Competition Between Intermolecular and Intramolecular Association in Polyatomic Molecules : Theory and Simulation

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Introduction

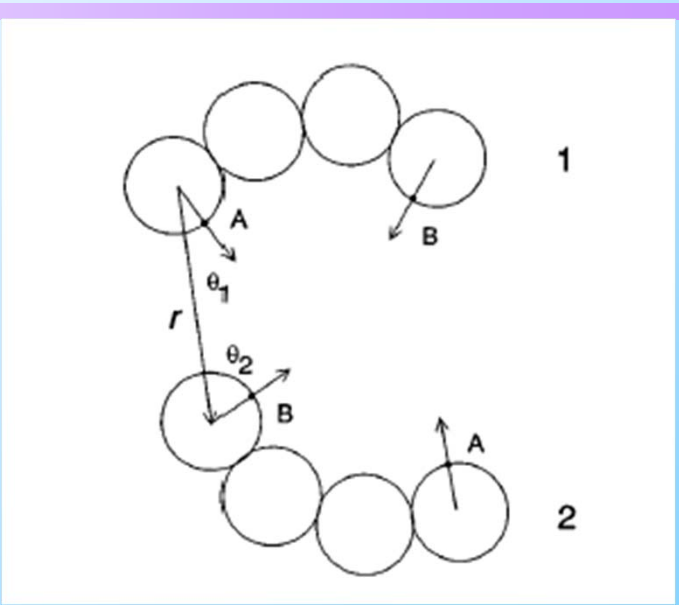
- Unusual phase behavior of associating polymers
  - Liquid-Liquid equilibria of Nylon-6 / tetrafluoroethanol / carbon ioxide at 373.15 K
  - Solutions of Telechelic polymers
  - The competition between **inter-** and **intramolecular** association
  - Wertheim's theory
    - Model for intermolecular associations
    - Unable to predict the intramolecular association

- This work
  - Development of the model for the intramolecular association
  - Comparison of Monte Carlo simulation results and the theory

Metropolis Monte Carlo Simulation

- Potential energy

$$\phi = \phi_{HS} + \phi_{\text{inter}}^{assoc} + \phi_{\text{intra}}^{assoc}$$



$$\phi_{HS}(\mathbf{r},\Omega_1,\Omega_2) = \begin{cases} \infty & \text{if } r_{ij} < \sigma \\ 0 & \text{otherwise} \end{cases}$$

$$\phi_{\text{inter}}^{\text{assoc}}(\mathbf{r},\Omega_{t1},\Omega_{t2}) = \begin{cases} -\varepsilon_{\text{inter}} & \text{if } r < r_c, \theta_1 < \theta_c, \text{and } \theta_2 < \theta_c \\ 0 & \text{otherwise} \end{cases}$$

$$\phi_{\text{intra}}^{\text{assoc}}(\mathbf{r},\Omega_{t1},\Omega_{t2}) = \begin{cases} -\varepsilon_{\text{intra}} & \text{if } r < r_c, \theta_1 < \theta_c, \text{and } \theta_2 < \theta_c \\ 0 & \text{otherwise} \end{cases}$$

Metropolis Monte Carlo Simulation

- NVT ensemble
  - Starting from an
    - Ordinary flexi
  - Association sites
  - Displacement and Reorientat “translational-jiggling” algorithm of Dickman and Hall [ ]
    - Rearrangement of atoms in chain molecules
    - Accepted ratio of 40 % of the configurations generated

(1) Random uniform displacement : $\mathbf{x}_i^{(j)} \rightarrow \mathbf{x}_i^{(j)} + \mathbf{a}$

(2) Bond vectors $\mathbf{e}_i^{(j)} = \mathbf{x}_i^{(j+1)} - \mathbf{x}_i^{(j)} \; (j = 1,\ldots,n-1)$ along chain to independent random displacements, where $\left|\mathbf{e}_i^{(j)}\right| = 1$ by adding a random vector $\mathbf{b}_j$ to $\mathbf{e}_i^{(j)}$ and normalizing the resultant to unit length

- NPT ensemble
  - The length of the simulation cell are changed to keep the pressure constant.
  - About 40 % of the volume changes are accepted

Theory for Intra- and Intermolecular Association

- The change in configurational Helmholtz free energy

$$\frac{A^{assoc}}{NkT} = \ln X_0 + X_0^{\text{intra}} - X_A$$

  - Solving nonlinear equations as follows

$$X_A = \frac{X_0^{\text{int}\,ra}}{1+\rho X_A \Delta_{AB}^{\text{int}\,er}} \qquad \Delta_{AB}^{\text{int}\,er} = 4\pi g_{HS}(\sigma) K_{AB}\left[\exp\left(\varepsilon_{AB}^{\text{int}\,er}/kT\right)-1\right]$$

$$X_0 = \frac{X_0^{\text{int}\,er}}{1+\Delta^{\text{int}\,ra}} \qquad \Delta^{\text{int}\,ra} = D\left[\exp\left(\varepsilon^{\text{int}\,ra}/kT\right)-1\right]$$

$$X_0 = X_A^2 / X_0^{\text{int}\,ra}$$

$$X_0^{\text{int}\,er} + X_0^{\text{int}\,ra} - X_0 = 1$$

Theory for Intra- and Intermolecular Association

- Thermodynamic variables
  - Configurational internal energy

$$\frac{\partial\left(A^{assoc}/NkT\right)}{\partial\beta}=\frac{1}{X_0}\frac{\partial X_0}{\partial\beta}-\frac{\partial X_A}{\partial\beta}+\frac{\partial X_0^{\text{int}\,ra}}{\partial\beta}=\frac{U}{N}$$

  - Compressibility factor (Equation of state)

$$Z^{assoc}=\eta\frac{\partial\left(A^{assoc}/NkT\right)}{\partial\eta}=\eta\left(\frac{1}{X_0}\frac{\partial X_0}{\partial\eta}-\frac{\partial X_A}{\partial\eta}+\frac{\partial X_0^{\text{int}\,ra}}{\partial\eta}\right)$$

where, $\eta=\pi\ m\rho\sigma^3/6$

- Equation of state for the reference state [Chapman et al. 1988]

$$Z=m\left(\frac{1+\eta+\eta^2-\eta^3}{\left(1-\eta^3\right)}\right)-(m-1)\eta\frac{5-2\eta}{(1-\eta)(2-\eta)}-(m-1)$$

Results and Discussions

- At low density, there is significant difference between Wertheim's theory and the present theory.

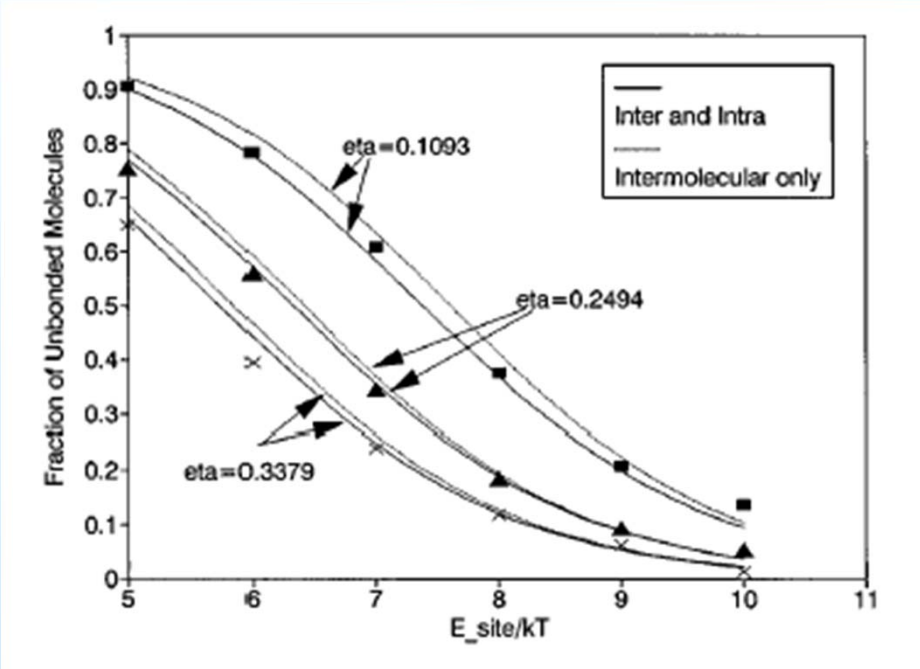


Fig. Fraction of unbonded molecules vs ε_{site}/kT at three densities; symbols represent simulation results

Results and Discussions

- As density increases, N_{inter}/N_{intra} also increases

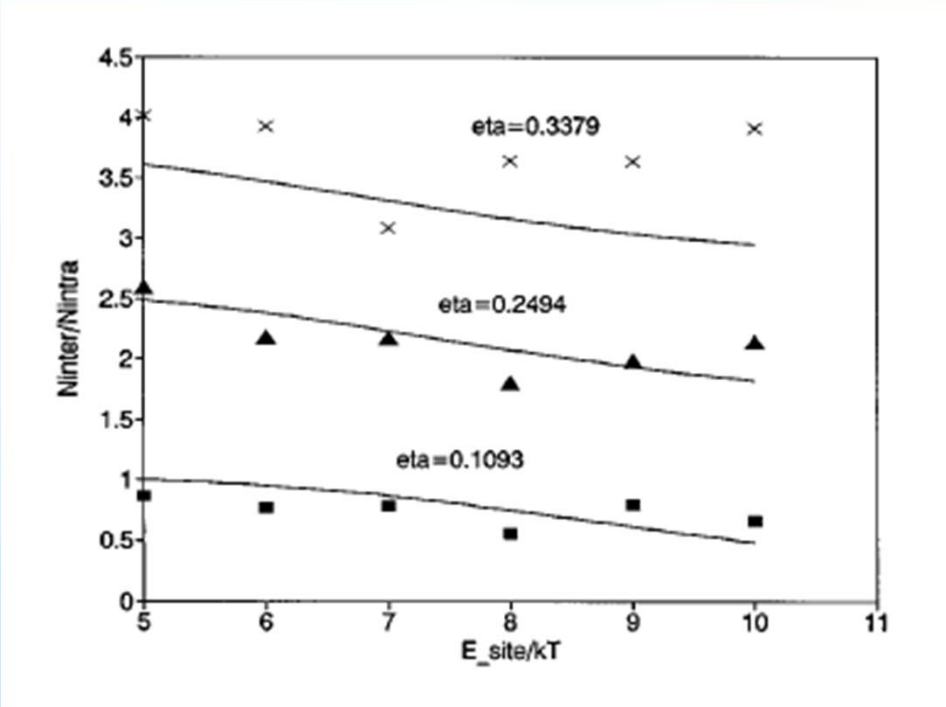


Fig. Ratio of the number of intermolecular bonds to the number of intramolecular bonds vs ε_{site}/kT at three densities

Results and Discussions

- At the highest density, the errors are increased at the high association energy.

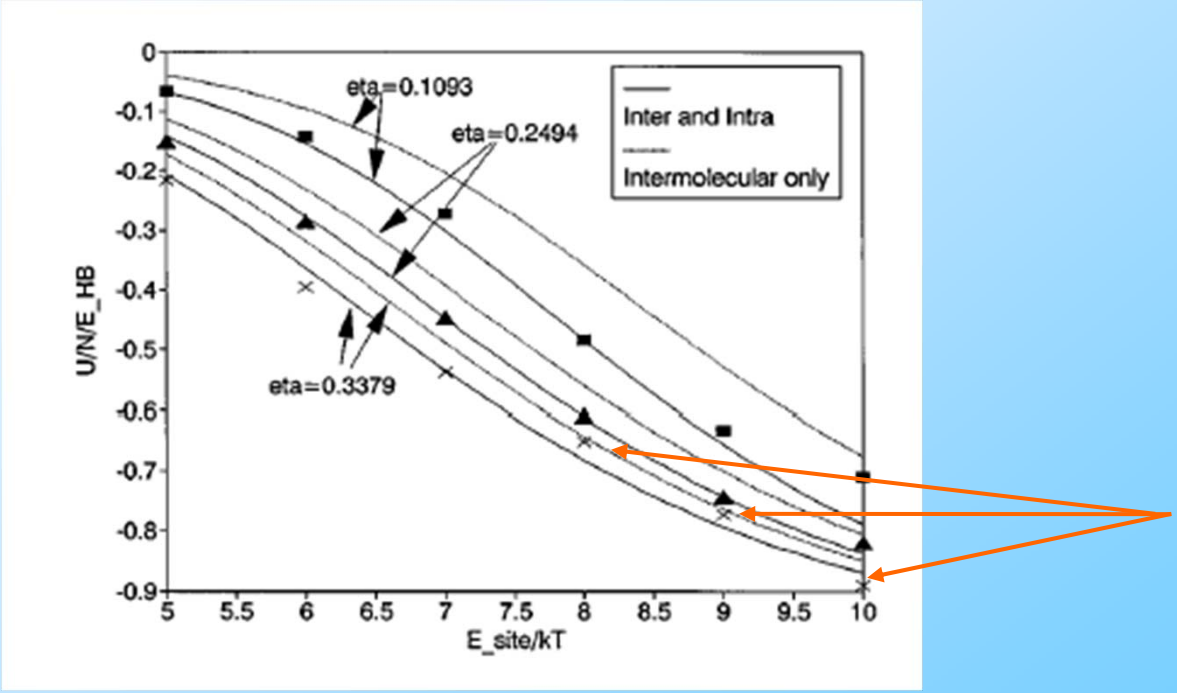


Fig. Configurational energy vs ε_{site}/kT at three densities

Results and Discussions

- The minimum in the compressibility factor
  - The competition between inter- and intramolecular association
  - At lower density, intramolecular association is dominated.

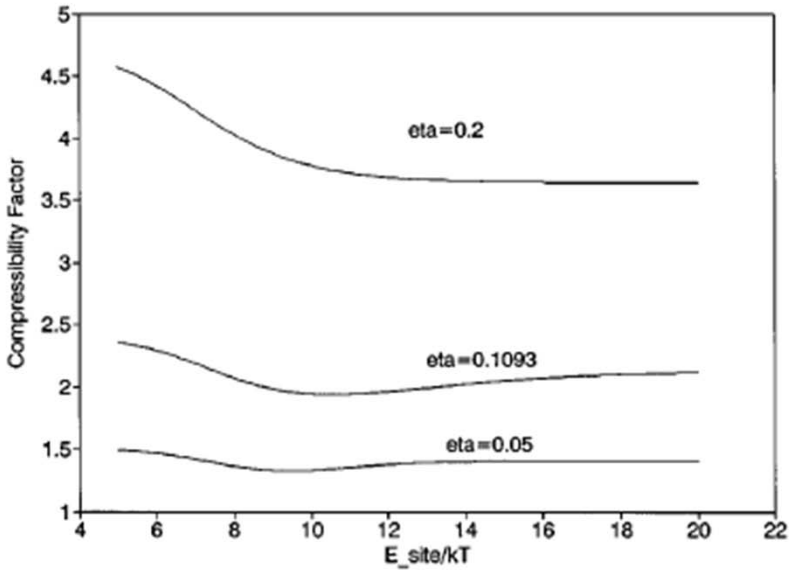


FIG. 5. Predictions from theory of compressibility factor vs ϵ_{site}/kT at η=0.2, 0.1093, and 0.05.

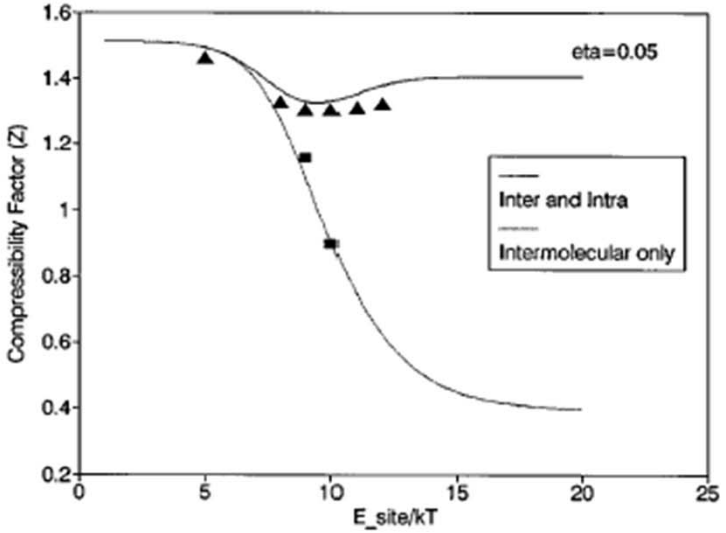


FIG. 6. Compressibility factor vs ϵ_{site}/kT at η=0.05. Symbols represent simulation results, solid triangles (inter- and intramolecular association), solid squares (no intramolecular association). Curves represent predictions from theory.

Conclusion

- Development of a theory to explain the competition between inter- and intramolecular association

- The good agreement with Monte Carlo simulation results for most of the conditions studied.

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