The Potential Distribution Theorem and Models of Molecular Solutions

An understanding of molecular statistical thermodynamic theory is fundamental to the appreciation of molecular solutions. This complex subject has been simplified by the authors with down-to-earth presentations of molecular theory. Using the potential distribution theorem (PDT) as the basis, the text provides an up-to-date discussion of practical theories in conjunction with simulation results. The authors discuss the field in a concise and simple manner, illustrating the text with useful models of solution thermodynamics and numerous exercises. Modern quasi-chemical theories that permit statistical thermodynamic properties to be studied on the basis of electronic structure calculations are given extended development, as is the testing of those theoretical results with *ab initio* molecular dynamics simulations. The book is intended for students undertaking research problems of molecular science in chemistry, chemical engineering, biochemistry, pharmaceutical chemistry, nanotechnology, and biotechnology.

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Preface

Molecular liquids are complicated because the defining characteristics that enliven the interesting cases are precisely molecular-scale details. We argue here that practical molecular theory can be simpler than this first observation suggests. Our argument is based upon the view that an effective tool for developing theoretical models is the potential distribution theorem, a local partition function to be used with generally available ideas for evaluating partition functions. An approach based upon the potential distribution theorem also allows functional theory to ride atop simulation calculations, clearly a prudent attitude in the present age of simulation.

This work is about molecular theory, and emphatically not about how to perform simulations. Molecular simulation is an essential component of modern research on solutions. There are a number of presentations of simulation techniques, but not of the molecular theory that we take up here. We offer this book as complementary theory with simulators in mind.

A goal of this book is, thus, to encourage those performing detailed calculations for molecular solutions to learn some of the theory and some of the sources. The physical insights permitted by those calculations are more likely to become apparent with an understanding of the theory that goes beyond the difficulties of executing molecular simulations. Confronting the enormity and lack of specificity of statistical mechanics usually would not be the practical strategy to achieve that goal.

This book also frequently attempts to persuade the reader that these problems can be simple. Extended discussions are directly *physical*, i.e., non-technical. This is consistent with our view that many of these problems *are* simple when viewed from the right perspective. Part of our view is, however, associated with a high-altitude style: in many instances, we are comfortable in presenting things simply and referring to comprehensive sources for background details (Münster, 1969,1974).

Thus, an introductory course in statistical thermodynamics, typically offered in graduate programs in chemistry and chemical engineering, is a prerequisite to this material. A few sections are at a level more advanced than that. But the references and access to a technical library, or to a knowledgeable teacher, would provide the natural supplement. We hope that this book will be accessible then to students with a strong background in a physical science, and specifically to graduate students embarking on research activities in molecular modeling of solutions in chemistry, chemical engineering, biophysics, pharmaceutical sciences, and in molecular biotechnology and nanotechnology.

We have made a conscious decision to emphasize aspects of the theory of molecular liquids different from the mature and familiar theory of atomic liquids. This decision is partly due to the fact that the theory of simple liquids is well described elsewhere, and partly due to the view that the specifically *molecular* aspects of solutions are essential to topics of current interest.

It is helpful to contrast the view we adopt in this book with the perspective of Hill (1986). In that case, the normative example is some separable system such as the polyatomic ideal gas. Evaluation of a partition function for a small system is then the essential task of application of the model theory. Series expansions, such as a virial expansion, are exploited to evaluate corrections when necessary. Examples of that type fill out the concepts. In the present book, we establish and then exploit the potential distribution theorem. Evaluation of the same partition functions will still be required. But we won't stop with an assumption of separability. On the basis of the potential distribution theorem, we then formulate additional simplified low-dimensional partition function models to describe many-body effects. Quasi-chemical treatments are prototypes for those subsequent approximate models. Though the design of the subsequent calculation is often heuristic, the more basic development here focuses on theories for discovery of those model partition functions. These deeper theoretical tools are known in more esoteric settings, but haven't been used to fill out the picture we present here.

Exercises are included all along, but not in the style of a textbook for a conventional academic discipline. Instead we intend the exercises to permit a more natural dialogue, e.g. by reserving technical issues for secondary consideration, or by framing consideration of an example that might be off the course of the main discussion.

The Platonic debate known as "The Learner's Paradox" suggests *if you don't know it, you can't learn it*. A judgment on the truth content of this assertion is tangential to the observation that learning is difficult in ways that are forgotten afterwards. A typical response to the Learner's Paradox is a discussion of example, organization of observations, and analogy. Learning does often result in "new concept $\mathcal{B}$ is like old concept $\mathcal{A}$." Our efforts that follow do introduce serious examples at an early stage, and do return to them later as the concepts develop further. With Mauldin[1] and Ulam, we thus accept Shakespeare's advice:

All things done without example, in their issue
Are to be fear'd.

Several important results are demonstrated more than once but from different perspectives.

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[1] Mauldin, R. D., Probability and nonlinear systems, *Los Alamos Science* (Special issue Stanislaw Ulam 1909–1984) **15**, 52 (1987).

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Glossary

α_p	Coefficient of thermal expansion at constant pressure, $\alpha_p = -(1/\mathcal{V})\,(\partial\mathcal{V}/\partial T)_p$.
β	Inverse temperature in energy units, $\beta = 1/kT$.
γ_α	Activity coefficient for species α.
ΔU_α	Binding energy of a molecule of type α to the solution.
$\Delta\tilde{U}_\alpha$	Reference system contribution, indicated by the tilde, to the binding energy of a distinguished molecule of type α to the solution.
ϵ	Dielectric constant.
κ_T	The isothermal compressibility $\kappa_T = (-1/\mathcal{V})\,(\partial\mathcal{V}/\partial p)_T$.
$\bar{\kappa}_{T\alpha}$	The isothermal compressibility for pure liquid α.
Λ_α	Thermal de Broglie wavelength, $\Lambda_\alpha = \sqrt{\frac{h^2\beta}{2\pi m_\alpha}}$, with m_α the mass of a molecule of type α.
μ_α	Chemical potential for molecular component α.
μ_α^{ex}	Interaction contribution to the chemical potential for molecular component α.
$\tilde{\mu}_\alpha^{\mathrm{ex}}$	Interaction contribution to the chemical potential of species α due to reference interactions between a distinguished molecule and the solution.
ξ_α	Available volume fraction for species α.
ρ_α	Number density of species α.
$\overline{\rho}_\alpha$	Number density of species α in pure liquid α.
$\rho(\mathcal{N}, \mathcal{N}')$	Thermal density matrix.
ϕ_α	Volume fraction of species α in Flory–Huggins treatment of polymer mixtures.
$\chi_{\alpha\gamma}$	Flory–Huggins interaction parameter for mixing of pure liquids of species α and γ.

$\mathcal{X}_{\alpha\gamma}$	Interaction parameter in Flory–Huggins treatment of polymer mixtures; after normalization on a per monomer basis this becomes $\chi_{\alpha\gamma}$, also susceptibilities in discussion of density functional theories.
$\varphi_{\alpha}(\mathcal{R}^n)$	Applied external field acting on species α in conformation $\mathcal{R}^n$.
$\varphi_{\alpha}(\boldsymbol{r})$	Applied external field as a function of position acting on species α.
$a^{(2)}_{\alpha\gamma}$	Contribution of attractive interactions to the second virial coefficient for species pair $\alpha\gamma$; also van der Waals coefficient.
$\mathcal{A}$	Helmholtz free energy, $\mathcal{A} = \mathcal{E} - T\mathcal{S}$.
$b_{\alpha}(j)$	Indicator function; equal to one (1) when solvent molecule j occupies the inner shell of a distinguished molecule of type α, and zero (0) when this solvent molecule is outside that region.
$b_{\alpha}(\mathcal{R}^n)$	Indicator function; equal to one (1) for configurations $\mathcal{R}^n$ recognized as forming a molecule of type α, and zero (0) otherwise.
$b^{(2)}_{\alpha\gamma}(T)$	Second virial coefficient for species pair $\alpha\gamma$, as a function of temperature T, *e.g.* $b^{(2)}_{\alpha\gamma}(T) = \tilde{b}^{(2)}_{\alpha\gamma} - a^{(2)}_{\alpha\gamma}/kT$.
$\tilde{b}^{(2)}_{\alpha\gamma}$	Second virial coefficient for species pair $\alpha\gamma$, for the case of reference interactions only.
B_k	Binomial moments, $\mathrm{B}_k \equiv \left\langle \binom{n}{k} \right\rangle_0$.
c_n	Concentration of a complex consisting of a specific solute of interest and n water molecules.
ε	Binding energy for a distinguished molecule to the solution.
$\mathcal{E}$	Internal energy.
$\mathcal{G}$	Gibbs free energy, $\mathcal{G} = \mathcal{H} - T\mathcal{S}$.
$\hbar$	Planck constant divided by 2π, $\hbar = h/2\pi$.
$\mathcal{H}$	Enthalpy, $\mathcal{H} = \mathcal{E} + p\mathcal{V}$.
$\mathbb{H}$	Hamiltonian, $\mathbb{H} = \mathbb{K} + \mathbb{V}$.
k	Boltzmann constant.
k_{α}	Henry's Law coefficient for species α.
$\mathbb{K}$	Kinetic energy.
K_n	Chemical equilibrium constant for the formation of a cluster of n water molecules with a specific solute of interest.
$m(x)$	For packing problems, the excess chemical potential as a function of available volume x, *e.g.* $m(x) = -\ln(1-x)$ is the primordial available volume theory.
M_{α}	Empirical polymerization index for species α.
$\boldsymbol{n}!$	Boltzmann–Gibbs total number of permutations of identical molecules, $\boldsymbol{n}! \equiv \prod_{\alpha} n_{\alpha}!$.
p	Pressure.
$\mathcal{P}^{(0)}_{\alpha}(\varepsilon)$	Probability distribution function for the binding energy of a distinguished molecule of type α to the solution in the case that these two subsystems are decoupled, as indicated by the superscript zero.

$\mathcal{P}_\alpha(\varepsilon)$	Probability distribution function for the binding energy for a distinguished molecule of type α to the solution in the case that these two subsystems are fully coupled.
$\tilde{\mathcal{P}}_\alpha(\varepsilon)$	Distribution of the perturbative contribution to the binding energy of a distinguished molecule of type α to the solution in the case, indicated by the tilde, that the binding energy is solely derived from the reference system $\Delta\tilde{U}_\alpha$.
q_α^{int}	Internal partition function of a molecule of species α.
$\mathcal{Q}(\boldsymbol{n})$	Canonical partition function with volume $\mathcal{V}$ and temperature T not specifically indicated, $\mathcal{Q}(\boldsymbol{n}) = \mathcal{Q}(\boldsymbol{n}, \mathcal{V}, T)$.
$\mathcal{Q}(n_\alpha = 1)$	Canonical partition function for the case of exactly one molecule of type α, with volume $\mathcal{V}$ and temperature T (not specifically indicated), $\mathcal{Q}(n_\alpha = 1) = \mathcal{V} q_\alpha^{\mathrm{int}} / \Lambda_\alpha^3$.
$\mathcal{R}^n$	Conformational coordinates for a molecule of n atoms.
$s_\alpha^{(0)}(\mathcal{R}^n)$	Distribution of conformational coordinates $\mathcal{R}^n$ for a molecule of type α with n atoms; in isolation as indicated by the superscript zero.
$\mathcal{S}$	Entropy.
T	Thermodynamic temperature.
$\bar{U}(\mathcal{N})$	Model potential energy function for incorporation of quantum mechanical effects in classical-limit configurational integral expressions for the canonical partition function.
$\bar{v}_\alpha$	Partial molar volume of pure liquid α, $\bar{v}_\alpha = 1/\bar{\rho}_\alpha$.
$\mathcal{V}$	Volume.
$\mathbb{V}$	Potential energy.
x_α	Mole fraction of species α.
z_α	Absolute activity of species α, $z_\alpha = \mathrm{e}^{\beta\mu_\alpha}$.
$\boldsymbol{z}^{\boldsymbol{n}}$	Product of absolute activities, $\boldsymbol{z}^{\boldsymbol{n}} \equiv \prod_\alpha z_\alpha{}^{n_\alpha}$.
$\langle A \vert B \rangle$	Conditional expectation, the mean of A conditional on B.
$\langle\langle \ldots \rangle\rangle_0$	Expectation of ‘…’ under the circumstances of no coupling, indicated by the subscript zero (0), between solution and distinguished molecule.
$\langle \ldots \vert \mathcal{R}^n \rangle_0$	Expectation of ‘…’ conditional on the conformation $\mathcal{R}^n$ of the distinguished molecule.