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Abstract. A theory based on a density-functional formalism is developed to obtain the solvent-induced potential between different sites on a polymer. The expression found for the potential surface is not pair decomposable. The theory brings to light a new approach for deriving solute-solvent correlation functions and computation of multipoint correlation functions in fluids.

The solvent-mediated interactions between solutes are well known to be of fundamental importance in the formation and stability of structures involving biopolymers [1, 2] and for an understanding of the coil-globule transition [3] in polymer solutions. However, despite the substantial advances which have been made in the theory of liquids and solutions in recent years [4] the details of the solvent-mediated forces between solutes at short range remain poorly resolved. The reason for this is simply related to the difficulty produced by the problems. Computer simulation involves an enormous computational investment [5] since, in a rough sense, even at infinite dilution each solute-solute separation corresponds to a separate simulation study of the magnitude of a single solute in solution. On the other hand, the theory of liquids has not yet developed to the extent that it can be reliably applied for quantitative results to polymer problems.

In this paper we develop a theory based on a density-functional formalism to obtain the solvent-induced potential surface for site-site (or monomer-monomer) interactions. The density-functional formalism is conceptually simple, containing as few independent approximations as appears presently feasible. It requires as input the solute-solvent *direct pair correlation function* as a function of number density and temperature. Therefore the theory must also give a method to compute the solute-solvent correlations.

Let the total free energy of a combined system of a polymer with P interaction sites constrained to the configuration $(r^{(1)}, r^{(2)}, \ldots, r^{(P)} \equiv \{r^{(\alpha)}\}$ and the one-component solvent in volume V be written as

$$\beta A\{r^{(\alpha)}\} = \beta A^s[\rho_s(r)] + \beta A_0^p\{r^{(\alpha)}\} + \beta \Delta\mu([\rho_s(r)], \{r^{(\alpha)}\}) \tag{1}$$

where $\beta A^s[\rho_s(r)]$ is the reduced free energy of the solvent having the single-particle density distribution $\rho_s(r)$ and β^{-1} is the Boltzmann constant times temperature. $\beta A_0^p\{r^{(\alpha)}\}$ is the reduced free energy of an unperturbed polymer of constrained configuration given by $\{r^{(\alpha)}\}$ and $\beta \Delta\mu ([\rho_s(r)], \{r^{(\alpha)}\})$ is the reduced excess free energy arising due to interactions between the solvent molecules and the polymer of given structure $\{r^{(\alpha)}\}$. $\beta \Delta\mu$ is a functional of both $\rho_s(r)$ and the polymer structure. These functional dependences are indicated, respectively, by square and curly brackets. Here for the

sake of simplicity we have assumed that each solvent molecule has one interaction site. Generalisation to many interaction sites and to a multicomponent solvent [6] is straightforward.

If we assume that, in the absence of the polymer, the solvent is a uniform system with the density distribution ρ_s, a constant independent of position, then the external potential responsible for creating the non-uniformity $\Delta\rho_s(r) = \rho_s(r) - \rho_s$ in the density distribution of the solvent is

$$\frac{\delta\beta\Delta\mu}{\delta\rho_s(r)}\bigg|_{T,v} = \beta\phi_s(r). \tag{2}$$

This external field is produced by the polymer and is therefore a functional of the structure of the polymer in addition to $\rho_s(r)$. The *solute-solvent direct pair correlation function* is defined in [7]

$$\frac{\delta(\beta\phi_s(r))}{\delta\rho_\alpha(r')} = -c_{\alpha s}(r, r') \tag{3}$$

where $\rho_\alpha(r')$ is the density distribution of a site α in the polymer. For the constrained polymer

$$\rho_\alpha(r) = \delta(r - r^{(\alpha)}). \tag{4}$$

Though not explicitly written, the functional dependence of ϕ_s, $c_{\alpha s}$ and $\beta\Delta\mu$ on $\rho_s(r)$ and the polymer structure should be kept in mind. The functional integration of (3) yields

$$-\beta\phi_s(r) = \sum_{\alpha=1}^{P} \int dr' \, \rho_\alpha(r')\bar{c}_{\alpha s}(r, r') \tag{5}$$

where

$$\bar{c}_{\alpha s}(r, r') = \int_0^1 d\lambda \, c_{\alpha s}(r, r'; \lambda\rho_\alpha).$$

The solvent-mediated external field acting on the site of the polymer is

$$\frac{\delta(\beta\Delta\mu)}{\delta\rho_\alpha(r)} = \beta\psi_\alpha(r). \tag{6}$$

Since $\beta\Delta\mu$ vanishes at zero polymer density we have, from functional integration of (6),

$$\beta\Delta\mu = \sum_{\alpha=1}^{P} \int dr \, \rho_\alpha(r)\beta\phi_\alpha(r) \tag{7}$$

where

$$\phi_\alpha(r) = \int_0^1 d\lambda \, \psi_\alpha[r, \lambda\rho_\alpha(r)] \tag{8}$$

and ϕ_α is a functional of both the solvent density and the polymer structure.

The functional Taylor expansion of (7) about the uniform density of the solvent, ρ_s, leads to

$$\beta\Delta\mu\{r^{(\alpha)}\} = \sum_{\alpha=1}^{P} \int dr \, \rho_\alpha(r)\beta\phi_\alpha(r, \rho_s) - \sum_{\alpha=1}^{P} \int dr \int dr' \, \rho_\alpha(r)\bar{c}_{\alpha s}(r, r'; \rho_s)\delta\rho_s(r') \tag{9}$$

where

$$c_{\alpha s}(\mathbf{r}, \mathbf{r}'; \rho_s) = \frac{\delta(-\beta\psi_\alpha(\mathbf{r}))}{\delta\rho_s(\mathbf{r}')}\bigg|_{\rho_s(\mathbf{r}') = \rho_s}. \tag{10}$$

Here $\psi_\alpha(\mathbf{r}, \rho_s)$ is the potential field exerted at site α in the polymer by the uniform solvent. $c_{\alpha s}$ is the solute–solvent direct pair correlation function. For an isolated system, $c_{\alpha s}$ defined by (3) and (10) are identical.

From the linear response theory one obtains

$$\delta\rho_s(\mathbf{r}) = \int \frac{\delta\rho_s(\mathbf{r})}{\delta(-\beta\phi_s(\mathbf{r}'))}\bigg|_{\phi_s(\mathbf{r}') = 0} (-\beta\phi_s(\mathbf{r}')) \, \mathrm{d}\mathbf{r}'$$

$$= \sum_{\eta=1}^{P} \int \mathrm{d}\mathbf{r}' \int \mathrm{d}\mathbf{r}'' \chi_{ss}(\mathbf{r}, \mathbf{r}') \tilde{c}_{\eta s}(\mathbf{r}', \mathbf{r}'') \rho_\eta(\mathbf{r}''). \tag{11}$$

Here use has been made of (5). χ_{ss} is the density–density correlation function of the uniform solvent, i.e.

$$\chi_{ss}(\mathbf{r}, \mathbf{r}') = \frac{\delta\rho_s(\mathbf{r})}{\delta(-\beta\phi_s(\mathbf{r}'))}\bigg|_{\Phi_s(\mathbf{r}') = 0}$$

$$= \rho_s\delta(\mathbf{r} - \mathbf{r}') + \rho_s^2 h_{ss}(\mathbf{r}, \mathbf{r}') \tag{12}$$

where $h_{ss}(r)$ is the total pair correlation function of the uniform solvent. The solvent-mediated field at $\mathbf{r}^{(\alpha)}$ due to a uniform fluid of density ρ_s is obtained by functional integration of (10) and (8), i.e.

$$\beta\phi_\alpha(\mathbf{r}^{(\alpha)}, \rho_s) = -\rho_s \int \mathrm{d}\mathbf{r} \int_0^1 \mathrm{d}\lambda \, \tilde{c}_{\alpha s}(\mathbf{r}^{(\alpha)}, \mathbf{r}; \lambda\rho_s). \tag{13}$$

Combining (9), (11), (13) and (14) we get the following expression for the solvent-induced energy surface for a constrained polymer of configuration $\{\mathbf{r}^{(\alpha)}\}$:

$$-\beta\Delta\mu\{\mathbf{r}^{(\alpha)}\} = \sum_{\alpha=1}^{P} \rho_s \int \mathrm{d}\mathbf{r} \int_0^1 \mathrm{d}\lambda \, \tilde{c}_{\alpha s}(\mathbf{r}, \mathbf{r}^{(\alpha)}; \rho_s) - \frac{1}{2}\sum_{\alpha \ne \eta = 1}^{P} v(\mathbf{r}^{(\alpha)}, \mathbf{r}^{(\eta)})$$

$$\tag{14}$$

with

$$v(\mathbf{r}^{(\alpha)}, \mathbf{r}^{(\eta)}) = -\int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \, \tilde{c}_{\alpha s}(\mathbf{r}^{(\alpha)}, \mathbf{r}) \chi_{ss}(\mathbf{r}, \mathbf{r}') \tilde{c}_{\eta s}(\mathbf{r}', \mathbf{r}^{(\eta)}). \tag{15}$$

A factor of $\frac{1}{2}$ is included here to avoid counting the same pair twice.

Our derivation clearly indicates that the function $c_{\alpha s}$ which appears in (15) is a functional of the polymer structure. Because of this the solvent-generated potential surfaces are not pair decomposable. This complexity seems central to the physics of the system. Indeed, consider the polymer in a tangled configuration for which the interior portion is shielded from the solvent by the exterior. The reversible work associated with moving a pair of monomers buried within the interior is clearly different than would be found when the polymer is untangled and the pair is exposed to the solvent. This fact implies that the potential of mean force associated with a pair of momoners in the polymer depends upon the configuration of many other monomers. It seems therefore, that in an essential way, $\beta\Delta\mu\{\mathbf{r}^{(\alpha)}\}$ cannot be pair decomposable.

In order to obtain an integral equation for solute-solvent correlation functions we generalise the method of Percus [8]. Let a site α of the polymer be localised at $r^{(\alpha)}$. The change induced in the density distribution of the solvent due to the polymer in linear response theory (see (11)) is

$$\delta\rho_s[r'/u_{\alpha s}(r^{(\alpha)}, r')]$$

$$= \sum_{\eta=1}^{P} \int dr'' \int dr''' \chi_{xx}(r', r'') \tilde{c}_{\eta s}(r'', r^{(\eta)}) \delta\rho_\eta[r'''/\phi_{\alpha\eta}(r^{(\alpha)}, r^{(\eta)})]. \tag{16}$$

Here $u_{\alpha s}$ indicates the pair interaction between a site of the polymer and a solvent molecule and $\phi_{\alpha\eta}$ the site-site interaction.

The basis of the Percus method is the interaction of the quantity $\rho(1 + h(r))$ as the local number density at a distance r from the origin, i.e. one particle of the system is known to be located at the origin, i.e. $\rho(r/\phi(r, 0)) = \rho[1 + h(r, 0)]$ where $\phi(r, 0)$ is the pair potential. The extension of this interpretation of our problem leads to

$$\delta\rho_s[r'/u_{\alpha s}(r^{(\alpha)}, r')] = \rho_s h_{\alpha s}(r^{(\alpha)}, r') \tag{17}$$

and

$$\rho_\eta[r'/\phi_{\alpha\eta}(r^{(\alpha)}, r')] = w_{\alpha\eta}(r^{(\alpha)}, r') \tag{18}$$

where $w_{\alpha\eta}$ is the intrapolymer pair correlation:

$$w_{\alpha\eta}(r, r') = \delta_{\alpha\eta}\delta(r - r') + s_{\alpha\eta}(r, r') \tag{19}$$

with

$$s_{\alpha\eta}(r, r') = (1 - \delta_{\alpha\eta})\langle\delta(r - r^{(\alpha)})\delta(r' - r^{(\eta)})\rangle \tag{20}$$

where $s_{\alpha\eta}$ gives the joint probability density of finding two different sites α and η at positions r and r', respectively. The factor $(1 - \delta_{\alpha\eta})$ ensures that α and η refer to different sites.

From (16)-(18) we get

$$\rho_s h_{\alpha s}(r^{(\alpha)}, r) = \sum_{\eta=1}^{P} \int dr' \int dr'' \chi_{ss}(r, r') \tilde{c}_{\eta s}(r', r'') w_{\alpha\eta}(r^{(\alpha)}, r''). \tag{21}$$

This is analogous to the equation obtained from the so-called RISM (reference interaction site model) theory [9]. χ_{ss} is obtained from either an experiment or a computer simulation on the pure solvent. With the known values of χ_{ss}, (21) is solved for $c_{\alpha s}$ with an appropriate closure. Motivated by the hypernetted chain (HNC) theory of simple fluids [7], one can use the following closure:

$$1 + h_{\alpha s}(r) = \exp[-u_{\alpha s}(r) + h_{\alpha s}(r) - c_{\alpha s}(r)]. \tag{22}$$

This theory for intermolecular pair correlation, usually referred to as the extended RISM equation, is known to be accurate for simple models of polyatomic systems [9]. The solutions $c_{\alpha s}$ and $h_{\alpha s}$ are non-linear functionals of the polymer structure, $w_{\alpha\eta}(r)$.

Equations (14) bears a striking relationship to the potential surface predicted from a Gaussian field theory [10]. We consider a model in which the solvent density fields, $\rho_s(r)$, obey Gaussian statistics with variance $\chi_{ss}(r, r')$ and a site is coupled to the solvent with the potential energy

$$-kT \sum_{\alpha=1}^{P} \int dr \rho_s(r) \tilde{c}_{\alpha s}(r^{(\alpha)}, r).$$

On performing the functional integration over density fields, one finds the pair correlation in this model is given by (21) and the potential surface is given very nearly by (14). The difference resides with the first term. This term in the Gaussian field theory is

$$\sum_{\alpha=1}^{P} \rho_s \int \mathrm{d}r \, \tilde{c}_{\alpha s}(r, \rho_s). \tag{23}$$

In another derivation of $-\beta \Delta \mu \{r^{(\alpha)}\}$, Singer and Chandler [11] started with a 'charging' formula and relations (21) and (22). For the first term they found

$$\rho_s \sum_{\alpha} \int \mathrm{d}r [c_{\alpha s}(r) - \tfrac{1}{2} h_{\alpha s}^2(r)]. \tag{24}$$

This owes its form to the closure relation (22). Both (23) and (24) can be regarded as approximate forms of the first term of (14).

To calculate the properties of the polymer we concentrate on the partition function of the polymer in the solvent, which in the continuum limit $P \to \infty$ is given by

$$Z = \int \! \int \mathrm{D}r(t) s^{(0)}[r(t)] y[r(t)]. \tag{25}$$

In this expression the weighting of configurations is determined by the solvent-induced interactions $\beta \Delta \mu[r(t)]$, as well as the intrapolymer energetics contained in $s^{(0)}[r(t)]$ which in turn is given in [12] as

$$s^{(0)}[r(t)] \propto \exp\left(-\frac{3}{2a} \int_0^L |\dot{r}(t)|^2 \, \mathrm{d}t - \tfrac{1}{2}\beta \int \! \int_0^L \phi[r(t) - r(t')] \, \mathrm{d}t \, \mathrm{d}t'\right) \tag{26}$$

where the integration is over all continuous curves $r(t)$, $0 \leq t \leq L$, such that $r(0) \equiv 0$, a is the size of the statistical unit and L is the total contour length along the chain, $L = Pa$. A constrained path $r(t)$ corresponds to a constrained conformation $\{r^{(\alpha)}\}$ of the polymer. In (25), $y[r(t)] = \lim_{P \to \infty} y\{r^{(\alpha)}\}$ is the Boltzmann factor for the solvent contribution to the potential of mean force for the P interaction sites on the polymer, i.e.

$$\ln y\{r^{(\alpha)}\} = -\beta \Delta \mu \{r^{(\alpha)}\}. \tag{27}$$

The pair correlation function for the polymer is determined by a functional integral similar to (25) but with two points on the path constrained to a fixed separation, in

$$w(r - r') = \langle \delta[r - r' - r(t) + r(t')] \rangle$$

$$= \int \! \int \mathrm{D}r(t) \delta[r - r' - r(t) + r(t')] s^{(0)}[r(t)] y[r(t)]. \tag{28}$$

Since the solvent-generated interactions and the 'long-range' intrapolymer interactions are in general not harmonic, the evaluation of the functional integrals of (26) and (28) is not easy. The competition between ϕ and v will, however, lead to many interesting features including θ point. The solvent-induced interaction v may favour a collapsed polymer structure. The physical reason for this behaviour is that, by making the polymer smaller, there is a smaller solvent free energy change required to accommodate the polymer. The compression of the polymer will, however, compete with the entropic preference of an extended structure. These effects may be sensitive to the details of the interactions present in the system.

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