with the dispersion interactions (e.g., screening of the dispersion interaction by correlations in the electrolytes). It has also been extended to charge distributions^{23,24}, where it can be used to examine the liquid crystalline phases.

However, most previous applications of the variational perturbation theory have been limited to a cumulant expansion truncated at first order, which leads to an approximation that is equivalent to the Debye-Hückel theory. This theory, however, is only accurate for systems where the electrostatic interactions are relatively weak. Physically, these arise from the poor description of short wavelength fluctuations in the systems.

In principle, this method can be systematically improved through use of a cumulant expansion. However, these corrections for the variational perturbation method have been examined beyond first order for classical fluids. In this work, we examine the variational perturbation theory of classical equilibrium systems from a diagrammatic perspective. This approach allows us to more clearly see how different approximation schemes are related to each other.

In the next section, we present the development of the variational perturbation approximation for the free energy functional of classical particle systems that interact with pairwise additive potentials. The functional integral representation of the grand partition function is quickly introduced, and then its approximation using the cumulant expansion is discussed. An exact diagrammatic representation of the cumulant expansion of the free energy functional is given. The summation of the infinite set of chain diagrams and ring diagrams is provided, and the addition of their contribution to the free energy is considered. In Sec. 3, the diagrammatic analysis is then applied specifically to electrolyte systems composed of mobile ions and fixed charges within a spatially varying dielectric continuum. In particular, we examine Debye-Hückel theory and splitting theory. These theories are applied to the classical one-component plasma in Sec. 4 to compare their relative accuracy. Finally, the main findings of the approach are summarized in Sec. 5, along with directions for future work.

2 Variational perturbation approximation

We consider an open, multicomponent system of particles in a fixed volume V and absolute temperature T . Particles of type α have a constant, uniform chemical potential μ_α and are coupled to an external one-body potential $k_B T v_\alpha^{(1)}(\mathbf{R})$, where \mathbf{R} denotes the position (and possibly also orientation) of the particle and k_B is the Boltzmann constant; we combine the chemical poten-

tial with the one-body potential a generalized chemical potential $\gamma_\alpha(\mathbf{R}) = \beta\mu_\alpha - v_\alpha^{(1)}(\mathbf{R})$, where $\beta = (k_B T)^{-1}$. The particles are assumed to interact with each other through a pairwise additive potential $k_B T v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$. The total energy H of these interactions is given by

$$\beta H = \frac{1}{2} \sum_{\alpha k, \alpha' k'} v_{\alpha\alpha'}(\mathbf{R}_{\alpha k}, \mathbf{R}_{\alpha' k'}) - \frac{\beta}{2} \sum_{\alpha k} e_\alpha^{\text{se}}(\mathbf{R}_{\alpha k}) \quad (1)$$

where $\mathbf{R}_{\alpha k}$ is the position (and possibly orientation) of the k th particle of type α , and $e_\alpha^{\text{se}}(\mathbf{R})$ is the self-energy of a particle of type α

$$\beta e_\alpha^{\text{se}}(\mathbf{R}) = \frac{1}{2} v_{\alpha\alpha}(\mathbf{R}, \mathbf{R}). \quad (2)$$

All static equilibrium properties of the system can be derived from its grand partition function Z_G , which is a functional of the generalized chemical potential. Typically, Z_G is given by an enumeration over all possible particle configurations in the system, weighted by their probability of occurrence¹. This representation can be converted to a functional integral over a set of fluctuating external fields ψ_α , through the use of the Hubbard-Stratonovich transformation^{5,6}. This gives

$$Z_G[\gamma] = \left\langle Z_G^{\text{ig}}[\gamma - i\psi + \beta e] \right\rangle_0 \quad (3)$$

where $\langle \langle \dots \rangle \rangle_0$ is an average over the Hamiltonian

$$\beta H_0[\psi] = \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \psi_\alpha(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}') \psi_{\alpha'}(\mathbf{R}'),$$

Z_G^{ig} is the grand partition function of an ideal gas

$$\ln Z_G^{\text{ig}}[\gamma - i\psi + \beta e] = \sum_\alpha \int d\mathbf{R} \Lambda_\alpha^{-d} e^{\gamma_\alpha(\mathbf{R}) - i\psi_\alpha(\mathbf{R}) + \beta e_\alpha^{\text{se}}(\mathbf{R})}, \quad (4)$$

and Λ_α is the thermal wavelength of particles of type α . We can interpret Eq. (3) as stating that a system with particles interacting with each other through a pairwise additive potential is physically equivalent to a system of particles that do not directly interact with each other but are coupled to a fluctuating external field. The configuration of the fields ψ_α are distributed according to a Gaussian distribution with a correlation given by the interaction potential between the particles $v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$.

The functional integral form of the grand partition function is formally exact, however, it is not possible to evaluate it explicitly and approximate methods must be employed. In this work, we use the variational perturbation method. In this method, the functional averages taken over a shifted Gaussian Hamiltonian of the general form:

$$\beta H_{\mathcal{X}}[\delta\psi] = \frac{1}{2} \int d\mathbf{R} d\mathbf{R}' [\bar{\psi}_\alpha(\mathbf{R}) + \delta\psi_\alpha(\mathbf{R})] \times v_{\mathcal{X}, \alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}') [\bar{\psi}_{\alpha'}(\mathbf{R}') + \delta\psi_{\alpha'}(\mathbf{R}')] \quad (5)$$

where $\bar{\psi}_\alpha$ is the nominal mean of the interaction field associated with particles of type α , $\delta\psi_\alpha$ is the deviation of the field from its mean value, and $v_{\mathcal{X}, \alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}')$ is the nominal correlation of the

fluctuations of the interaction fields $\delta\psi_\alpha(\mathbf{R})$ that are given by

$$v_{\mathcal{K},\alpha\alpha'}^{-1}(\mathbf{R},\mathbf{R}') = v_{\alpha\alpha'}^{-1}(\mathbf{R},\mathbf{R}') + \mathcal{K}_{\alpha\alpha'}(\mathbf{R},\mathbf{R}'),$$

and $\mathcal{K}_{\alpha\alpha'}$ is related to the screening of the interactions between particles.

The grand partition function can be written as an average over the new Hamiltonian $H_{\mathcal{K}}$

$$\begin{aligned} \ln Z_G[\gamma] = & -\frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \bar{\psi}_\alpha(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R},\mathbf{R}') \bar{\psi}_{\alpha'}(\mathbf{R}') \\ & - \frac{1}{2} \text{Tr} \ln(1 + \mathcal{K} v) + \ln \langle e^{-\beta \delta H_{\mathcal{K}}[\delta\psi]} \rangle_{\mathcal{K}} \end{aligned} \quad (6)$$

where $\langle (\dots) \rangle_{\mathcal{K}}$ is an average with respect to the Hamiltonian $H_{\mathcal{K}}$, and $\delta H_{\mathcal{K}}[\delta\psi]$ is defined as

$$\begin{aligned} -\beta \delta H_{\mathcal{K}}[\delta\psi] = & \sum_{\alpha} \int d\mathbf{R} z_{\alpha}(\mathbf{R}) \\ & + \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i \delta\psi_{\alpha}(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R},\mathbf{R}') i \bar{\psi}_{\alpha'}(\mathbf{R}') \\ & - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i \delta\psi_{\alpha}(\mathbf{R}') \mathcal{K}_{\alpha\alpha'}(\mathbf{R},\mathbf{R}') i \delta\psi_{\alpha'}(\mathbf{R}'), \end{aligned} \quad (7)$$

where $z_{\alpha}(\mathbf{R})$ is the fugacity of particles of type α , which is given by

$$z_{\alpha}(\mathbf{R}) = \Lambda_{\alpha}^{-d} e^{\gamma_{\alpha}(\mathbf{R}) - i \bar{\psi}_{\alpha}(\mathbf{R}) - i \delta\psi_{\alpha}(\mathbf{R}) + \beta e_{\alpha}^{*}(\mathbf{R})}. \quad (8)$$

The first term on the right side of Eq. (7) is the partition function of an ideal gas and represents the coupling of the fluctuating field to a particle. The second term is the interaction of the fluctuating field with the mean value of the field, and the final term is the interaction of the field with itself.

Equation (6) is exact, however, in order to make practical calculations, approximations must be made to evaluate the functional average in the final term. Using different approximations for this term will lead to different theories. For example, completely neglecting this term (i.e. setting it equal to zero) will lead to the mean-field approximation. In the remainder of this section, we will discuss the use of the cumulant expansion.

2.1 Cumulant expansion

One method to approximately evaluate the average over the fluctuating fields $\delta\psi_{\alpha}(\mathbf{R})$ in Eq. (6) (i.e. the final term) is to use a cumulant expansion²⁵, which is given by

$$\begin{aligned} \ln \langle e^{-\beta \delta H_{\mathcal{K}}} \rangle_{\mathcal{K}} &= \langle e^{-\beta \delta H_{\mathcal{K}}} - 1 \rangle_{\mathcal{K}}^{(c)} \\ &\approx \langle (-\beta \delta H_{\mathcal{K}}) \rangle_{\mathcal{K}}^{(c)} + \frac{1}{2!} \langle (-\beta \delta H_{\mathcal{K}})^2 \rangle_{\mathcal{K}}^{(c)} \\ &\quad + \frac{1}{3!} \langle (-\beta \delta H_{\mathcal{K}})^3 \rangle_{\mathcal{K}}^{(c)} + \dots \end{aligned} \quad (9)$$

where the superscript denotes the cumulant average.

Each of the terms that arise in the cumulant expansion of the grand partition function (see Eq. (6)) is a functional average with

respect to the Hamiltonian $H_{\mathcal{K}}$ of products of various combinations of the three terms that make up Eq. (7). The required averages can be evaluated with the help of the relation

$$\left\langle e^{-\sum_{\alpha} \int d\mathbf{R} b_{\alpha}(\mathbf{R}) i \delta\psi_{\alpha}(\mathbf{R})} \right\rangle_{\mathcal{K}} = e^{-\frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' b_{\alpha}(\mathbf{R}) v_{\mathcal{K},\alpha\alpha'}^{-1}(\mathbf{R},\mathbf{R}') b_{\alpha'}(\mathbf{R}')}.$$

By taking necessary functional derivatives with respect to b on both sides of the equation and setting it to an appropriate value (e.g., $b_{\alpha}(\mathbf{R}) = 0$ or $b_{\alpha}(\mathbf{R}) = \delta_{\alpha\alpha'} \delta^d(\mathbf{R} - \mathbf{R}')$) in order to obtain the required average.

The first order cumulant is given by

$$\langle (-\beta \delta H_{\mathcal{K}}) \rangle_{\mathcal{K}}^{(c)} = \sum_{\alpha} \int d\mathbf{R} \bar{z}_{\alpha}(\mathbf{R}) + \frac{1}{2} \text{Tr} \mathcal{K} G_{\mathcal{K}}, \quad (10)$$

and the second order cumulant is

$$\begin{aligned} \frac{1}{2!} \langle (-\beta \delta H_{\mathcal{K}})^2 \rangle_{\mathcal{K}}^{(c)} = & -\frac{1}{2} \sum_{\alpha} \int d\mathbf{R} \bar{z}_{\alpha}(\mathbf{R}) [v_{\mathcal{K}} \mathcal{K} v_{\mathcal{K}}]_{\alpha\alpha}(\mathbf{R},\mathbf{R}) \\ & + \sum_{\alpha} \int d\mathbf{R} d\mathbf{R}' \bar{z}_{\alpha}(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R},\mathbf{R}') i \bar{\psi}_{\alpha'}(\mathbf{R}') \\ & + \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \bar{z}_{\alpha}(\mathbf{R}) f_{\alpha\alpha'}(\mathbf{R},\mathbf{R}') \bar{z}_{\alpha'}(\mathbf{R}') \\ & - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i \bar{\psi}_{\alpha}(\mathbf{R}) \\ & \quad \times [v^{-1} v_{\mathcal{K}} v^{-1}]_{\alpha\alpha'}(\mathbf{R},\mathbf{R}') i \bar{\psi}_{\alpha'}(\mathbf{R}') \\ & + \frac{1}{4} \text{Tr}(\mathcal{K} v_{\mathcal{K}})^2. \end{aligned} \quad (11)$$

where $\bar{z}_{\alpha}(\mathbf{R})$ is the fugacity of the ions of type α

$$\bar{z}_{\alpha}(\mathbf{R}) = \Lambda_{\alpha}^{-d} e^{\gamma_{\alpha}(\mathbf{R}) - \bar{\psi}_{\alpha}(\mathbf{R}) - \frac{1}{2} \Delta v_{\mathcal{K},\alpha\alpha}(\mathbf{R},\mathbf{R})}, \quad (12)$$

and $\Delta v_{\mathcal{K},\alpha\alpha} = v_{\mathcal{K},\alpha\alpha'} - v_{\alpha\alpha'}$ is the shift of the self interaction energy. The short ranged interactions are grouped together with the non-electrostatic interactions. These are collected into a set of “ f -bonds”, defined as

$$f_{\alpha\alpha'}(\mathbf{R},\mathbf{R}') = e^{-v_{\mathcal{K},\alpha\alpha'}(\mathbf{R},\mathbf{R}')} - 1. \quad (13)$$

This differs from the typical definition of the f -bond in that the screened interaction $v_{\mathcal{K},\alpha\alpha'}$, rather than the bare interaction $v_{\alpha\alpha'}$, appears in the argument of the exponential. If we set $\mathcal{K} = 0$, then the f -bond will reduce back to its conventional definition.

Including the first and second order cumulant terms gives the

following approximation for the grand partition function

$$\begin{aligned}
\ln Z_G = & + \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i\tilde{\psi}_\alpha(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') \\
& - \frac{1}{2} \text{Tr} \ln(1 + \mathcal{K}v) \\
& + \sum_\alpha \int d\mathbf{R} \bar{z}_\alpha(\mathbf{R}) + \frac{1}{2} \text{Tr} \mathcal{K}v_{\mathcal{K}} \\
& - \frac{1}{2} \sum_\alpha \int d\mathbf{R} \bar{z}_\alpha(\mathbf{R}) [v_{\mathcal{K}} \mathcal{K} v_{\mathcal{K}}]_{\alpha\alpha}(\mathbf{R}, \mathbf{R}) \\
& + \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \bar{z}_\alpha(\mathbf{R}) [v_{\mathcal{K}} v^{-1}]_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') \\
& + \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \bar{z}_\alpha(\mathbf{R}) f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \bar{z}_{\alpha'}(\mathbf{R}') \\
& - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i\tilde{\psi}_\alpha(\mathbf{R}) [v^{-1} v_{\mathcal{K}} v^{-1}]_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') \\
& + \frac{1}{4} \text{Tr} (\mathcal{K}v_{\mathcal{K}})^2 + \dots
\end{aligned} \tag{14}$$

All the static equilibrium properties of a system can be determined directly from its grand partition function. For example, the density distribution of the ions can be determined through the relation:

$$\rho_\alpha(\mathbf{R}) = \frac{\delta \ln Z_G[\gamma]}{\delta \gamma_\alpha(\mathbf{R})}$$

The corresponding expression for the particle density in the second order cumulant approximation is:

$$\begin{aligned}
\rho_\alpha(\mathbf{R}) = & \bar{z}_\alpha(\mathbf{R}) \left[1 - \frac{1}{2} [v_{\mathcal{K}} \mathcal{K} v_{\mathcal{K}}]_{\alpha\alpha}(\mathbf{R}, \mathbf{R}) \right. \\
& + \sum_{\alpha'} \int d\mathbf{R}' [v_{\mathcal{K}} v^{-1}]_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') \\
& \left. + \int d\mathbf{R}' f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \bar{z}_{\alpha'}(\mathbf{R}') + \dots \right]
\end{aligned} \tag{15}$$

2.2 Legendre transform

Often it is more convenient to work with a where the particle density profiles are the independent variables of the system rather than the chemical potentials. The Helmholtz free energy is defined through the Legendre transform of the grand partition function:

$$F[\rho] = \sum_\alpha \int d\mathbf{R} \rho_\alpha(\mathbf{R}) \gamma_\alpha(\mathbf{R}) - \ln Z_G[\gamma]. \tag{16}$$

To perform the Legendre transform, we require expressions for the generalized chemical potentials γ_α in terms of the particle densities ρ_α , which can be obtained by inversion of Eq. (15). For

the second order cumulant approximation, this leads to

$$\begin{aligned}
\gamma_\alpha(\mathbf{R}) = & \ln \rho_\alpha(\mathbf{R}) \Lambda_\alpha^d + \frac{1}{2} \Delta v_{\mathcal{K}, \alpha\alpha}(\mathbf{R}, \mathbf{R}) + i\tilde{\psi}_\alpha(\mathbf{R}) \\
& + \frac{1}{2} [v_{\mathcal{K}} \mathcal{K} v_{\mathcal{K}}]_{\alpha\alpha}(\mathbf{R}, \mathbf{R}) \\
& - \sum_{\alpha'} \int d\mathbf{R}' f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}') \\
& - \sum_{\alpha'} \int d\mathbf{R}' (v_{\mathcal{K}} v^{-1})_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') + \dots
\end{aligned} \tag{17}$$

Using this expression for the chemical potential, the Helmholtz free energy can be written as a functional of the particle densities

$$\begin{aligned}
F[\rho] = & F^{\text{ig}}[\rho] + \frac{1}{2} \sum_\alpha \int d\mathbf{R} \rho_\alpha(\mathbf{R}) \Delta v_{\mathcal{K}, \alpha\alpha}(\mathbf{R}, \mathbf{R}) \\
& + \sum_\alpha \int d\mathbf{R} \rho_\alpha(\mathbf{R}) i\tilde{\psi}_\alpha(\mathbf{R}) \\
& - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i\tilde{\psi}_\alpha(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') \\
& + \frac{1}{2} \text{Tr} \ln(1 + \mathcal{K}v) - \frac{1}{2} \text{Tr} \mathcal{K}v_{\mathcal{K}} \\
& + \frac{1}{2} \sum_\alpha \int d\mathbf{R} \rho_\alpha(\mathbf{R}) [v_{\mathcal{K}} \mathcal{K} v_{\mathcal{K}}]_{\alpha\alpha}(\mathbf{R}, \mathbf{R}) \\
& - \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \rho_\alpha(\mathbf{R}) (v_{\mathcal{K}} v_0^{-1})_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') \\
& - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \rho_\alpha(\mathbf{R}) f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}') \\
& + \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i\tilde{\psi}_\alpha(\mathbf{R}) [v^{-1} v_{\mathcal{K}} v^{-1}]_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') \\
& - \frac{1}{4} \text{Tr} (\mathcal{K}v_{\mathcal{K}})^2 + \dots
\end{aligned} \tag{18}$$

where F^{ig} is free energy functional of an ideal gas

$$F^{\text{ig}} = \sum_\alpha \int d\mathbf{R} \rho_\alpha(\mathbf{R}) [\ln \rho_\alpha(\mathbf{R}) \Lambda_\alpha^d - 1]. \tag{19}$$

The free energy given in Eq. (18) is only correct to second order in the cumulant expansion. In principle, this expression can be improved by adding higher order cumulant terms, however, the number and complexity of these additional terms increases rapidly as the order increases. Diagrammatic methods can be used to facilitate the enumeration of these terms and to aid their evaluation. We discuss this approach in the following section.

2.3 Diagrammatic representation

the contributions to the free energy, given in Eq. (18), of the terms that arise from the cumulant expansion can be written as diagrams. A diagram consists of two types of elements: vertices and bonds. For the systems that we consider, there are three types of

vertices:

- ρ -circles: These are represented by a large black circle and are associated with the term $\bar{z}_\alpha(\mathbf{R})$ (or $\rho_\alpha(\mathbf{R})$).
- \mathcal{H} -vertex: These are represented with a wavy line with small black circles at either end and come with a factor $-\frac{1}{2}\mathcal{H}_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$. The small circle on one side of the line is associated with the particle type index α and particle configuration \mathbf{R} and the other circle is associated with α' and \mathbf{R}' .
- $i\bar{\psi}v^{-1}$ -vertex: These are represented with a dashed line, representing the function $v_{\alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}')$, with a small gray circle on one end, representing $i\bar{\psi}_\alpha(\mathbf{R})$, and a small black circle on the other end. This vertex is associated with a factor $-v^{-1}i\bar{\psi}$.

The vertices are connected to each other by two types of bonds:

- $v_{\mathcal{H}}$ -bond: These are represented by a straight, thin line with two small black circles at either end. This represents the function $-v_{\mathcal{H},\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$, where one circle is associated with a particle of type α in configuration \mathbf{R} and the other circle with a particle of type α' in configuration \mathbf{R}' .
- f -bond: These are given by a thick line with a large black circle on either end. This is associated with the function $f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$.

The value associated with a diagram is a product of the integral over the functions associated with the elements and a numerical prefactor that is composed of two parts. The first part of the prefactor $1/(n_1!n_2!n_3!)$, where n_1 is the number ρ -circles, n_2 is the number \mathcal{H} -bonds, and n_3 is the number of $i\bar{\psi}v^{-1}$ -vertices in the diagram; this is related to the number of ways of selecting these elements. The second part is a combinatorial factor equal to the number of ways that the elements can be connect to yield the same diagram, topologically.

The diagrams that contribute to the free energy at first order, second order, and third order of the cumulant expansion are shown in Figs. 1(a), (b), and (c), respectively. As example of evaluating a diagram, the value of the first diagram in Fig. 1(c) is

$$-\frac{1}{2} \int d\mathbf{R} \rho_\alpha(\mathbf{R}) [v_{\mathcal{H}} \mathcal{H} v_{\mathcal{H}} v_{\mathcal{H}} \mathcal{H} v_{\mathcal{H}}]_{\alpha\alpha}(\mathbf{R}, \mathbf{R})$$

For this diagram, there is one ρ -circle and two \mathcal{H} -vertices; in addition, there are four distinct ways to bond the \mathcal{H} -vertices to the ρ -circle. Therefore, the numerical prefactor is $4/(1!2!0!) = 2$. Finally, recall that each \mathcal{H} vertex carries a factor of $-1/2$, and each $v_{\mathcal{H}}$ -bond carries a factor of -1 .

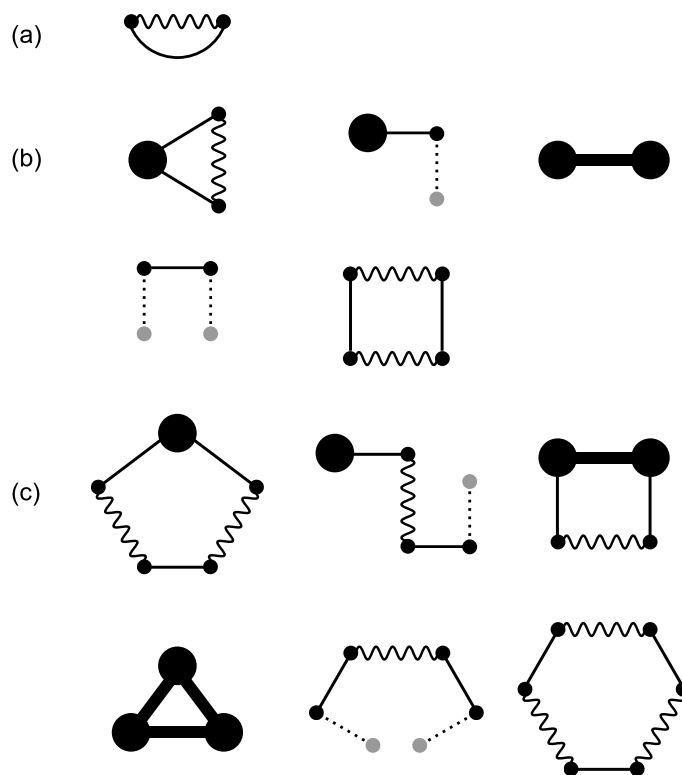


Fig. 1 Diagrams contributing to the (a) first-order, (b) second-order, and (c) third-order term in the cumulant expansion.

In terms of diagrams, the free energy can be written exactly as

$$\begin{aligned}
 F[\rho, \Sigma] = & F^{\text{ig}}[\rho] + \frac{1}{2} \sum_{\alpha} \int d\mathbf{R} \rho_{\alpha}(\mathbf{R}) \Delta v_{\mathcal{H}}(\mathbf{R}, \mathbf{R}) \\
 & + \sum_{\alpha} \int d\mathbf{R} \rho_{\alpha}(\mathbf{R}) i\bar{\psi}_{\alpha}(\mathbf{R}) \\
 & - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i\bar{\psi}_{\alpha}(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}') i\bar{\psi}_{\alpha'}(\mathbf{R}') \quad (20) \\
 & + \frac{1}{2} \text{Tr} \ln(1 + \mathcal{H}v) \\
 & - \text{sum of all allowed diagrams.}
 \end{aligned}$$

The allowed diagrams obey the following restrictions

- The diagram must consist of one or more vertices (i.e. ρ -circle, \mathcal{H} -vertex, or $v^{-1}i\bar{\psi}$ -vertex); the diagram consisting of a single ρ -circle is not allowed.
- The diagram must be connected. There must be a path from every vertex to another.
- Two ρ -circles can be connected by at most one f -bond; f -bonds can only be incident to ρ -circles (i.e., they cannot directly attach to a $v^{-1}i\bar{\psi}$ -vertex or either end of \mathcal{H} -vertex. ρ -circles can be incident to any number of $v_{\mathcal{H}}$ -bonds.
- The ρ -circles must not be nodal; that is, the diagram must not become disconnected if a ρ -circle is removed.

- Both ends of a \mathcal{K} -bond must be incident to a $v_{\mathcal{K}}$ -bond.
- Every $v^{-1}i\tilde{\psi}$ -vertex must be incident to a $v_{\mathcal{K}}$ -bond.

Note that when \mathcal{K} is set to zero, this representation will lead to the Mayer cluster expansion for a simple fluid.

This expression for the Helmholtz free energy functional is formally exact; the difficulty in evaluating it is the contribution of the infinite number of terms that is represented by the sum over allowed diagrams. In the following, we will discuss methods to approximate this term. The first method is the cumulant expansion, and the second is a summation of subsets of diagrams.

The cumulant expansions typically used in the field theory of electrolytes are typically truncated at first or second order, such as that presented in the previous section. The n th order cumulant term only has diagrams composed of n vertices. Only a finite set of diagrams are included at a given order of the expansion, and the contribution of all other diagrams are neglected. We can obtain a higher order approximation by summing over an infinite set of diagrams. In particular, we can exactly sum over all linear and ring diagrams (diagrams with at most one loop). We will consider this in later sections. In the following, we will discuss in more detail the issues involved in using approximate expressions for the free energy. In the next section, we begin our analysis with the first order cumulant expansion.

2.4 First order cumulant approximation

The first order cumulant approximation consists of just using the single diagram given in Fig. 1(a). The corresponding expression for the Helmholtz free energy is

$$\begin{aligned}
 F = F^{\text{ig}}[\rho] &+ \frac{1}{2} \sum_{\alpha} \int d\mathbf{R} \rho_{\alpha}(\mathbf{R}) \Delta v_{\mathcal{K},\alpha\alpha}(\mathbf{R}, \mathbf{R}) \\
 &+ \sum_{\alpha} \int d\mathbf{R} \rho_{\alpha}(\mathbf{R}) i\tilde{\psi}_{\alpha}(\mathbf{R}) \\
 &- \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i\tilde{\psi}_{\alpha}(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}') \\
 &+ \frac{1}{2} \text{Tr} [\ln(1 + \mathcal{K}v) - \mathcal{K}v_{\mathcal{K}}] + \dots
 \end{aligned} \tag{21}$$

In order to complete the specification of the theory, we need some manner to determine the values of the arbitrary functions $\tilde{\psi}_{\alpha}$ and $\mathcal{K}_{\alpha\alpha'}$. For the exact free energy, the choice of $\tilde{\psi}$ and \mathcal{K} (or equivalently $v_{\mathcal{K}}$) is completely arbitrary, and, consequently, none of the physically observable properties of the system should depend on the values of these quantities. As all static equilibrium properties of the system can, in principle, be derived from the partition function, the exact partition function should be independent of the variables $\tilde{\psi}$ and \mathcal{K} . This implies that the functional derivatives of the free energy with respect to these functions at all orders should vanish:

$$\frac{\delta^{m+n} F}{\delta \tilde{\psi}_{\alpha_1}(\mathbf{r}_1) \cdots \delta \tilde{\psi}_{\alpha_m}(\mathbf{r}_m) \delta \mathcal{K}_{\alpha'_1 \alpha''_1}(\mathbf{r}'_1, \mathbf{r}''_1) \cdots \delta \mathcal{K}_{\alpha'_n \alpha''_n}(\mathbf{r}'_n, \mathbf{r}''_n)} = 0.$$

Although the exact free energy functional is independent of the choice of $\tilde{\psi}$ and \mathcal{K} , an approximate free energy will, in general,

have a dependence. There is then the question as to what is the optimal choice for these parameters.

One obvious criterion to determine the functions is to make the first order derivative of the free energy with respect to the function equal to zero. In this case, the value of the mean interaction potentials $\tilde{\psi}_{\alpha}(\mathbf{R})$ are given by

$$\frac{\delta F}{\delta i\tilde{\psi}_{\alpha}(\mathbf{R})} = 0. \tag{22}$$

For the first order cumulant approximation, this yields:

$$\tilde{\psi}_{\alpha}(\mathbf{R}) = \sum_{\alpha\alpha'} \int d\mathbf{R} v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}'). \tag{23}$$

So we see that $\tilde{\psi}_{\alpha}(\mathbf{R})$ can be identified with the interaction field that a particle of type α experiences in the system. The value of the screening function \mathcal{K} is determined by making the free energy stationary:

$$\frac{\delta F}{\delta \mathcal{K}_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')} = 0. \tag{24}$$

For the first order cumulant approximation, the screening function is given by:

$$\mathcal{K}_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = \delta_{\alpha\alpha'} \delta^d(\mathbf{R} - \mathbf{R}') \rho_{\alpha}(\mathbf{R}). \tag{25}$$

This criterion for selecting the mean field and screening function has the additional technical benefit that the first order derivatives of the free energy with respect to any of the properties of the system (e.g., ρ_{α} or $v_{\alpha\alpha}$) only needs to be performed on terms where these properties explicitly appear. That is, the implicit dependence of $\tilde{\psi}$ and \mathcal{K} can be neglected.

Interestingly, at first order, the cumulant expansion possesses a variational condition: the value of the free energy for any arbitrary value of $\tilde{\psi}$ and \mathcal{K} will be greater than the exact value of the free energy. Consequently, it is natural to choose the values of these functions such that the approximate free energy is minimized.

Imposing the stationary condition only removes the dependence of the approximation free energy functional on \mathcal{K} at first order. Higher order functional derivative of the free energy will, in general, still be non-zero. The fact that for the first order cumulant approximation the stationary condition minimizes the system free energy relies on the second functional derivative of the free energy being positive.

For the exact free energy functional, this property should also hold for the higher order derivatives; however, it is not true for a general approximate free energy functional. Non-vanishing values of the higher order derivatives will lead to inconsistencies in the theory that are related to higher order correlation functions computed through different routes. This will also lead to inconsistencies in the evaluation of various thermodynamic properties (e.g., virial and compressibility routes of computing the pressure).

As an example, consider the total correlation function h . This can be determined from the free energy through the relation¹

$$\frac{\delta F}{\delta v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')} = \frac{1}{2} \rho_{\alpha}(\mathbf{R}) [1 + h_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')] \rho_{\alpha'}(\mathbf{R}') \tag{26}$$

The total correlation function for the first cumulant approximation is given by

$$h_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = -v_{\mathcal{K}, \alpha\alpha'}(\mathbf{R}, \mathbf{R}'). \quad (27)$$

This is the Debye-Hückel approximation for the total correlation function, which consists of “chains” of convolutions of the interactions between particles.

From the total correlation function, the direct correlation function $c_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$ can be defined through the Ornstein-Zernike equation,

$$h_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = c_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') + \sum_{\alpha''} \int d\mathbf{R}'' c_{\alpha\alpha''}(\mathbf{R}, \mathbf{R}'') \rho_{\alpha''}(\mathbf{R}'') h_{\alpha\alpha'}(\mathbf{R}'', \mathbf{R}').$$

With this, we find

$$c_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = -v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$$

Within this approximation, the direct correlation function is just the bare interaction between particles. Note that is precisely the mean-spherical approximation, which has been used extensively to model electrolyte systems such as the primitive model, for systems without a hard-core, excluded volume interaction (e.g., the ultrasoft electrolyte model^{26,26}). This approximation yields the correct long range behavior.

The direct correlation function can also be determined from the second functional derivative of the free energy with respect to density:

$$\frac{\delta^2 F}{\delta \rho_{\alpha}(\mathbf{R}) \delta \rho_{\alpha'}(\mathbf{R}')} = \frac{\delta_{\alpha\alpha'}}{\rho_{\alpha}(\mathbf{R})} \delta^d(\mathbf{R} - \mathbf{R}') - c_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}'). \quad (28)$$

This gives:

$$c_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = v_{\mathcal{K}, \alpha\alpha'}^2(\mathbf{R}, \mathbf{R}') - v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') + \dots$$

This expression for the direct correlation function is not consistent with the pair correlation function derived previously. This represents an inconsistency in the expression for the free energy functional.

The first order cumulant approximation can, in principle, be improved by including higher order terms. Unfortunately, the accuracy does not improve very quickly with the addition of these terms. In the next sections, we will consider adding the contribution of infinite sets of diagrams.

2.5 Chain diagrams

The first infinite set of diagrams that we can exactly sum are chains. These are diagrams that consist of elements that are linked in a linear manner. Examples of diagrams in this set are shown in Fig. 2. The class of chain diagrams can be divided into three different categories, depending on the number of ρ -circles they contain. In the following, we separately describe each of these classes of diagrams and present their contributions to the free energy.

C0: The first class of chain diagrams that we consider are those with no ρ -circles. These diagrams all consist of terminal $i\tilde{\psi}v^{-1}$ -vertices which are each directly connected to $v_{\mathcal{K}}$ -bonds, followed then by a series of alternating \mathcal{K} -bonds and $v_{\mathcal{K}}$ -bonds. Examples of diagrams in this class are shown in Fig. 2(C0).

The sum of all linear diagrams with no ρ -circles leads to

$$-\frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' i\tilde{\psi}_{\alpha}(\mathbf{R}) v_{\alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}') i\tilde{\psi}_{\alpha'}(\mathbf{R}').$$

The first term will exactly cancel the term that couples $i\tilde{\psi}$ to itself (see Eq. (20)), the second term cancels the coupling of the fixed charge distribution with $i\tilde{\psi}$, and the third term is the electrostatic interaction energy of the fixed charge with itself.

C1: The next category of chain diagrams that we consider are those that contain exactly one ρ -circle. In these diagrams, the ρ -circle appears on one end of the chain and an $i\tilde{\psi}v^{-1}$ -vertex on the other side. These two elements are connected by an alternating series of \mathcal{K} -bonds and $v_{\mathcal{K}}$ -bonds. The first three of these diagrams are shown in Fig. 2(C1).

The sum of all linear diagrams with exactly one ρ -circle leads to

$$\sum_{\alpha} \int d\mathbf{R} \rho_{\alpha}(\mathbf{R}) i\tilde{\psi}_{\alpha}(\mathbf{R}).$$

The first term will cancel the term that couples the ions to $i\tilde{\psi}$, and the second term is the electrostatic interaction energy between the mobile ions and the fixed charge.

C2: The final set of chain diagrams that we consider are those with precisely two ρ -circles. The ρ -circles appear on both ends of the diagrams and are connected to each other through a chain of alternating $v_{\mathcal{K}}$ -bonds and \mathcal{K} -bonds. Examples of diagrams in this set are shown in Fig. 2(R2).

The sum of all linear diagrams with two ρ -circles contributes

$$\frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \rho_{\alpha}(\mathbf{R}) C_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}')$$

where the function c is a shifted f -bond and is given by

$$C_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') + \Delta v_{\mathcal{K}}(\mathbf{R}, \mathbf{R}'),$$

and $\Delta v_{\mathcal{K}} = v_{\mathcal{K}} - v$.

If we add the contribution of all the chain diagrams to the first cumulant approximation of the free energy, we get

$$F[\rho] = F^{\text{ig}}[\rho] + \frac{1}{2} \sum_{\alpha} \int d\mathbf{R} \rho_{\alpha}(\mathbf{R}) \Delta v_{K, \alpha\alpha}(\mathbf{R}, \mathbf{R}) - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \rho_{\alpha}(\mathbf{R}) C_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}') + \frac{1}{2} \text{Tr}[\ln(1 + \mathcal{K}v) - \mathcal{K}v_{\mathcal{K}}] - \dots$$

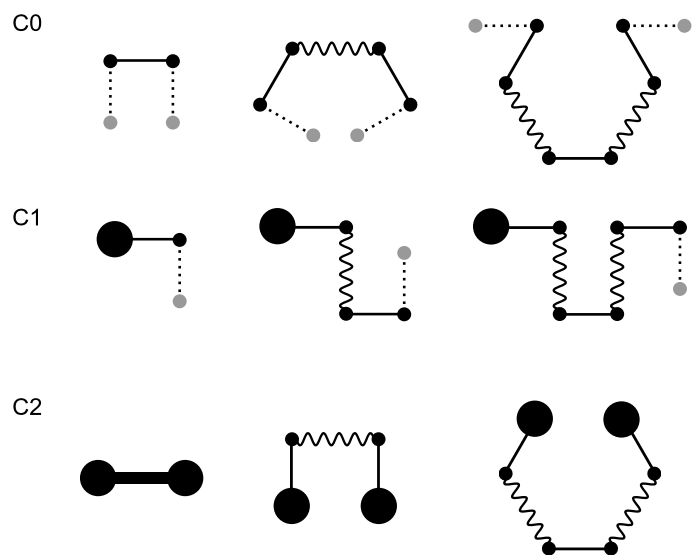


Fig. 2 Example of chain diagrams contributing to the free energy with (C0) no ρ -circles, (C1) one ρ -circle, and (C2) two ρ -circles.

where the ellipses represent the contributions of all the allowed diagrams with one or more loops, with the exception of the diagram in Fig. 1(a).

Note that within this approximation, there is no dependence of the interaction fields $\psi_\alpha(\mathbf{R})$, so there is no need to compute them. If we use the stationary condition to determine the screening function, we get

$$\begin{aligned} \mathcal{H}_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') &= \rho_\alpha(\mathbf{R})\delta_{\alpha\alpha'}\delta^d(\mathbf{R}-\mathbf{R}') \\ &+ \rho_\alpha(\mathbf{R})f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')\rho_{\alpha'}(\mathbf{R}') + \dots \end{aligned} \quad (29)$$

Given this form for the screening function, the total correlation function (as determined by Eq. (26)) is given by

$$\begin{aligned} h_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') &= f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \\ &- \sum_{\alpha''\alpha'''} \int d\mathbf{R}'' d\mathbf{R}''' (1+f\rho)_{\alpha\alpha''}(\mathbf{R}, \mathbf{R}'') \\ &\times v_{\mathcal{K}, \alpha''\alpha'''}(\mathbf{R}'', \mathbf{R}''') (1+\rho f)_{\alpha''\alpha'}(\mathbf{R}'', \mathbf{R}') \\ &+ \dots \end{aligned} \quad (30)$$

2.6 Ring diagrams

Another infinite set of diagrams that can be summed exactly are the rings, which are diagrams that consist of a single loop. Some examples of diagrams in this class are shown in Fig. 3. These diagrams can be divided into three classes, according to the number of ρ -circles that they contain.

R0: The first class of ring diagrams that we consider are those with no ρ -circles. The simplest of these diagrams is that shown in Fig. 1(a), which is the contribution of the first order cumulant. All the other ring diagrams consist of alternating $v_{\mathcal{K}}$ -bonds and \mathcal{K} bonds. First three of these diagrams is

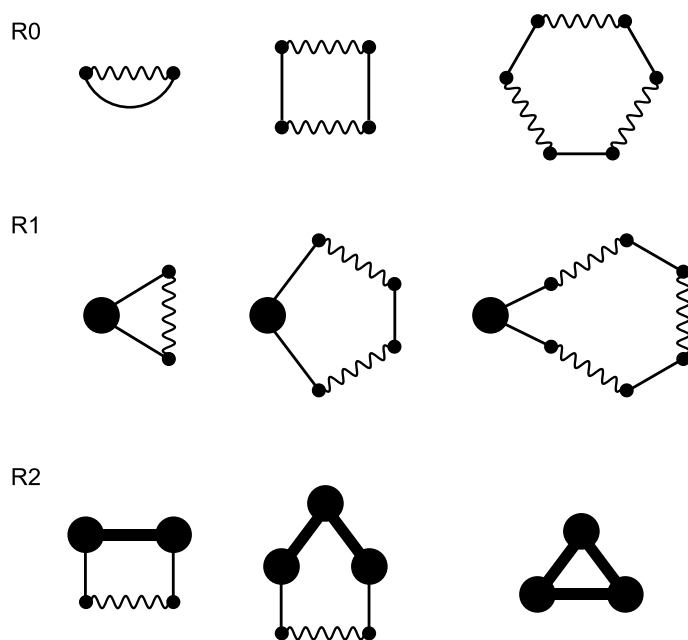


Fig. 3 Example of ring diagrams contributing to the free energy with (R0) no ρ -circles, (R1) one ρ -circle, and (R2) two or more ρ -circles.

shown in Fig. 3(R0). These represent the free energy of the freely fluctuating interaction fields ψ_α .

The sum of all ring diagrams with no ρ -circles is equal to

$$\frac{1}{2}\text{Tr}\ln(1+\mathcal{K}v).$$

This term will precisely cancel the ratio of the normalization factors in the original free energy (the final term in Eq. (20)).

R1: The next class of diagrams that we consider are the ring diagrams with exactly one ρ -circle. In these diagrams, there are ρ -circle is directly connected to two $v_{\mathcal{K}}$ -bonds. The remainder of the diagram consists of alternating \mathcal{K} -bonds and $v_{\mathcal{K}}$ -bonds. The first three of these diagrams are shown in Fig. 3(R1).

The sum of all diagrams in this class contributes

$$\frac{1}{2}\text{Tr}\rho\Delta v_{\mathcal{K}}.$$

This term will exactly cancel with the self-energy terms in the free energy.

R2: The final class of diagrams are the ring diagrams with two or more ρ -circles. In these diagrams, the ρ -circles must not be directly incident to a \mathcal{K} -bond. Two ρ -circles can only be directly connected by an f -bond or by an alternating series of $v_{\mathcal{K}}$ -bonds and \mathcal{K} -bonds. Examples of diagrams in this class are shown in Fig. 3(R2). Note that the smallest of these diagrams is the first one shown in Fig. 3(R2).

The sum of all these ring diagrams gives

$$-\frac{1}{4}\text{Tr}(\rho f)^2 - \frac{1}{2}\text{Tr}\rho C - \frac{1}{2}\text{Tr}\ln(1 - \rho C).$$

Including the contribution of the chain and the ring diagrams leads to the following expression for the Helmholtz free energy functional

$$F[\rho] = F^{\text{ig}}[\rho] - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \rho_{\alpha}(\mathbf{R}) C_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}') + \frac{1}{4} \text{Tr}(\rho f)^2 + \frac{1}{2} \text{Tr}[\rho C + \ln(1 - \rho C)] \quad (31)$$

– all allowed diagrams with two or more loops,

The diagrams that appear in the final term do not depend on $\tilde{\psi}$, so the free energy is completely independent of $\tilde{\psi}$.

By applying the stationary condition, the screening function is given by the solution of the integral equation

$$f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = [C(1 - \rho C)^{-1}]_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') + \dots \quad (32)$$

where the ellipses denote contributions from functional derivatives of the diagrams with two or more loops. So, we see that the f -bond can be decomposed as a sum of convolutions of the C interactions, in the identical manner in which the total correlation function is related to the direct correlation function (i.e. through the Ornstein-Zernike equation).

By taking the functional derivative of the free energy with respect to the bare interaction potential (see Eq. (26)), we find that the total correlation function is given by

$$h_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = [C(1 - \rho C)^{-1}]_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') + \dots \quad (33)$$

Neglecting the contribution of diagrams with two and more loops and comparing this with the equation for the screening function, we find that the f -bond can be approximately identified with the total correlation function h (i.e. $f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \approx h_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$), and, consequently, C can be identified with the direct correlation function (i.e. $C_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \approx c_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$).

The definition of the f -bond, given in Eq. (13), can be written as

$$1 + f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = e^{-v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') + f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') - C_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')}. \quad (34)$$

In approximating the total correlation function with the f -bond and the direct correlation with C , the above equation is exactly the hypernetted chain closure relation¹.

Interestingly, we have recovered hypernetted chain approximation by only summing up to chain and one-loop diagrams. In the standard Mayer cluster analysis for classical fluids, the hypernetted chain approximation appears as the sum of diagrams with up to one loop, however, in this expansion, the f -bonds have been renormalized to h -bonds^{27–29}. Using the stationary condition with the variational perturbation method appears to have performed this renormalization.

3 Electrolyte systems

In this section, we examine the application of the variational perturbation theory to electrolyte systems — specifically, multicomponent systems of mobile ions in the presence of a fixed charge distribution $\Sigma(\mathbf{r})$ and dissolved in a spatially varying continuous dielectric medium $\varepsilon(\mathbf{r})$. The ions can have an arbitrary internal charge distribution, such that the charge density due to an ion of type α located at position \mathbf{R} is $Q_{\alpha}(\mathbf{r} - \mathbf{R})$.

The electrostatic interaction energy of the system is given by

$$H = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \left[\sum_k Q_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha k}) + \Sigma(\mathbf{r}) \right] \times G_0(\mathbf{r}, \mathbf{r}') \left[\sum_{k'} Q_{\alpha'}(\mathbf{r} - \mathbf{R}_{\alpha' k'}) + \Sigma(\mathbf{r}') \right] - \sum_{\alpha k} e_{\alpha}^{\text{se}}(\mathbf{R}_{\alpha k}) \quad (35)$$

where $\mathbf{R}_{\alpha k}$ is the position of ion k of type α , G_0 is the Green's function of the Poisson equation for the system:

$$-\frac{1}{4\pi} \nabla \cdot \varepsilon(\mathbf{r}) \nabla G_0(\mathbf{r}, \mathbf{r}') = \delta^d(\mathbf{r} - \mathbf{r}'), \quad (36)$$

$e_{\alpha}^{\text{se}}(\mathbf{R})$ is the electrostatic self-energy of an ion of type α

$$e_{\alpha}^{\text{se}}(\mathbf{R}) = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' Q_{\alpha}(\mathbf{R} - \mathbf{r}) G_{\text{free}}(\mathbf{r}, \mathbf{r}') Q_{\alpha}(\mathbf{r}' - \mathbf{R}), \quad (37)$$

and G_{free} is the Green's function for the Poisson equation with a spatially uniform dielectric constant. The bare electrostatic interaction energy $v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$ between an ion of type α and an ion of type α' is

$$v_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = \int d\mathbf{r} d\mathbf{r}' Q_{\alpha}(\mathbf{R} - \mathbf{r}) G_{\text{free}}(\mathbf{r}, \mathbf{r}') Q_{\alpha'}(\mathbf{r}' - \mathbf{R}').$$

In order to simplify the presentation, we limit ourselves to the case where only electrostatic interactions are present. Non-electrostatic interactions can be included, however, this will complicate the vertices that appear in the diagrams. The grand partition function for this type of system can be written as

$$\ln Z_G[\gamma, \Sigma] = \ln \left\langle e^{-\beta \delta H[\psi]} \right\rangle_0 - \frac{1}{2} \text{Tr} \frac{G_0^{-1}}{G_{\text{free}}^{-1}} \quad (38)$$

where $\langle \dots \rangle_0$ is an average over the Hamiltonian

$$-\beta H_0[\psi] = -\frac{1}{2\beta} \int d\mathbf{r} d\mathbf{r}' \psi(\mathbf{r}) G_0^{-1}(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}').$$

and δH is the Hamiltonian

$$-\beta \delta H[\psi] = \sum_{\alpha} \int d\mathbf{R} \Lambda_{\alpha}^{-d} e^{\gamma_{\alpha}(\mathbf{R}) - \int d\mathbf{r} Q_{\alpha}(\mathbf{R} - \mathbf{r}) i\psi(\mathbf{r}) + \beta e_{\alpha}^{\text{se}}(\mathbf{R})} - \int d\mathbf{r} \Sigma(\mathbf{r}) i\psi(\mathbf{r}), \quad (39)$$

Unlike the case for the particle systems discussed in the previous section, there is only one fluctuating field, which is associated with the electrostatic potential generated by the charges in the

system, both mobile and fixed. Also, the final term in the expression for the grand partition function does not appear Eq. (6) for the particle system. This term captures the zero frequency dispersion interactions in the system^{30,31}, resulting from fluctuations in the electrostatic potential due to quantum effects. In the absence of charged particles, this leads to Lifshitz theory.

Applying the variational perturbation method, the average over the fluctuation field ψ is taken with respect to the Gaussian Hamiltonian

$$-H_{\mathcal{K}} = -\frac{1}{2\beta} \int d\mathbf{r} d\mathbf{r}' [\bar{\psi}(\mathbf{r}) + \delta\psi(\mathbf{r})] G_{\mathcal{K}}^{-1}(\mathbf{r}, \mathbf{r}') [\bar{\psi}(\mathbf{r}') + \delta\psi(\mathbf{r}')] \quad (40)$$

where $G_{\mathcal{K}}^{-1} = G_0^{-1} + \mathcal{K}$. The grand partition function then becomes

$$\ln Z_G = \ln \langle e^{-\beta \delta H_{\mathcal{K}}[\delta\psi]} \rangle_{\mathcal{K}} - \frac{1}{2} \text{Tr} \ln \frac{G_{\mathcal{K}}^{-1}}{G_{\text{free}}^{-1}} - \frac{1}{2\beta} \int d\mathbf{r} d\mathbf{r}' \bar{\psi}(\mathbf{r}) G_0^{-1}(\mathbf{r}, \mathbf{r}') \bar{\psi}(\mathbf{r}') - \int d\mathbf{r} \Sigma(\mathbf{r}) i\bar{\psi}(\mathbf{r}), \quad (40)$$

where $\delta H_{\mathcal{K}}$ is the Hamiltonian

$$\begin{aligned} -\beta \delta H_{\mathcal{K}}[\delta\psi] = & \sum_{\alpha} \int d\mathbf{R} \Lambda_{\alpha}^{-d} e^{\gamma_{\alpha}(\mathbf{R}) - \int d\mathbf{r} Q_{\alpha}(\mathbf{R}-\mathbf{r}) [i\bar{\psi}(\mathbf{r}) + i\delta\psi(\mathbf{r})] + \beta e_{\alpha}^{\text{sc}}(\mathbf{R})} \\ & - \int d\mathbf{r} d\mathbf{r}' i\delta\psi(\mathbf{r}) \beta^{-1} G_0^{-1}(\mathbf{r}, \mathbf{r}') i\bar{\psi}(\mathbf{r}') \\ & - \int d\mathbf{r} \Sigma(\mathbf{r}) i\delta\psi(\mathbf{r}) \\ & - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' i\delta\psi(\mathbf{r}) \mathcal{K}(\mathbf{r}, \mathbf{r}') i\delta\psi(\mathbf{r}'). \end{aligned} \quad (41)$$

The grand partition function can be Legendre transformed to obtain the free energy functional, which is given by

$$\begin{aligned} F[\rho, \Sigma] = & F^{\text{ig}}[\rho] \\ & + \frac{1}{2} \sum_{\alpha} \int d\mathbf{R} d\mathbf{r} d\mathbf{r}' \rho(\mathbf{R}) Q_{\alpha}(\mathbf{R}-\mathbf{r}) \\ & \quad \times [\Delta G_{\mathcal{K}}(\mathbf{r}, \mathbf{r}') + \Delta G_0(\mathbf{r}, \mathbf{r}')] Q_{\alpha}(\mathbf{r}'-\mathbf{R}) \\ & + \int d\mathbf{r} \mathcal{Q}(\mathbf{r}) i\bar{\psi}(\mathbf{r}) - \frac{1}{2\beta} \int d\mathbf{r} d\mathbf{r}' i\bar{\psi}(\mathbf{r}) G_0^{-1}(\mathbf{r}, \mathbf{r}') i\bar{\psi}(\mathbf{r}') \\ & + \frac{1}{2} \text{Tr} \ln(1 + \mathcal{K} G_0) + \frac{1}{2} \text{Tr} \ln \frac{G_0^{-1}}{G_{\text{free}}^{-1}} \\ & - \text{sum of all allowed diagrams} \end{aligned} \quad (42)$$

where $\Delta G_{\mathcal{K}} = G_{\mathcal{K}} - G_0$, $\Delta G_0 = G_0 - G_{\text{free}}$, and $\mathcal{Q}(\mathbf{r})$ is the total charge density in the system, which is given by

$$\mathcal{Q}(\mathbf{r}) = \sum_{\alpha} \int d\mathbf{R} \rho_{\alpha}(\mathbf{R}) Q_{\alpha}(\mathbf{r}-\mathbf{R}) + \Sigma(\mathbf{r}). \quad (43)$$

The diagrams that appear in Eq. (42) are exactly the same as

those that appear in Eq. (20). The only difference is that the dotted lines represent $(\beta^{-1} G_0^{-1} i\bar{\psi} - \Sigma)$ -vertices, and the thin straight lines represent $G_{\mathcal{K}}$ -bonds. The f -bond is defined as in Eq. (13), with the screened interaction potential $v_{\mathcal{K}, \alpha\alpha'}$ between ions of type α and α' given by

$$v_{\mathcal{K}, \alpha\alpha'}(\mathbf{R}, \mathbf{R}') = \int d\mathbf{r} d\mathbf{r}' Q_{\alpha}(\mathbf{R}-\mathbf{r}) \beta G_{\mathcal{K}}(\mathbf{r}, \mathbf{r}') Q_{\alpha'}(\mathbf{r}'-\mathbf{R}'). \quad (44)$$

3.1 Debye-Hückel theory

Taking the first order cumulant approximation to the average, which amounts to including only the single diagram in Fig. 1(a), we find

$$\begin{aligned} F[\rho, \Sigma] \approx & F^{\text{ig}}[\rho] \\ & + \frac{1}{2} \sum_{\alpha} \int d\mathbf{R} d\mathbf{r} d\mathbf{r}' \rho(\mathbf{R}) Q_{\alpha}(\mathbf{R}-\mathbf{r}) \\ & \quad \times [\Delta G_{\mathcal{K}}(\mathbf{r}, \mathbf{r}') + \Delta G_0(\mathbf{r}, \mathbf{r}')] Q_{\alpha}(\mathbf{r}'-\mathbf{R}) \\ & + \int d\mathbf{r} \mathcal{Q}(\mathbf{r}) i\bar{\psi}(\mathbf{r}) - \frac{1}{2\beta} \int d\mathbf{r} d\mathbf{r}' i\bar{\psi}(\mathbf{r}) G_0^{-1}(\mathbf{r}, \mathbf{r}') i\bar{\psi}(\mathbf{r}') \\ & + \frac{1}{2} \text{Tr} [\ln(1 + \mathcal{K} G_0) - \mathcal{K} G_{\mathcal{K}}] + \frac{1}{2} \text{Tr} \ln \frac{G_0^{-1}}{G_{\text{free}}^{-1}} \end{aligned} \quad (45)$$

where $\Delta G_{\mathcal{K}} = G_{\mathcal{K}} - G_0$. This approximation is related to the mean spherical approximation.

The screening function can be determined through use of the stationary principle

$$\mathcal{K}(\mathbf{r}, \mathbf{r}') = \beta \sum_{\alpha} \int d\mathbf{R} Q_{\alpha}(\mathbf{r}-\mathbf{R}) \rho_{\alpha}(\mathbf{R}) Q_{\alpha}(\mathbf{R}-\mathbf{r}') \quad (46)$$

Note that while the stationary principle ensures that the first functional derivative of the free energy vanishes (as required from physical considerations and the arbitrariness of the particular choice of the function), it does not guarantee that the higher order derivatives also vanish. In fact, the variational principle given by this approximation (where the optimal form of the screening function is the one which minimizes the free energy functional) is reliant on the fact that the second functional derivative of the free energy is positive.

The pair correlation function between ions is given by

$$h_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = - \int d\mathbf{r} d\mathbf{r}' Q_{\alpha}(\mathbf{R}-\mathbf{r}) \beta G_{\mathcal{K}}(\mathbf{r}, \mathbf{r}') Q_{\alpha'}(\mathbf{r}'-\mathbf{R}'). \quad (47)$$

At sufficiently close particle distances, the pair correlation within this approximation will become negative, which is unphysical, between ions with charges of the same sign. One manner to try to improve the theory is to restrict the allowed form that the screening function can sample in order to ensure that it leads to physically reasonable behavior (e.g., positive pair correlation functions).

3.2 Chain diagrams

The first correction we can make is to add all the linear (chain) diagrams that contribute to the free energy to the first order cumulant approximation. This leads to:

$$\begin{aligned}
 F[\rho, \Sigma] = & F^{\text{ig}}[\rho] \\
 & + \frac{1}{2} \sum_{\alpha} \int d\mathbf{R} d\mathbf{r} d\mathbf{r}' \rho_{\alpha}(\mathbf{R}) Q_{\alpha}(\mathbf{r} - \mathbf{R}) \\
 & \quad \times [\beta \Delta G_{\mathcal{H}}(\mathbf{r}, \mathbf{r}') + \beta \Delta G_0(\mathbf{r}, \mathbf{r}')] Q_{\alpha}(\mathbf{r}' - \mathbf{R}) \\
 & + \frac{\beta}{2} \int d\mathbf{r} d\mathbf{r}' \mathcal{Q}(\mathbf{r}) G_0(\mathbf{r}, \mathbf{r}') \mathcal{Q}(\mathbf{r}') \\
 & - \frac{1}{2} \sum_{\alpha} \int d\mathbf{R} d\mathbf{R}' d\mathbf{r} d\mathbf{r}' \rho_{\alpha}(\mathbf{R}) Q_{\alpha}(\mathbf{r} - \mathbf{R}) \\
 & \quad \times \beta G_{\mathcal{H}}(\mathbf{r}, \mathbf{r}') Q_{\alpha'}(\mathbf{r}' - \mathbf{R}') \rho_{\alpha'}(\mathbf{R}') \\
 & - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \rho_{\alpha}(\mathbf{R}) f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}') \\
 & + \frac{1}{2} \text{Tr}[\ln(1 + \mathcal{H} G_0) - \mathcal{H} G_{\mathcal{H}}] + \frac{1}{2} \text{Tr} \ln \frac{G_0^{-1}}{G_{\text{free}}^{-1}} \\
 & - \dots,
 \end{aligned} \tag{48}$$

where the ellipses represent the contributions of the diagrams with one or more loops excluding the first cumulant.

If we use the stationary principle with the free energy, the screening function is given by

$$\begin{aligned}
 \mathcal{H}(\mathbf{r}, \mathbf{r}') = & \beta \sum_{\alpha} \int d\mathbf{R} Q_{\alpha}(\mathbf{r} - \mathbf{R}) \rho_{\alpha}(\mathbf{R}) Q_{\alpha}(\mathbf{R} - \mathbf{r}') \\
 & + \beta \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' Q_{\alpha}(\mathbf{r} - \mathbf{R}) \rho_{\alpha}(\mathbf{R}) \\
 & \quad \times f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}') Q_{\alpha'}(\mathbf{R}' - \mathbf{r}')
 \end{aligned} \tag{49}$$

The first contribution to the screening is the same as found in the first order cumulant approximation, while the second term is due to interactions between the ions.

The total correlation function between ions is given (cf. Eq. (30)):

$$\begin{aligned}
 h_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = & f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \\
 & - \sum_{\alpha''\alpha'''} \int d\mathbf{R}'' d\mathbf{R}''' d\mathbf{r}'' d\mathbf{r}''' (1 + f\rho)_{\alpha\alpha''}(\mathbf{R}, \mathbf{R}'') \\
 & \quad \times Q_{\alpha''}(\mathbf{R}'' - \mathbf{r}'') G_{\mathcal{H}}(\mathbf{r}'', \mathbf{r}''') Q_{\alpha'''}(\mathbf{r}''' - \mathbf{R}''') \\
 & \quad \times (1 + \rho f)_{\alpha'''\alpha'}(\mathbf{R}''', \mathbf{R}') + \dots
 \end{aligned} \tag{50}$$

3.2.1 Splitting theory

The standard Debye-Hückel theory works well only when the electrostatic interactions are relatively weak. In order to produce an approximate free energy that would be accurate for sys-

tems also when the interactions become extremely strong, a splitting approach was developed by Hatlo and Lue^{32,33}. In this method, the electrostatic interactions are divided into short-wavelength G_s and long-wavelength G_l contributions by separating the Green's function G_0 as

$$G_0 = G_s + G_l,$$

where $G_l = \mathcal{P}G_0$, and \mathcal{P} is a filter operator that depends on a length scale σ that divides short wavelength phenomena ($< \sigma$) from long wavelength phenomena ($> \sigma$); σ is used as a variational parameter to make the free energy stationary to first order.

The long range fluctuations associated with G_l are approximated using a field theoretic method (e.g., mean field theory or a variational perturbation expansion), and the interactions associated with G_s are treated with a virial expansion. The resulting theory is found to be accurate for systems from the electrostatic interactions are weak all the way through to where the interactions are strong.

If we identify G_s with $G_{\mathcal{H}}$ and G_l with $-\Delta G_{\mathcal{H}}$, then the filter operator is given by

$$\mathcal{P} = 1 - G_{\mathcal{H}} G_0^{-1}$$

By introducing the long range electrostatic potential $\tilde{\psi}_l(\mathbf{r}) = \mathcal{P}\tilde{\psi}(\mathbf{r})$, the free energy can be written in a form that closely resembles the splitting theory

$$\begin{aligned}
 F[\rho, \Sigma] = & F^{\text{ig}}[\rho] + \sum_{\alpha} \int d\mathbf{R} \rho_{\alpha}(\mathbf{R}) \beta u_{\alpha}(\mathbf{R}) \\
 & - \frac{1}{2} \sum_{\alpha\alpha'} \int d\mathbf{R} d\mathbf{R}' \rho_{\alpha}(\mathbf{R}) f_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rho_{\alpha'}(\mathbf{R}') \\
 & + \frac{\beta}{2} \int d\mathbf{r} d\mathbf{r}' \Sigma(\mathbf{r}) G_{\mathcal{H}}(\mathbf{r}, \mathbf{r}') \Sigma(\mathbf{r}') \\
 & - \frac{1}{2\beta} \int d\mathbf{r} d\mathbf{r}' i\tilde{\psi}_l(\mathbf{r}) G_l^{-1}(\mathbf{r}, \mathbf{r}') i\tilde{\psi}_l(\mathbf{r}') + \int d\mathbf{r} \mathcal{Q}(\mathbf{r}) i\tilde{\psi}_l(\mathbf{r}) \\
 & + \frac{1}{2} \text{Tr}[\ln(1 + \mathcal{H} G_0) - \mathcal{H} G_{\mathcal{H}}] + \frac{1}{2} \text{Tr} \ln \frac{G_0^{-1}}{G_{\text{free}}^{-1}} - \dots,
 \end{aligned} \tag{51}$$

where the ellipses represent the contribution of diagrams with one or more loops excluding first cumulant, and $u_{\alpha}(\mathbf{R})$ is a one-body potential defined as

$$\begin{aligned}
 u_{\alpha}(\mathbf{R}) = & \int d\mathbf{r} d\mathbf{r}' Q_{\alpha}(\mathbf{R} - \mathbf{r}) G_{\mathcal{H}}(\mathbf{r}, \mathbf{r}') \Sigma(\mathbf{r}') \\
 & + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' Q_{\alpha}(\mathbf{R} - \mathbf{r}) \Delta G_{\mathcal{H}}(\mathbf{r}, \mathbf{r}') Q_{\alpha}(\mathbf{R} - \mathbf{r}') \\
 & + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' Q_{\alpha}(\mathbf{R} - \mathbf{r}) \Delta G_0(\mathbf{r}, \mathbf{r}') Q_{\alpha}(\mathbf{r}' - \mathbf{R}).
 \end{aligned} \tag{52}$$

The first term in the one-body potential is the short-ranged interaction of the ion charge with the fixed charge, the second term is related to the long-ranged self energy of the ion charge, and the final term is the image charge interaction of the ion with any

dielectric inhomogeneities. This is essentially the form of the free energy given by the splitting theory at the second order cumulant expansion of the short wavelength fluctuating field. This theory has been successfully used to model the properties of systems interacting with the Yukawa potential³⁴. The main exception is the presence of the next to final term in Eq. (51), which represents the free fluctuations of the electrostatic potential. This term vanishes, however, if we also include the ring diagrams with no ρ -circles (i.e. R0 diagrams).

In principle the free energy should be independent of the form selected for the filter function, however, in practice, different choices will lead to approximations with different accuracies. Using the form proposed by Santangelo³⁵, $\mathcal{P} = (1 - \sigma^2 \nabla^2)$, corresponds to choosing the screening function

$$\mathcal{K}(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi\sigma^2} \delta^d(\mathbf{r} - \mathbf{r}').$$

For the choice of the filter function $\mathcal{P} = (1 - \sigma^2 \nabla^2 + \sigma^4 \nabla^4)^{-1}$ (e.g., see Ref. 30), the corresponding expression for the screening function is

$$\mathcal{K}(\mathbf{r}, \mathbf{r}') = \frac{\epsilon}{4\pi\sigma^2} (1 - \sigma^2 \nabla^2)^{-1} \delta^d(\mathbf{r} - \mathbf{r}').$$

3.2.2 Dressed ion theory

An important aspect of electrolyte systems is the long range correlations between charge objects. This dictates the potential of mean force between colloidal particles immersed within an electrolyte solution and, consequently, their aggregation behavior.

The dressed ion theory developed by Kjellander and Mitchell³⁶ provides an exact formalism to directly analyze the long range behavior of the pair correlation function.

The direct correlation function decays exactly as $c_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') \rightarrow -\beta v_{\alpha\alpha'}(\mathbf{R} - \mathbf{R}')$. We divide the direct correlation function into short-ranged c_s and long-ranged contributions c_l , such that $c = c_s + c_l$, and define the short ranged direct correlation function c_s by subtracting the long-range asymptotic decay

$$c_{s,\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = c_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}') + \int d\mathbf{r} d\mathbf{r}' Q_\alpha(\mathbf{R} - \mathbf{r}) \beta G_0(\mathbf{r}, \mathbf{r}') Q_{\alpha'}(\mathbf{r}' - \mathbf{R}'). \quad (53)$$

Similarly, we divide the total correlation function as $h = h_s + h_l$ and define the short-range contribution of the total correlation function h_s through an Ornstein-Zernike relation

$$h_{s,\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = c_{s,\alpha\alpha'}(\mathbf{R}, \mathbf{R}') + \sum_{\alpha''} \int d\mathbf{R}'' c_{s,\alpha\alpha''}(\mathbf{R}, \mathbf{R}'') \rho_{\alpha''}(\mathbf{R}'') h_{s,\alpha\alpha'}(\mathbf{R}'', \mathbf{R}'). \quad (54)$$

The key result of dressed ion theory is that if the long range decay of the direct correlation function can be factorized, then the long range decay of the total correlation function also factorizes.

The long-range decay of the total correlation function is given

by a screened interaction with an effective charge.

$$h_{l,\alpha\alpha'}(\mathbf{R}, \mathbf{R}') = - \int d\mathbf{r} d\mathbf{r}' Q_\alpha^*(\mathbf{R} - \mathbf{r}) G_{\mathcal{K}}^*(\mathbf{r}, \mathbf{r}') Q_{\alpha'}^*(\mathbf{R}' - \mathbf{r}'), \quad (55)$$

where Q_α^* is the dressed charge of α ions

$$Q_\alpha^*(\mathbf{R} - \mathbf{r}) = \sum_{\alpha'} \int d\mathbf{R}' (1 - c_s \rho)_{\alpha\alpha'}^{-1}(\mathbf{R}, \mathbf{R}') Q_{\alpha'}(\mathbf{R}' - \mathbf{r}), \quad (56)$$

$G_{\mathcal{K}}^*(\mathbf{r}, \mathbf{r}')$ is a screening interaction, defined with respect to the the screening function

$$\mathcal{K}^*(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\alpha'} \int d\mathbf{R} Q_\alpha(\mathbf{r} - \mathbf{R}) \rho_\alpha(\mathbf{R}) Q_{\alpha'}^*(\mathbf{R} - \mathbf{r}'),$$

through the relation $G_{\mathcal{K}}^{*-1} = G_0^{-1} + \mathcal{K}^*$.

If we identify $G_{\mathcal{K}}^*$ with $G_{\mathcal{K}}$, then comparing this expression with that in Eq. (49), we find the following relationship between f and c_s :

$$\delta_{ab} + f_{ab} \rho_b = (1 - c_s \rho)_{ab}^{-1}.$$

This is just an Ornstein-Zernike relation, with f playing the role of the total correlation function, and c_s playing the role of the direct correlation function. This implies $h_s = f$.

4 One-component plasma

In order to gauge the relative accuracy of the various approximations discussed in the previous section, we apply them to a one-component plasma of point charges. The charge density of the particles is given by $Q(\mathbf{r}) = q \delta^d(\mathbf{r})$, and their charge is neutralized by a uniform background $\Sigma = -\rho q$. The key parameter that characterizes the strength of the electrostatic interactions in the system is the coupling parameter Γ , which is defined as

$$\Gamma = \left(\frac{4\pi}{3} \rho l_B^3 \right)^{1/3}$$

where $l_B = \beta q^2$ is the Bjerrum length. For large values of Γ , the ions are closely spaced compared to the range l_B of the Coulomb interactions, and the system is strongly coupled. For small values of Γ , the electrostatic coupling is weak compared to the thermal motion of the ions.

4.1 Cumulant approximation

The first approximations we will consider are the first and second order cumulant expansions. At first order, the theory reduces to the Debye-Hückel approximation, where the Helmholtz free energy is given by:

$$\frac{F}{V} = \frac{F^{\text{ig}}}{V} - \frac{\kappa^3}{12\pi}, \quad (57)$$

with $\kappa^2 = 4\pi\rho l_B = 4\Gamma^3/l_B^2$, and κ is the inverse Debye screening length. In this case, the stationary principle was used to determine the screening function, giving $\hat{\mathcal{K}}(\mathbf{p}) = 4\pi\kappa^2$, where the $\hat{\cdot}$ denotes the Fourier transform of a function. The corresponding expression for the electrostatic interaction energy is $\beta U/N = \sqrt{3}\Gamma^{3/2}/2$, where N is the number of ions in the system.

At second order in the cumulant expansion, the Helmholtz free energy is

$$\begin{aligned} \frac{F}{V} = & \frac{F^{\text{ig}}}{V} + \frac{l_B}{2} \rho \int_{\mathbf{p}} [\Delta \hat{G}_{\mathcal{K}}(\mathbf{p}) + \mathcal{K}(\mathbf{p}) \hat{G}_{\mathcal{K}}^2(\mathbf{p})] \\ & - \frac{l_B}{2} \rho^2 \hat{G}_{\mathcal{K}}(0) - \frac{1}{2} \rho^2 \hat{f}(0) \\ & + \frac{1}{2} \int_{\mathbf{p}} \left[\ln(1 + \mathcal{K}(\mathbf{p}) \hat{G}_0(\mathbf{p})) \right. \\ & \left. - \mathcal{K}(\mathbf{p}) \hat{G}_{\mathcal{K}}(\mathbf{p}) - \frac{1}{2} (\mathcal{K}(\mathbf{p}) \hat{G}_{\mathcal{K}}(\mathbf{p}))^2 \right] \end{aligned} \quad (58)$$

The stationary condition provides the following integral equation to be solved for the screening function:

$$\mathcal{K}(\mathbf{p}) \hat{G}_{\mathcal{K}}(\mathbf{p}) \mathcal{K}(\mathbf{p}) = 2\rho l_B \mathcal{K}(\mathbf{p}) \hat{G}_{\mathcal{K}}(\mathbf{p}) + \rho l_B \hat{f}(\mathbf{p}). \quad (59)$$

The electrostatic interaction energy U is

$$\frac{\beta U}{N} = \frac{l_B}{2} \int_{\mathbf{p}} [\Delta \hat{G}_{\mathcal{K}}(\mathbf{p}) + \mathcal{K}(\mathbf{p}) \hat{G}_{\mathcal{K}}^2(\mathbf{p})] + \frac{l_B}{2} \int_{\mathbf{p}} \hat{G}_{\mathcal{K}}(\mathbf{p}) \rho \hat{f}(\mathbf{p}) \quad (60)$$

4.2 Chain approximation

As mentioned in the previous section, including the chain diagrams as well as the ring diagrams with no ρ -circles leads to a theory very similar to the splitting theory. For the one-component plasma, this approximation leads to the free energy

$$\frac{F}{V} \approx \frac{F^{\text{ig}}[\rho]}{V} + \frac{l_B}{2} \rho \int_{\mathbf{p}} \Delta \hat{G}_{\mathcal{K}}(\mathbf{p}) - \frac{l_B}{2} \rho^2 \hat{G}_{\mathcal{K}}(0) - \frac{1}{2} \rho^2 \hat{f}(0), \quad (61)$$

The corresponding expression for the electrostatic interaction energy is given by

$$\frac{\beta U}{N} = \frac{l_B}{2} \int_{\mathbf{p}} \Delta \hat{G}_{\mathcal{K}}(\mathbf{p}) + \frac{l_B}{2} \int_{\mathbf{p}} \hat{G}_{\mathcal{K}}(\mathbf{p}) \rho \hat{f}(\mathbf{p}). \quad (62)$$

In the splitting theory, we restrict the form of the screening function to

$$\hat{\mathcal{K}}(\mathbf{p}) = \frac{1}{4\pi\sigma^2} (1 + p^2\sigma^2)^{-1},$$

where σ is used as a variational parameter.

$$G_{\mathcal{K}}(r) = \frac{e^{-\frac{\sqrt{3}r}{2\sigma}}}{r} \left(\cos \frac{r}{2\sigma} + \sqrt{3} \sin \frac{r}{2\sigma} \right)$$

This implies that $\hat{G}_{\mathcal{K}}(0) = 4\pi\sigma^2$ and $\Delta G_{\mathcal{K}}(0) = -(\sqrt{3}\sigma)^{-1}$. The value of the parameter σ is determined from the condition:

$$\frac{\partial F}{\partial \sigma} = 0. \quad (63)$$

Finally, we note that adding both the chain and ring diagrams leads to the well-known hypernetted chain approximation.

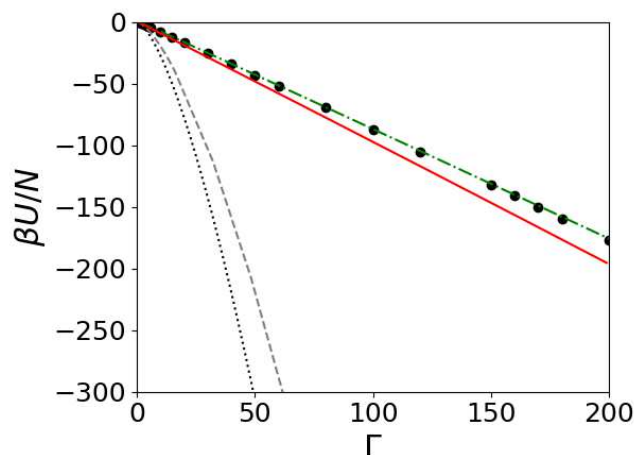


Fig. 4 Electrostatic interaction energy of a one-component plasma of point charges. The symbols are the Monte Carlo simulation data from Ref. 38, the black dotted line is the first order cumulant approximation (i.e. Debye-Hückel theory), and the black dotted line is the prediction of the second order cumulant approximation. The solid red line is the prediction of the chain + R0 approximation, and the green dashed-dotted line is the prediction of the hypernetted chain approximation.

4.3 Comparison with simulation data

In order to assess the accuracy of the various approximations, we compare their predictions with Monte Carlo^{37,38} and molecular dynamics simulation data for the residual electrostatic interaction energy per ion. The results are presented in Fig. 4. The symbols are the results of the simulation data.

The accuracy of the Debye-Hückel theory (black dotted line) degrades quite rapidly as the strength of the electrostatic interactions increases. Adding the second order correction (black dashed line) does improve the results of the theory, although not substantially. Both approximations severely overestimate the strength of the Coulomb interactions. This is due to the poor description of the short-wavelength fluctuations.

One method that has been used to improve the predictions of the Debye-Hückel theory is to modify the short lengthscale features of the theory by including an exclusion zone around the ions to keep the pair correlation function non-negative^{39,40} or by introducing a short-wavelength cutoff⁴¹⁻⁴³. This approach has led to approximate theories that yield extremely good descriptions of the interaction energy.

Adding the chain and R0 diagrams (solid red line), along with restricting the form of the screening function, leads to significant improvement of the predictions. This might be expected, as this approximation is closely related to the splitting theory²⁴. The hypernetted chain theory provides very good predictions for the interaction energy over the entire range of coupling parameters.

5 Conclusions

In this work, we have presented a diagrammatic representation of the variational perturbation method for classical particle systems interacting through pairwise additive potentials. Previously, this

method has only been applied for low orders of the cumulant expansion of the free energy functional, which leads to theories that are only accurate in the weak coupling limit. At first order in the expansion, this theory is related to the mean spherical approximation. We discuss the role and choice of the screening function $\mathcal{H}_{\alpha\alpha'}(\mathbf{R}, \mathbf{R}')$ and consider the use of the criterion of making the free energy stationary at first order.

The diagrammatic representation of the free energy functional allow us to consider approximations involving an infinite number of terms in the cumulant expansion. In particular, we consider the corrections associated with the set of all chain diagrams and the set of all ring diagrams. We show that by including these corrections leads to the hypernetted chain approximation.

This diagrammatic approach was then applied specifically to electrolyte systems immersed in systems with a fixed background charge and (possibly) varying dielectric continuum. At first order, the approach reduces to the extended Debye-Hückel theory, which has been successfully to describe the influence of dielectric inhomogeneities on ion distribution and interactions, as well as the coupling between electrostatic and dispersion interactions. Including the chain diagrams in free energy leads to the splitting theory developed by Hatlo and Lue^{32,33}, which has been very successful in describing electrolyte systems from the weak to strong coupling limits. The link between the dressed ion theory and the splitting theory is analyzed.

The relatively simple structure of the theory is in large part due to the use of the ideal gas reference system. If another reference system is chosen, such as a hard sphere fluid, the diagrammatic structure of the theory will become more complicated. In particular, there will be a variety of “particle” circles that will appear in the diagrammatic series, each corresponding to a different order direct correlation function (i.e. higher order functional derivatives of the free energy with respect to density). This extension will allow the application of the method to electrolyte systems that include non-electrostatic interactions.

One important factor in the variational perturbation method is the choice of the screening function. Typically, this is chosen by making the free energy functional stationary to first order. Although this choice provides substantial technical benefits, it does not always lead to physically reasonable results, as discussed previously in the case of the pair correlation function at short distances. One interesting manner that can be might be address this issue is to restrict the form that the screening function can take. This is what is done in the case of the splitting theory, when the form of the filter function is selected. This is also what is done in the hole corrected Debye-Hückel theory⁴⁰ for the one-component plasma, where a correlation hole is introduced in order to ensure that the pair correlation function is positive. In the case of the variational perturbation theory, the connection between the screening function and the pair correlation will depend on the particular approximation made for the free energy functional.

Even if the stationary principle is used, the higher order functional derivatives of the free energy with respect to the screening function may still non-zero, which call lead to inconsistencies in the theory. This is due to the neglect of the contribution of the remaining diagrams to the free energy functional. As a result, the

value of a property will depend on the route by which it is calculated (e.g., virial versus compressibility pressure). One way that this might be addressed is to add a term to the free energy functional that would compensate for these missing diagrams. This term could be adjusted to constrain certain higher order functional derivatives to zero in order to remove various inconsistencies which may arise.

The precise role of this term will depend on the level of approximation of the free energy (i.e. the set of diagrams that are included in the approximation). In the case where the linear and ring diagrams are included, which leads to the HNC approximation, the additional term will be related to the contribution of the bridge diagrams¹, and its form will lead to different approximations to the closure relation. A similar idea is taken in the development of self-consistent closure relations for integral equation theories^{44–47}. In these approaches, parameters are included in the closure relation which are then adjusted so that the certain self-consistency criteria are satisfied.

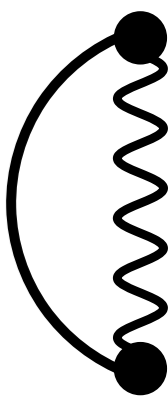
These are some of the directions we plan to pursue in future to develop an approximate theory for electrolyte systems that is accurate but simple enough that it can be readily applied to nonuniform systems in complex geometries.

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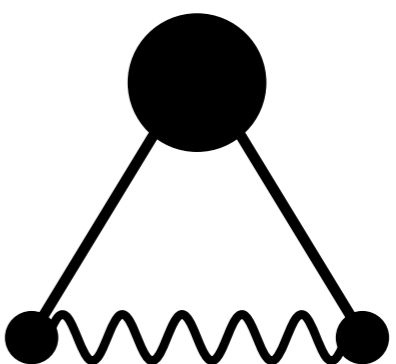
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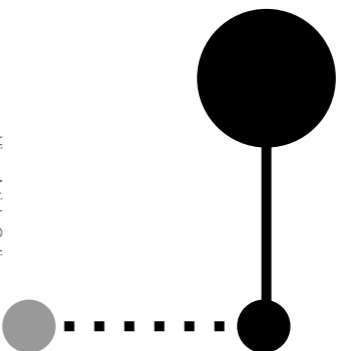
(a)



(b)



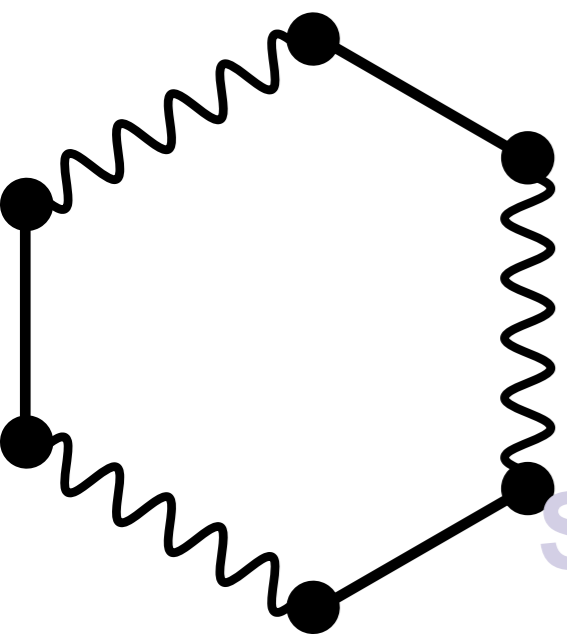
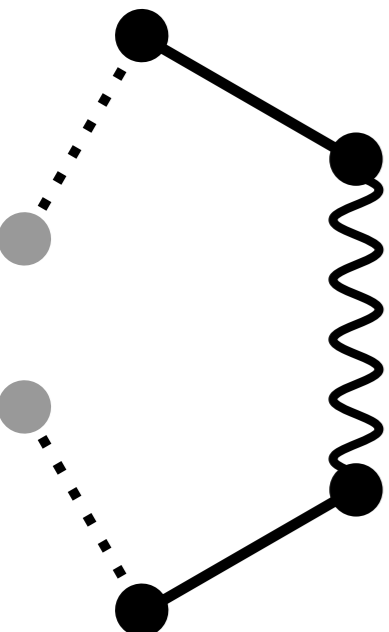
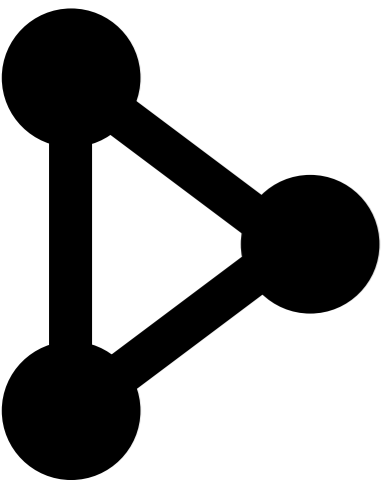
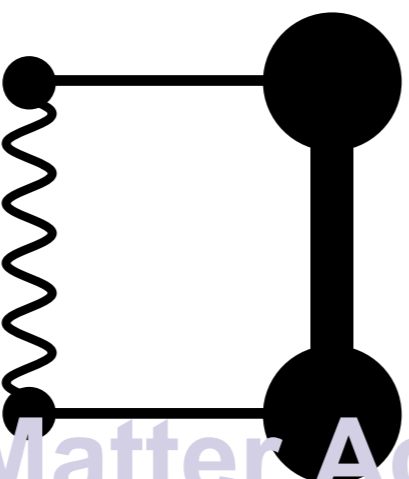
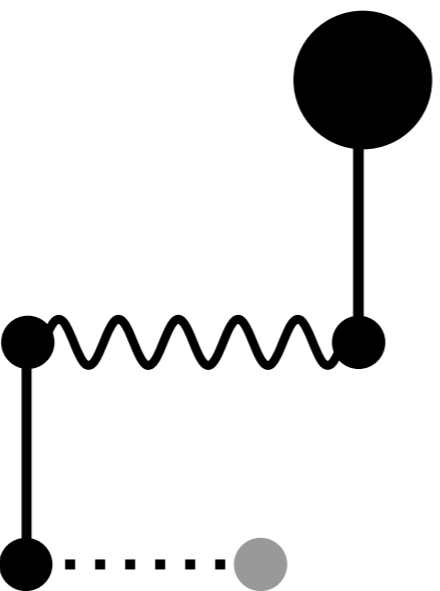
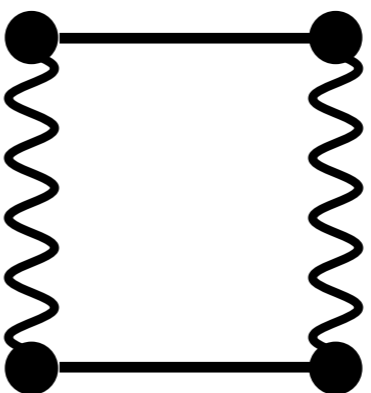
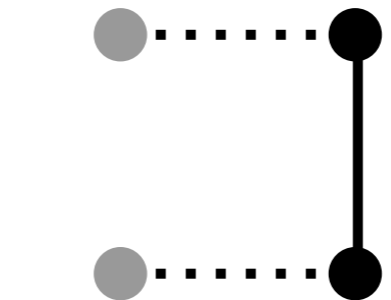
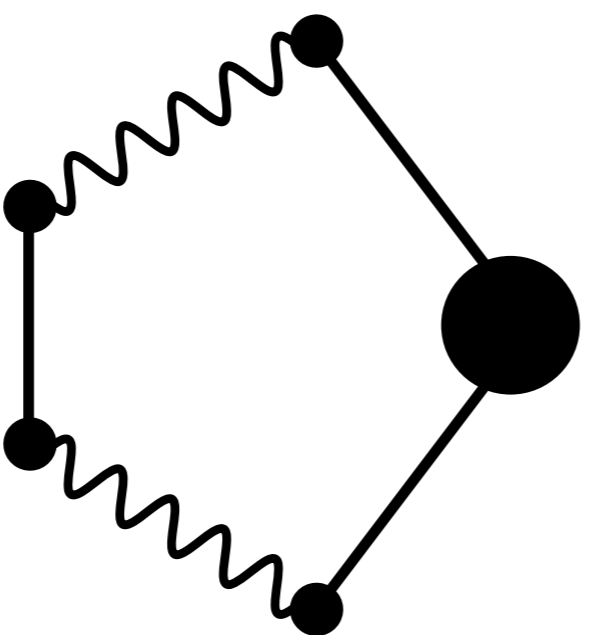
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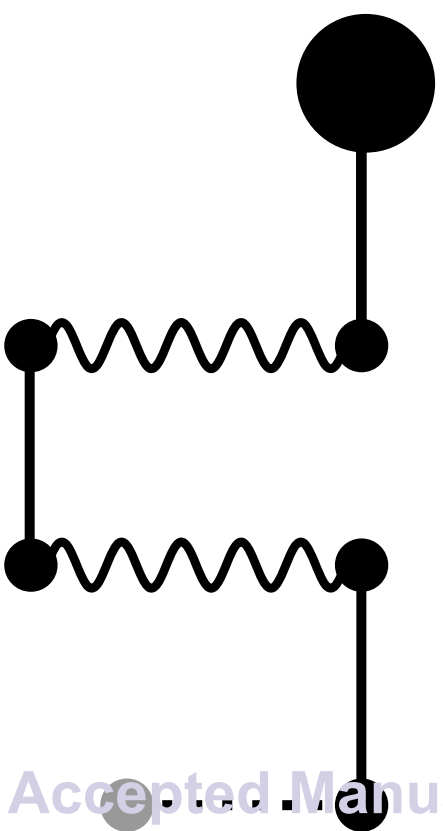
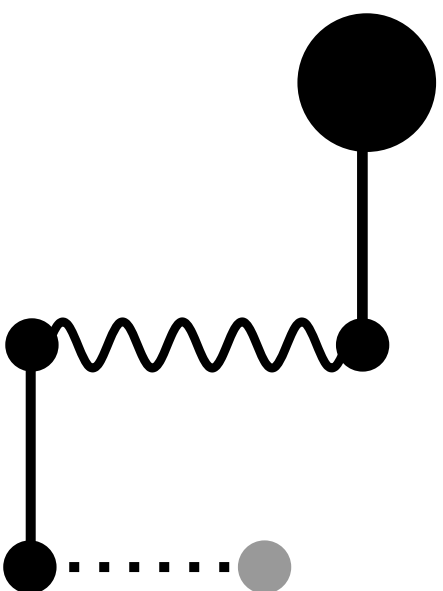
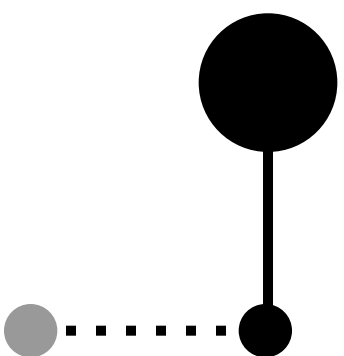
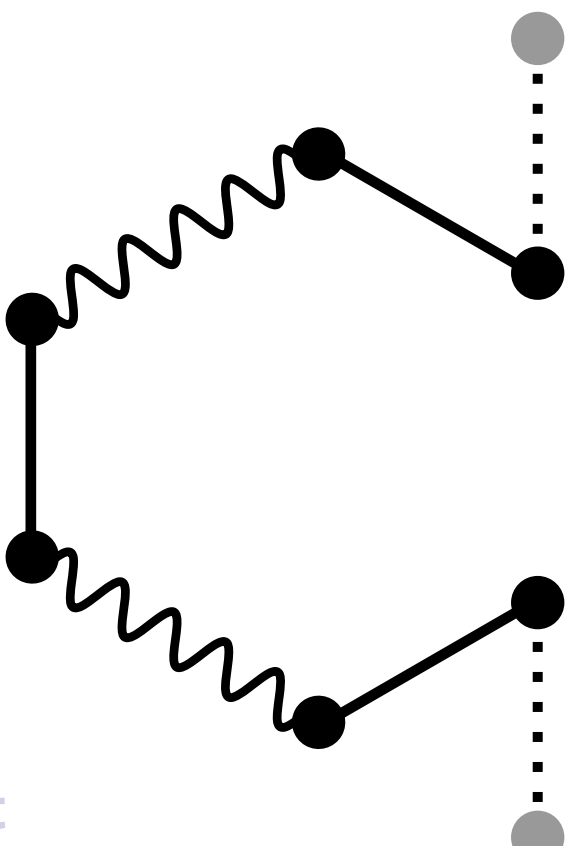
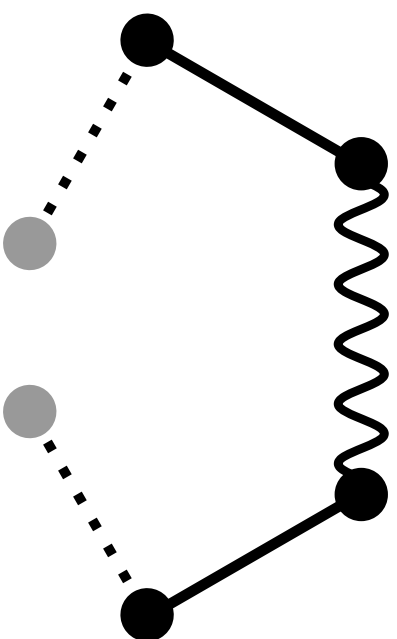
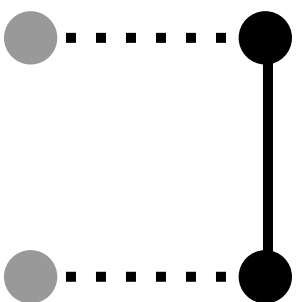
Soft Matter

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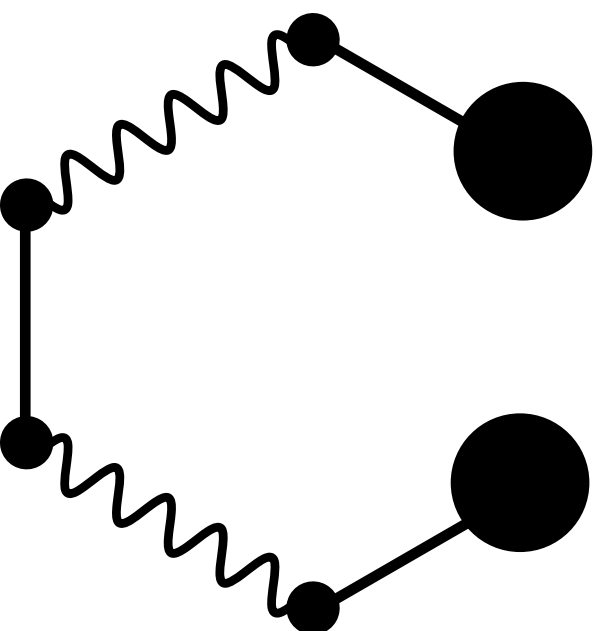
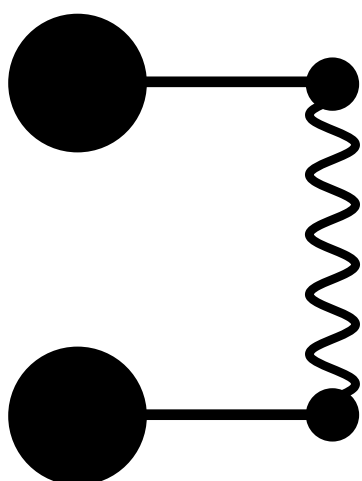
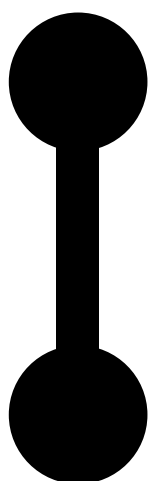
(c)



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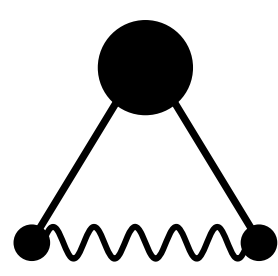
C2



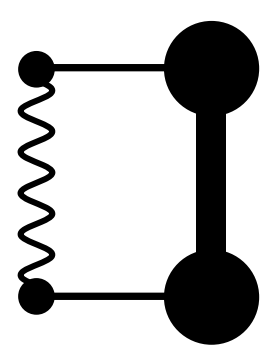
R0



R1



R2



Soft Matter

