5.62 Physical Chemistry II
Spring 2008

5.62 Lecture #19: Configurational Integral: Cluster Expansion

Goal: For $U(\underset{\sim}{q}) \neq 0$, calculate Z to obtain corrections for non-ideal contributions to the equation of state.

$$Z = \int \cdots \int d\underset{\sim}{q}^{3N} e^{-U(\underset{\sim}{q})/kT}$$

where $U(\underset{\sim}{q})$ = Total Interaction Potential Energy

Simplifications based on form of $U(\underset{\sim}{q})$:

1. Assume $U(\underset{\sim}{q})$ is sum over pairs of atoms ("pair potential") — *pairwise additive interactions.*

2. Assume $U(\underset{\sim}{q})$ depends only on the distance between pairs of atoms, $\left|r_i - r_j\right|$.

$$U(\underset{\sim}{q}) = \sum_{i<j} u_{ij}\left(\left|r_i - r_j\right|\right)$$

r_{ij} = distance between atoms i and j

sum over pairs, i< j prevents double counting

$u_{ij} \equiv$ pair interaction potential (Hard Sphere, Square Well, Sutherland, LJ, dipole-dipole, etc.), which is a function of $\left|\underset{\sim}{r}_i - \underset{\sim}{r}_j\right|$.

$\underset{\sim}{r}_i \equiv$ position of i^{th} atom

Therefore —

$$Z = \int \cdots \int d\underset{\sim}{q}^{3N} e^{-\sum_{i<j} u_{ij}/kT} = \int \cdots \int d\underset{\sim}{q}^{3N} \prod_{i<j} e^{-u_{ij}/kT}$$

The next step is a USEFUL TRICK …

For distant particles $u_{ij} = 0 \Rightarrow e^{-u_{ij}/kT} = 1$

For convenience we define

$$e^{-u_{ij}/kT} \equiv \left(1+f_{ij}\right) \Rightarrow f_{ij} = e^{-u_{ij}/kT} - 1$$

giving $f_{ij} = 0$ when particles have no interaction.

$$Z = \int \cdots \int \; d\underset{\sim}{q}^{3N} \prod_{i<j} \left(1+f_{ij}\right)$$ evaluate as "cluster expansion"

$$Z = \int \cdots \int \; d\underset{\sim}{q}^{3N} (1+f_{12})(1+f_{13})(1+f_{14})\ldots(1+f_{1N})(1+f_{23})(1+f_{24})\ldots$$
$$(1+f_{2N})(1+f_{34})(1+f_{35})\ldots(1+f_{3N})\ldots$$
$$Z = \int \cdots \int \; d\underset{\sim}{q}^{3N} \left[1+\left(f_{12}+f_{13}+f_{14}+\ldots f_{N-1,N}\right)+\left(f_{12}f_{13}+f_{12}f_{34}+f_{12}f_{56}+f_{12}f_{23}+\ldots f_{N-2N-1}f_{N-1N}\right)+\right.$$
$$\left.\left(f_{12}f_{34}f_{56}+\ldots+f_{12}f_{23}f_{34}+\ldots\right)+\ldots\right]$$

Define "Cluster Integrals"

$z_1 = \int \cdots \int d\underset{\sim}{q}^{3N}(1) = V^N$ term involving no interactions

$z_2 = \int \cdots \int d\underset{\sim}{q}^{3N}(f_{12}+f_{13}+f_{14}+\ldots+f_{N-1,N})$ terms for independent two-particle interactions

$z_3 = \int \cdots \int d\underset{\sim}{q}^{3N}(f_{12}f_{34}+f_{12}f_{56}+\ldots+f_{12}f_{23}+\ldots)$ terms for 2 simultaneous pair interactions

$z_4 = \int \cdots \int d\underset{\sim}{q}^{3N}(f_{12}f_{34}f_{56}+\ldots+f_{12}f_{23}f_{34}+\ldots)$ terms for 3 simultaneous pair interactions

Note that terms linked by one common-particle interaction, e.g. $f_{12}f_{23}$, are included in z_3. But this causes no trouble because such integrals are trivially factorizable

$$\iiint d^3\underset{\sim}{q}_1\, d^3\underset{\sim}{q}_2\, d^3\underset{\sim}{q}_3\, f_{12}f_{23} = \iiint d^3\underset{\sim}{q}_{cm12}\, d^3\underset{\sim}{q}_{12}\, f_{12} d^3\underset{\sim}{q}_{23}\, f_{23}$$
$$= V\int d^3\underset{\sim}{q}_{12}\, f_{12} \int d^3\underset{\sim}{q}_{23}\, f_{23}$$

We get V^{N-3} from the N–3 independent particles, and $V\beta^2$ from the singly linked cluster. β is a two particle interaction integral. It has dimension of volume. See pages 263-266 and 277-291 of "Statistical Mechanics" by Mayer and Mayer (Wiley, 1940). A diagrammatic method for classifying interactions, a precursor to Feynmann diagrams, is presented.

The fact that the 1,2 and 2,3 interaction integrals may be independently evaluated means that no approximations need to be made about excluding terms from the z_2 and z_3 integrals. There is, however, a class of term that cannot be factored; and this class first appears in the z_4 integral when integrals over $f_{12}f_{23}f_{13}$ type *doubly linked* terms must be evaluated. For our present purposes it is sufficient to remark that the neglected terms in the z_4 (triples) and higher terms result in a dependence of Z on powers of the density higher than 1,

$$Z = \left[Ve^{\beta_1\rho}e^{\beta_2\rho^2}\ldots\right]^N$$

where

$$\rho = N/V.$$

The assumption of independent binary collisions (Boltzmann's *stosszahl ansatz*) is valid when the mean time between collisions is long relative to the time of one collision. When the inter-particle interaction is 1/r (Coulomb), the interaction length is infinite and there is no such thing as independent binary collisions. When the density is very high, the mean time between collisions can become comparable to the duration of a collision.

So, $Z = z_1 + z_2 + z_3 + z_4 + \ldots$

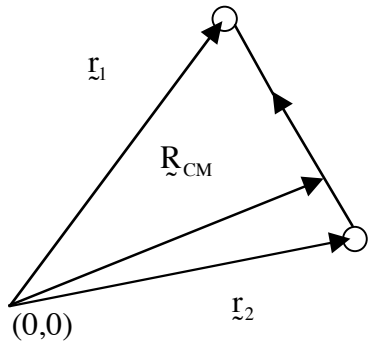
try to simplify these integrals —

$$z_2 = \int d\underset{\sim}{q}^{3N}\left(f_{12} + f_{13} + f_{14} + \ldots + f_{N-1,N}\right)$$
$$= \int d\underset{\sim}{q}^{3N}\left[\left(e^{-u_{12}/kT} - 1\right) + \left(e^{-u_{13}/kT} - 1\right) + \left(e^{-u_{14}/kT} - 1\right) + \ldots\right]$$

Each term $\left(e^{-u_{ij}/kT} - 1\right)$ has the same functional form, so z_2 is just equal to (# of terms) × (configurationally averaged value of any term). The # of terms is just the number of ways of choosing pairs from N molecules, which is $\frac{N(N-1)}{2}$.

$$z_2 = \int\cdots\int d^3\underset{\sim}{r}_1\, d^3\underset{\sim}{r}_2 \ldots d^3\underset{\sim}{r}_N \left[\frac{N(N-1)}{2}\right]\underbrace{\left[\left(e^{-u_{12}/kT} - 1\right)\right]}_{f_{12}}$$
$$= \frac{N(N-1)}{2}\int\cdots\int d^3\underset{\sim}{r}_1\, d^3\underset{\sim}{r}_2\, f_{12}\int\cdots\int d^3\underset{\sim}{r}_3\, d^3\underset{\sim}{r}_N$$
$$= \frac{N(N-1)}{2}V^{N-2}\int\cdots\int d^3\underset{\sim}{r}_1\, d^3\underset{\sim}{r}_2\, f_{12}\left(\underset{\sim}{r}_1, \underset{\sim}{r}_2\right)$$

Change from laboratory coordinates $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ to center of mass and relative coordinates, since f_{12} depends only on $\left|\underset{\sim}{r}_1 - \underset{\sim}{r}_2\right|$.



$\underset{\sim}{r}_{12} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2$ relative coordinates

(NOTE: CM is not at midpoint of $\underset{\sim}{r}_{12}$ when $m_1 \neq m_2$)

Coordinate transformation $\underset{\sim}{r}_{12} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2$ $\qquad \underset{\sim}{R}_{CM} = \frac{1}{2}\left(\underset{\sim}{r}_1 + \underset{\sim}{r}_2\right) \qquad \left[m_1 = m_2\right]$

$$z_2 = \frac{N(N-1)}{2}V^{N-2}\int d^3\underset{\sim}{R}_{CM}\int d^3\underset{\sim}{r}_{12}\left(e^{-u_{12}/kT} - 1\right)$$
$$= \frac{N(N-1)}{2}V^{N-1}\int d^3\underset{\sim}{r}_{12}\left(e^{-u_{12}/kT} - 1\right)$$

get one factor of V from d^3R_{CM} integral

Define $\beta \equiv \int d^3\underset{\sim}{r}_{12}\left(e^{-u_{12}/kT}-1\right)$ Cartesian coordinates

$\equiv 4\pi \int dr\, r^2\left(e^{-u(r)/kT}-1\right)$ Spherical coordinates

(integrated over θ, ϕ)

So

$$z_2 = \frac{N(N-1)}{2}V^{N-1}\beta = \frac{N(N-1)}{2}V^N\left(\frac{\beta}{V}\right)$$

for large N, $z_2 \approx \frac{N^2}{2}V^N\left(\frac{\beta}{V}\right)$

Look at z_3

$$z_3 = \int\cdots\int d\underset{\sim}{q}^{3N}\left(f_{12}f_{34}+f_{12}f_{56}+\ldots+f_{12}f_{23}+\ldots\right)$$

$$= \frac{N(N-1)(N-2)(N-3)}{2\cdot 2\cdot 2}\int\int\int\int d^3\underset{\sim}{r}_1 d^3\underset{\sim}{r}_2 d^3\underset{\sim}{r}_3 d^3\underset{\sim}{r}_4 f_{12}f_{34}\int\cdots\int d^3\underset{\sim}{r}_5\cdots d^3\underset{\sim}{r}_N$$

$2\cdot 2\cdot 2$ comes from 1,2 pair times 3,4 pair times 1,2 and 3,4 order

N large, so $\approx N^4$

$$= \frac{N^4}{2^3}V^{N-4}\int\int d^3\underset{\sim}{r}_1 d^3\underset{\sim}{r}_2 f_{12}\int\int d^3\underset{\sim}{r}_3 d^3\underset{\sim}{r}_4 f_{34}$$

$$= \frac{N^4}{2^3}V^{N-2}\beta^2 = \frac{N^4}{2^3}V^N\left(\frac{\beta}{V}\right)^2$$

IN GENERAL

$$Z = z_1 + z_2 + z_3 + z_4 + \ldots$$

$$Z = V^N + V^N\frac{N^2}{2}\left(\frac{\beta}{V}\right) + V^N\frac{N^4}{2^3}\left(\frac{\beta}{V}\right)^2 + \ldots$$

$$= V^N\left(1+\frac{N\beta}{2}\left(\frac{N}{V}\right)+\frac{1}{2}\left(\frac{N\beta}{2}\right)^2\left(\frac{N}{V}\right)^2+\ldots\right)$$

$$= V^N\exp\left[\frac{N\beta}{2}\left(\frac{N}{V}\right)\right] \qquad \text{since } e^x = 1+x+\frac{x^2}{2!}+\ldots$$

$$Z = \left[Ve^{\beta N/2V}\right]^N$$

where $\beta = \beta(T) = 4\pi\int_0^\infty\left[e^{-u(r)/kT}-1\right]r^2dr$

So we have summed over all orders of interaction. Everything is expressed in terms of one pair-interaction potential. So each simplified form of u(r) gives an explicit way to compute the contribution to Z!