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The free energy of a system containing  $N_1, N_2, \dots, N_M$  molecules of types  $1, 2, \dots, M$  can be written as a sum of three terms, the entropy, intra- and inter-molecular terms, all written in terms of  $kT$ ,

$$F = -\langle S \rangle + \langle H^{intra} \rangle + \langle H^{inter} \rangle \quad (1)$$

where the angular brackets denote the average over the probability distribution function (pdf)  $\rho$  of the system,  $\langle \dots \rangle = \int \dots \rho d\rho$ . This function contains all information about the equilibrium state of the whole system. If there are no strong correlations between interacting particles, such as ion pair formation or bonds formation, we can neglect the correlations between the molecules and use the mean field approximation: the pdf  $\rho$  of many component system factorizes into the product of single molecules pdfs  $\rho_\alpha(\Gamma_{\alpha i})$ ,

$$\rho \approx \prod_{\alpha=1}^M \prod_{i=1}^{N_\alpha} \rho_\alpha(\Gamma_{\alpha i}) \quad (2)$$

where  $\Gamma_{\alpha i}$  is the conformation of  $i$ -th molecule of type  $\alpha$ . Such factorization into contributions of individual molecules allows us to derive a close set of equations for  $\rho_\alpha(\Gamma_{\alpha i})$ .

The entropy term in the expression (1) is written as

$$\langle S \rangle = -\langle \ln \rho \Lambda \rangle, \quad (3)$$

where the factor  $\Lambda$  is the de Broglie length which has a quantum mechanics origin,

$$\Lambda = \prod_{\alpha=1}^M \Lambda_\alpha^{N_\alpha} N_\alpha! \approx \prod_{\alpha=1}^M \left( \frac{N_\alpha \Lambda_\alpha}{e} \right)^{N_\alpha} \quad (4)$$

Since the constants  $\Lambda_\alpha$  do not appear in the final expressions, they can be treated as unknown normalization constants. Thus, after factorizing the pdf  $\rho$  (2), the entropy

term (3) reads

$$\langle S \rangle \approx - \sum_{\alpha=1}^M N_{\alpha} \left\langle \ln \frac{\rho_{\alpha} N_{\alpha}}{e} \Lambda_{\alpha} \right\rangle \quad (5)$$

where the brackets on the right hand side denote the average over the single molecule pdf  $\rho_{\alpha}$ . Similar arguments allow us to write the intra-molecular energy of the system as a sum of contributions of the single molecules of different types

$$\langle H^{intra} \rangle \approx \sum_{\alpha=1}^M N_{\alpha} \langle H_{\alpha}^{intra} \rangle \quad (6)$$

Before writing a similar expression for the inter-molecular part, we assume that molecules of each type  $\alpha$  comprise of subunits with different chemical structure, and thus different energy parameters. Subunits can represent Kuhn segments in the chain or, in case of coarse-graining description, the groups of atoms or beads in a coarse-grained model. Thus, the interaction energy between a molecule of type  $\alpha$  in the conformation state  $\Gamma_{\alpha}$  and a molecule of type  $\beta$  in the conformation state  $\Gamma_{\beta}$ , can be written as a sum over the types of beads  $a$  as

$$H_{\alpha\beta}^{inter}(\Gamma_{\alpha}, \Gamma_{\beta}) = \sum_a \int u_{\alpha}^a(\Gamma_{\alpha}, \mathbf{r}) c_{\beta}^a(\Gamma_{\beta}, \mathbf{r}) d\mathbf{r} \quad (7)$$

In this expression  $c_{\beta}^a(\Gamma_{\beta}, \mathbf{r})$  is the concentration of units of type  $a$  at the point  $\mathbf{r}$  of a molecule of type  $\beta$  in the conformation state  $\Gamma_{\beta}$ . These units interact with the field  $u_{\alpha}^a(\Gamma_{\alpha}, \mathbf{r})$  created by the molecules of type  $\alpha$ . Thus, factorizing the pdf  $\rho$  (2) one can write the inter-molecular interaction free energy in the form

$$\langle H^{inter} \rangle \approx \frac{1}{2} \sum_{\alpha, \beta=1}^M N_{\alpha} (N_{\beta} - \delta_{\alpha\beta}) \sum_a \int \langle u_{\alpha}^a(\mathbf{r}) \rangle \langle c_{\beta}^a(\mathbf{r}) \rangle d\mathbf{r} \quad (8)$$

where  $\delta_{\alpha\beta}$  is the delta symbol. Thus, the interaction free energy is represented by the interaction of the average concentration of beads with the average fields at each point.

The free energy is usually coupled with the incompressibility condition implying that the sum of the concentrations of all components in a solution is fixed. However, this condition implies the hard core repulsion between all beads in the system, and thus

creates computational problems in converging the SCMF equations. To overcome this problem, we introduce the explicit incompressibility condition in every point  $\mathbf{r}$  in the system,

$$\sum_{\alpha=1}^M N_{\alpha} \langle \phi_{\alpha}(\mathbf{r}) \rangle = \phi_0 \quad (9)$$

where  $\langle \phi_{\alpha}(\mathbf{r}) \rangle$  is the average volume fraction occupied by a molecule of type  $\alpha$  in the point  $\mathbf{r}$ , while  $\phi_0$  is the total volume fraction occupied by the molecules of all types.

Combining all terms (5), (6), (8) together with the incompressibility condition (9), the free energy of the system can be written as

$$\begin{aligned} F[\rho_1, \rho_2, \dots, \rho_M] \approx & \sum_{\alpha=1}^M N_{\alpha} \left\langle \ln \frac{\rho_{\alpha} N_{\alpha}}{e} \Lambda_{\alpha} \right\rangle + \sum_{\alpha=1}^M N_{\alpha} \langle H_{\alpha}^{intra} \rangle + \\ & + \frac{1}{2} \sum_{\alpha, \beta=1}^M N_{\alpha} (N_{\beta} - \delta_{\alpha\beta}) \sum_a \int \langle u_{\alpha}^a(\mathbf{r}) \rangle \langle c_{\beta}^a(\mathbf{r}) \rangle d\mathbf{r} + \\ & + \int \lambda(\mathbf{r}) \left( \phi_0 - \sum_{\alpha=1}^M N_{\alpha} \langle \phi_{\alpha}(\mathbf{r}) \rangle \right) d\mathbf{r} \end{aligned} \quad (10)$$

where  $\lambda(\mathbf{r})$  is a Lagrange multiplier and all the averages are taken over the single-molecule pdfs  $\rho_{\alpha}$ . Minimization of this functional with respect to  $\rho_{\alpha}$  gives the pdf of a single molecule of type  $\alpha$

$$\begin{aligned} \rho_{\alpha}(\Gamma_{\alpha}) = & \frac{1}{Z_{\alpha}} \exp \left( -H_{\alpha}^{intra}(\Gamma_{\alpha}) - \sum_{\beta=1}^M (N_{\beta} - \delta_{\alpha\beta}) \times \right. \\ & \left. \sum_a \int u_{\alpha}^a(\Gamma_{\alpha}, \mathbf{r}) \langle c_{\beta}^a(\mathbf{r}) \rangle d\mathbf{r} + \int \lambda(\mathbf{r}) \phi_{\alpha}(\Gamma_{\alpha}, \mathbf{r}) d\mathbf{r} \right) \end{aligned} \quad (11)$$

where  $Z_{\alpha}$  is a normalization constant which is found from the normalization condition  $\int \rho_{\alpha}(\Gamma_{\alpha}) d\Gamma_{\alpha} = 1$ . This constant has a meaning of a partition function of the system at equilibrium and  $-\ln Z_{\alpha}$  is the total free energy of the system at equilibrium.

Once the average concentrations  $\langle c_{\beta}^a(\mathbf{r}) \rangle$  and the volume fractions  $\langle \phi_{\beta}(\mathbf{r}) \rangle$  are known, this expression allows to calculate the probabilities of each conformation  $\rho_{\alpha}(\Gamma_{\alpha})$  for all molecules in the system. In turn, if the probabilities  $\rho_{\alpha}(\Gamma_{\alpha})$  are known, the average concentrations and volume fractions, being the the molecular fields in this problem

are found from the self-consistency conditions,

$$\begin{aligned}\langle c_\alpha^a(\mathbf{r}) \rangle &= \int c_\alpha^a(\Gamma_\alpha, \mathbf{r}) \rho_\alpha(\Gamma_\alpha) d\Gamma_\alpha \\ \langle \phi_\alpha(\mathbf{r}) \rangle &= \int \phi_\alpha(\Gamma_\alpha, \mathbf{r}) \rho_\alpha(\Gamma_\alpha) d\Gamma_\alpha,\end{aligned}\quad (12)$$

representing the averages over the probabilities of conformations.

The probability of each conformation can be written as  $\rho_\alpha(\Gamma_\alpha) = \frac{1}{Z_\alpha} \exp[-H_{eff}(\Gamma_\alpha)]$ , where  $H_{eff}(\Gamma_\alpha)$  is the effective Hamiltonian given by (11), which describes the system at equilibrium. The last term in the effective Hamiltonian corresponds to the steric repulsion of beads of all types. If one of the components is a one bead solvent, the only degree of freedom of the solvent molecules is the position in space,  $\mathbf{r}$ . Hence, the volume fraction of the solvent, can be found from the incompressibility condition (9)

$$\phi_s(\mathbf{r}) = \phi_0 - \sum_{\alpha=1, \alpha \neq s}^M N_\alpha \langle \phi_\alpha(\mathbf{r}) \rangle \quad (13)$$

In addition, the Lagrange multiplier  $\lambda(\mathbf{r})$  can be expressed through the concentration of the solvent. The pdf of the solvent  $\rho_s(\mathbf{r})$ , the concentration  $c_s(\mathbf{r})$  and the volume fraction occupied by the solvent  $\phi_s(\mathbf{r})$  are related via the following expressions

$$\rho_s(\mathbf{r}) = \frac{c_s(\mathbf{r})}{N_s} = \frac{\phi_s(\mathbf{r})}{v_s N_s} \quad (14)$$

where  $N_s$  is the number and  $v_s$  is the volume of the solvent molecule, while the molecular field

$$\phi_s(\mathbf{r}, \mathbf{r}') \approx v_s \delta(\mathbf{r} - \mathbf{r}') \quad (15)$$

where  $\delta(\mathbf{r} - \mathbf{r}')$  is the Dirac delta-function. Substitution of (14) and (15) into (11) gives the approximate expression for the Lagrange multiplier  $\lambda(\mathbf{r})$

$$v_s \lambda(\mathbf{r}) \approx \ln \phi_s(\mathbf{r}) + \sum_{\beta=1}^M (N_\beta - \delta_{s\beta}) \sum_a \int u_s^a(\mathbf{r}, \mathbf{r}') \langle c_\beta^a(\mathbf{r}') \rangle d\mathbf{r}' \quad (16)$$

where we have assumed that  $H_s^{intra}(\mathbf{r}) = 0$  and omitted few constants, which will cancel out by the normalization of  $\rho_\alpha$ .

It is noteworthy, that in our equations the fields  $\langle\phi_\alpha(\mathbf{r})\rangle$  and  $\langle c_\alpha^a(\mathbf{r})\rangle$  formally are not related although they both correspond to the concentration of monomers. They are indeed related through the volume of the monomers only if the molecules are composed of *non-overlapping* beads, when the distance between the centers is larger than the diameter. However, if we want to conserve the possibility of describing the overlapping beads, the coefficient of proportionality between  $\langle\phi_\alpha(\mathbf{r})\rangle$  and  $\langle c_\alpha^a(\mathbf{r})\rangle$  is not known a priori and we keep them as independent variables.

The equations (11),(12),(13) and (16) form a closed set of non-linear equations of the SCMF theory. The solution of these equations gives the equilibrium structures, the self-consistent molecular fields such as the concentration profiles of the beads of each type and the distribution of the solvent, and the probabilities of each conformation of the molecules in the fields and the accurate measure of equilibrium free energies.