Appendix A
Statistical Mechanical Derivation of the Free Volume Theory

Here we present a statistical mechanical derivation of the grand potential. According to statistical mechanics (see for instance T.L. Hill, *An Introduction to Statistical Thermodynamics*. Addison-Wesley, New York, 1962) the grand potential is given by

$$\Omega(N_c, V, T, \mu_d) = -kT \ln \Xi(N_c, V, T, \mu_d), \quad (A.1)$$

where $\Xi$ is the grand canonical partition function

$$\Xi = \sum_{N_d=0}^{\infty} \exp(\mu_d N_d / kT) Q(N_c, V, T, N_d). \quad (A.2)$$

Here $Q$ is the canonical partition function

$$Q = \frac{1}{\Lambda_c^{3N_c}\Lambda_d^{3N_d} N_c!N_d!} \int \exp[-(U_c + U_{cd})/kT] \, dR^{N_c} d\mathbf{r}^{N_d}, \quad (A.3)$$

where $U_c$ is the interaction between the $N_c$ hard spheres and $U_{cd}$ the interaction between the $N_c$ hard spheres and the $N_d$ (depletants). The latter term in the interaction limits the integration over the position of the penetrable hard spheres to the free volume which is a function of the positions $\mathbf{R}^{N_c}$ of the $N_c$ hard spheres. This leads to

$$Q = \frac{1}{\Lambda_c^{3N_c}\Lambda_d^{3N_d} N_c!N_d!} \int \exp[-U_c/kT] \langle V_{\text{free}} \rangle^{N_d} d\mathbf{r}^{N_d}. \quad (A.4)$$

Substituting (A.4) in (A.2) and taking into account that

$$\sum_{N_d=0}^{\infty} \frac{\exp(\mu_d N_d / kT) \langle V_{\text{free}} \rangle^{N_d}}{\Lambda_d^{3N_d} N_d!} = \exp[P \langle V_{\text{free}} \rangle / kT], \quad (A.5)$$
where we have used that the right hand side of (A.5) is just the grand canonical partition of the penetrable hard spheres with chemical potential $\mu_d$ in a volume $\langle V_{\text{free}} \rangle$, we obtain

$$
\Xi = \frac{1}{N_c^{N_c} N_c!} \int \exp[-(U_c - P_d^R \langle V_{\text{free}} \rangle)/kT] \, d\mathbf{R}^{N_c}
$$

(A.6)

where $Q(N_c, V, T)$ is the canonical partition function of the $N_c$ hard spheres and the pointed brackets with subscript 0 indicate an average over the unperturbed configurations of the hard spheres. Substitution of (A.6) in (A.1) leads to

$$
\Omega = -kT \ln Q(N_c, V, T) - kT \ln \left( \exp \left( \frac{P^R \langle V_{\text{free}} \rangle}{kT} \right) / \left( \exp \left( \langle V_{\text{free}} \rangle / kT \right) \right) \right) \bigg|_0
$$

(A.7)

This expression for $\Omega$ is exact but, from a point of view of calculating it, difficult to handle. To make progress we replace the average of the exponent by the exponent of the average and obtain the following approximate expression for the grand potential

$$
\bar{\Omega} = F_0(N_c, V, T) - P^R \langle V_{\text{free}} \rangle_0
$$

(A.8)

This is precisely expression (3.24) we obtained from the thermodynamic integration route using the approximation (3.22). Using the well-known result that for an arbitrary probability distribution the following inequality holds

$$
\langle \exp(x) \rangle \geq \exp(\langle x \rangle)
$$

it follows immediately that the approximate grand potential obeys the inequality

$$
\bar{\Omega} \geq \Omega.
$$

(A.9)

We could have surmised this result also from our thermodynamic integration approach. As addition of depletants leads to some “clustering” of the hard spheres one expects that

$$
\langle V_{\text{free}} \rangle \geq \langle V_{\text{free}} \rangle_0
$$

and hence using the approximation (3.22) in the integration (3.18) leads to an approximate grand potential that is larger than the exact one. The statistical mechanical derivation presented above presents a rigorous proof of this supposition.
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