行政院國家科學委員會專題研究計畫 期中進度報告

聚合物介面粗粒化分子勢能之研究(1/2)

計畫類別：個別型計畫
計畫編號：NSC93-2119-M-002-036-
執行期間：93年11月01日至94年07月31日
執行單位：國立臺灣大學應用力學研究所

計畫主持人：趙聖德

計畫參與人員：李皇德

報告類型：精簡報告

處理方式：本計畫可公開查詢

中 華 民 國 94年5月30日

行政院國家科學委員會補助專題研究計畫期中進度報告

聚合物介面粗粒化分子勢能之研究（1/2）

Coarse-Grained Intermolecular Potentials for Polymers at Interfaces

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成果報告類型(依經費核定清單規定繳交)：■精簡報告□完整報告

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中文摘要

在第一年計畫裡面，我們報告建立電腦模擬實驗室的成果及現有的研究結果。我們也對之前所提的研究計畫達成度做了評估。以下列出主要的幾點：（1）我們已經在我們自己的實驗室建立了 5-node，雙 CPU，AMD250 的 PC-cluster。（2）我們繼續發展粗粒化模型的理論並對從小的官能基到大的聚合物系統界面做數值分析測試。（3）我們也完成一些較高層級（MP2 層級）的 *ab initio* 計算，並使用較大的基底，來計算小的官能基分子（水、甲烷、乙烷、丙烷、乙醇、二甲醚）。（4）我們正在研究兩個碳球並使用 Brenner-Tersoff 的力場來作為建構粗粒化的分子間勢能方法。（5）我們正在研究有關苯環的粗粒化分子力學模擬，以及液態甲烷的分子動力學模擬。（6）我們也初步做了有關複雜性生物巨分子之生物感測器的分子力學與動力學分析。我們評估使用高性能的計算來達到方法學發展和數值實驗分析是很有可為的。

關鍵詞：

聚合物、粗粒化、分子間勢能、*ab initio* 計算、分子動力學、分子力學、生物感測器

Abstract

In the first year of this start-up project, we report the progress in establishing a simulation laboratory and current research results. We also evaluate the anticipated goals we promised to achieve in the research proposal. The notable points are: (1) We have built a 5-node dual-processor AMD250 PC cluster situated at our home Institution. (2) We continue to develop theoretical methodology to improve the coarse-grained rigid blob (CGRB) model and perform numerical tests on its applicability to systems starting from small functional groups towards polymeric systems at interfaces. (3) We have performed *ab initio* quantum chemistry calculations on small functional groups (water, methane, ethane, propane, ethanol and dimethylether) at the MP2 theory level using large basis sets. (4) We have been studying the fullerene dimer using the Brenner-Tersoff type force field to construct the coarse grained intermolecular potential. (5) We are performing coarse-grained molecular mechanics simulations for benzene clusters and molecular dynamics simulations for methane liquids. (6) We have performed preliminary molecular mechanics and kinetics analysis of the interactions between biomoleculaes involved in the biosensors. Our mid-stage evaluation about the methodology development and the numerical experimenting using high performance computing facilities are very promising.

Keywords: polymer, coarse-grained, intermolecular potential, *ab initio* calculation, molecular dynamics, molecular mechanics, biosensor

1. Background of the Project

Recently, single-chain block copolymers with controllable arm-lengths and combination of polymer varieties have been synthesized by Moore and coworkers at the UIUC [1]. These building blocks can be grafted and assembled into nanoscale star-shaped composites with novel responsive functionalities in liquid interfaces. On the other hand, microcantilever beams and miniaturized actuators and detectors have been fabricated by Huang and coworkers [2]. These elements can be integrated to build lightweight biosensors with perspective medical applications in physiological solutions. A fundamental understanding of the interfacial interactions among the nanostructures is vital for successful assembling. The ability to render such an understanding eventually depends on the inventive progress to probe the nanoscale and mesoscale interfaces from both the experimental and theoretical advances.

Employing theoretical modeling to study the interfacial properties among heterogeneous, multiphase, and anisotropic materials poses a number of notorious challenges [3]. The grand challenge is to incorporate multiscale features of the polymeric system without sacrificing efficiency and accuracy. For example, the full atomistic molecular dynamics simulation is usually too expensive to study the dynamics of a polymeric system which often involves a wide range of spatiotemporal active scales. Therefore, the continuing pursuit for a predictable theoretical modeling can help track down the parameter space to a manageable level. One of the most popular strategies to mitigate the problem is to divide the full simulation into four stages with descending subtlety on the system parameters [4]: (1) performing *ab initio* calculations to obtain raw data for intermolecular potentials, (2) constructing atomistic models and performing simulations, (3) constructing mesoscopic models and performing coarse-grained simulations, and (4) integrating macroscopic continuum dynamics. Clearly, the most fundamental task in this procedure is to obtain accurate *ab initio* potential data in stage (1). For polymeric systems, we replace the atomistic simulations by an equivalently accurate but much more efficient simulation approach. We have developed a new simulation scheme where the attention was paid to obtain a theoretically based functional form for the coarse grained intermolecular potential starting out from the microscopic information [5]. It is this methodology we would like to devote to its further development and tests in this project.

3. Progress Reports

3.1. Laboratory Establishment and Student Training

We have set up a computer simulation laboratory and built our own computational facilities situated at the Institute of Applied Mechanics. We have a 5-node dual processor AMD cluster with shared air conditioning and power-UPS system. We have a 1-node dual-processor Intel server and four single-processor Acer PC's. Current members include one Ph. D. student and two MS students.

This project provides opportunities for one perspective Ph.D. student and two enthusiastic MS students to learn how to perform first principles electronic structure calculations and how to construct coarse-grained intermolecular interactions from the calculated data. This training definitely fuels their knowledge and ability in performing front-line researches and inspire their unexplored genius.

3.2. CGRB Methodology Development

Consider two blobs, *i* and *j*, with centers of mass $\vec{R}_i$ and $\vec{R}_j$, respectively. The positions of the particles in the blobs are $\vec{\rho}_{ia}$, $a=1,2,3,\ldots,N_i$, for the particle *a* in the blob *i*, and $\vec{\rho}_{jb}$, $b=1,2,3,\ldots,N_j$, for the particle *b* in the blob *j*, with the origins situated at $\vec{R}_i$ and $\vec{R}_j$. The corresponding position vectors are denoted by $\vec{r}_{ia}$ and $\vec{r}_{jb}$, with respect to a common origin *O*. We set for notational convenience $\vec{R} = \vec{R}_i - \vec{R}_j$ and $\vec{\rho}_{ab} = \vec{\rho}_{ia} - \vec{\rho}_{jb}$. In the CGRB model, the inter-blob potential is obtained by summing over all the particle pairs between the blobs

$$V_{ij} = \sum_{(p,q)} V_{ij}^{(pq)} \Theta_{ij}^{(pq)}$$

where

$$V_{ij}^{(pq)} = \frac{1}{q!(p-q)!!} R^q \left(\frac{1}{R} \frac{\partial}{\partial R} \right)^{\frac{p+q}{2}} U_{ij}(R)$$

$$\Theta_{ij}^{(pq)} = \sum_{ab} (\hat{R} \cdot \vec{\rho}_{ab})^q \rho_{ab}^{(p-q)}$$

The integers *p* and *q* run over pairs of the form

$$q = \begin{cases} p, p-2, p-4, \cdots, 0 & p \text{ even} \\ p, p-2, p-4, \cdots, 1 & p \text{ odd} \end{cases}$$

We summarize the advantages of using this formula as compared with other coarse-grained potential models as follows.

(1) It is based on a rigorous theoretical framework and is designed to connect the theories in different scales. Therefore, by choosing suitable blobs, it can serve a starting point to perform a hierarchy of multiscale simulations.

(2) It provides formally separated intermolecular and intramolecular properties and thus serves as a good parallel algorithm.

(3) It is computationally efficient in reducing the cost of calculating intermolecular interactions by employing a controllable approximation. It also simplifies the intricate intramolecular processes by using the rigid blob construct.

(4) For many cases, the molecular shape and symmetry can be realized in the formula.

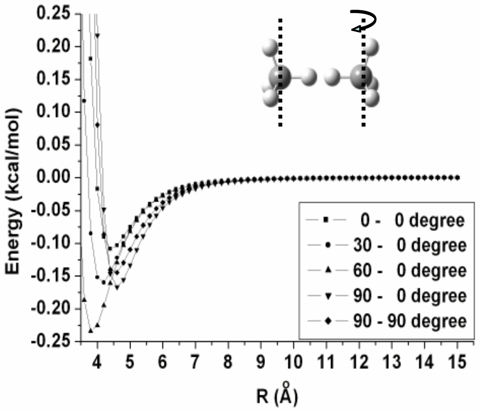
The whole methodology, including detailed derivation and case applications have been accepted to be published in the *Journal of Chemical Physics* (to appear in 2005) [6].

3.3. Ab initio calculation of Intermolecular potential database

The first general purpose of this project is to build a database of intermolecular potentials for common functional groups toward practically useful multiscale simulations. The accuracy of thermodynamics properties obtained from molecular dynamics or Monte Carlo simulations is basically limited by the efficacy of the intermolecular potential models. Recent progresses in developing very accurate potentials for dimers of inert gas and small molecules from post-Hartree-Fock *ab initio* calculations using large basis sets together with counterpoise corrections (CPC) to the basis set superposition error (BSSE) are very promising [7]. Application of this standard procedure to more complex molecules has been very active in the literature [8]. We will apply this procedure to dimers of molecules starting from alkanes and water and gradually increasing the size to larger functional groups. One of the distinguishing points of our study from others is that we choose to perform full relaxed geometry minimization instead of using rigid molecules assumption.

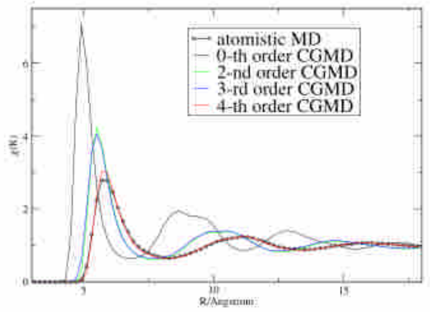
3.3.1 Methane, ethane, propane

We have performed preliminary *ab initio* calculations on dimers of methane, ethane and propane at several relative configurations, using the Gaussian 03 package [9]. The calculations were performed at the MP2 theory level using a series of basis sets, such as STO-3G, 6-31G, 6-31G*, 6-311G*, 6-311G**, 6-311+G**, and 6-311++G(2df, 2pd). The last basis set is pretty large and has been used to calibrate empirical force fields for liquid alkane in the literature [10]. The energy scans were performed for a quite dense grid of spatial points for each definite configuration. Counterpoise corrections to the basis set superposition error were performed using the new counterpoise feature in Gaussian 03 [9].

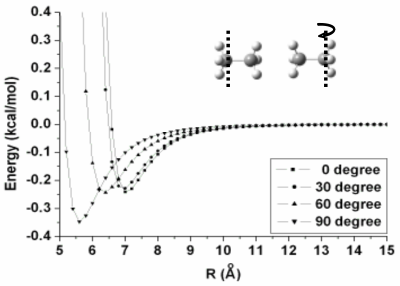


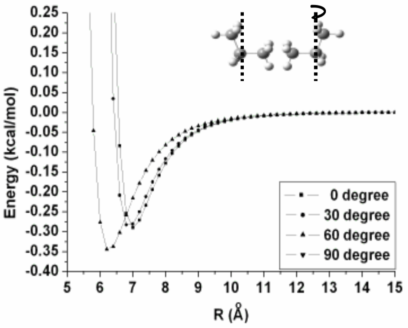
In Fig. 1 we present the potential energies of methane dimer from the MP2/6-311++G(2df,2pd) calculations for the five orientations designated by the rotational angles with respect to the rotational axes depicted in the inserts. Because the high symmetry in the methane dimer, these orientations have covered the main interaction geometries for the close encounters of two methane molecules. The relative stability of the dimer at different orientations has been studied in the literature. Our results are consistent with the published results [11]. One point of discrepancy is for the strong repulsive part of the potential. Because our calculations do not fix metrically the monomer methane, there would be some distorted electron distribution from the rigid molecule assumption used in previous publications. This discrepancy is expected to become significant for larger molecules. From our calculations we also verify the least basis set rendering reasonable energetic for methane dimer is 6-31G*, using CPC. Without CPC, the least basis set is 6-311+G** at the MP2 theory level.

Keeping the potential expansion to the 4-th order terms, we fit the potential function with adjustable parameters to the calculated potential energy data using nonlinear regression. We performed a molecular dynamics simulation for a system of model liquid methane using both the atomic force field (CFF91) [12] and the constructed coarse grained force field. In Fig. 2 we compare the calculated radial distribution functions from both simulations. As can be seen, the simulations using the coarse grained model potentials (lines, in ascending order) approach to the atomistic simulation result within the 4-th order. We should emphasize the calculation time is significantly less than that used in the atomistic MD simulation because we do not calculate pair-atom interactions.



The potential energies of ethane and propane dimers are shown in Fig. 3 and Fig. 4, respectively. These calculations are from the MP2/6-311G** calculations for the four orientations designated in the inserts. These orientations have covered quite a large range of interaction geometries for the close encounters of two monomers. The relative stability of the dimer at different orientations has been studied in the literature. Our results are consistent with the published results [13]. The discrepancy for the strong repulsive part of the potential is also observed. This series of calculations can provide the potential raw data for modeling the backbone of a polymer in molecular simulations.

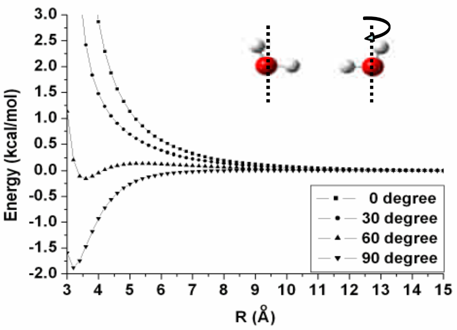




3.3.2 Water, methanol, ethanol

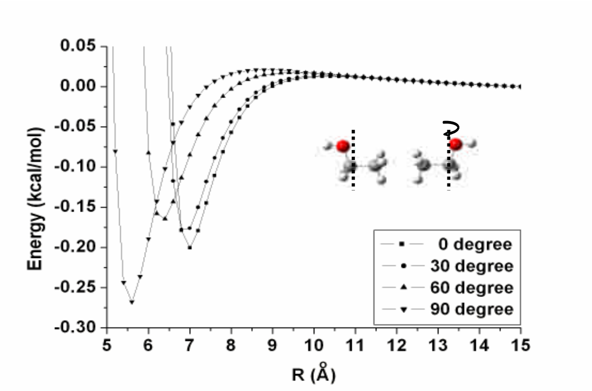
Hydrogen-boned complexes are very important in biological studies. The intermolecular interaction potentials are highly anisotropic and responsive, especially for water. We have made some preliminary studies on this category of molecules and used *ab initio* calculations to model the intermolecular potentials.

In Fig. 5 we present the potential energies of water dimer from the MP2/6-311++G**



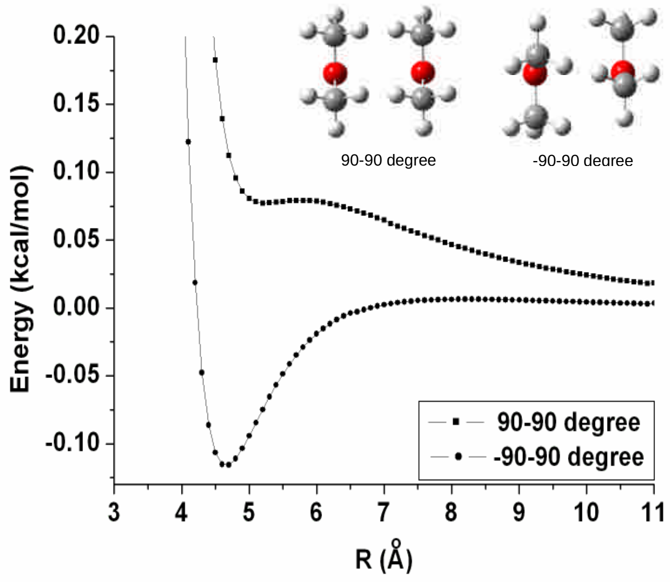
calculations for the four orientations designated by the rotational angles with respect to the rotational axes depicted in the inserts. These orientations should have covered the main interaction geometries for the close encounters of two water molecules, especially for the most stable hydrogen bond structure. The discrepancy from the rigid molecule assumption is also expected to be significant for hydrogen boned molecules.

In Fig. 6 we present the potential energies of ethanol dimer from the MP2/6-311G** calculations for the four orientations designated by the rotational angles with respect to the rotational axes depicted in the inserts. We have not seen much potential energy data published. It might be due to the large computational cost for this molecule. An interesting observation about the calculated data is a "bump" around R=8~9 Angstroms with energies higher than the asymptotic value. Whether this long range repulsive part is due to a repulsive term or an artifact remains to be resolved while we are doing higher level calculations.



3.3.3 Dimethylether

We have initiated a calculation for dimethylether (DME) which we will use to model the backbone segment of a polyethylenglycol (PEG). The molecule is pretty big so the computational burden is much heavier than small molecules we studied in the above. In Fig. 7 we present the potential energies of DME dimer from the MP2/6-311G** calculations for the two orientations depicted in the inserts. These orientations have covered part of the main interaction geometries for the close encounters of two DME molecules. The relative stability of the dimer at different orientations has not been studied in the literature. Our results could be the first to deal with DME dimer from the *ab initio* calculations for such large range of sample geometries. The discrepancy from the rigid molecule assumption is also expected to be significant.



4. Evaluation and Concluding Remarks

Overall in the first year we have achieved the anticipated goals we set in our proposal. The major computational works are currently going on smoothly. We have one paper accepted for publication and one manuscript in preparation. The tasks in action are listed as follows. (1) We are performing *ab initio* calculations of the intermolecular potentials for dimethylether, amide, ammonia, acrylamide, and benzene dimers. The calculation will be performed at the MP2 theory level with various basis sets, up to 6-311++G(2df,2pd). (2) We are studying the fullerene dimer using the Brenner-Tersoff type force field to construct the coarse grained intermolecular potential. (3) We are performing coarse-grained molecular mechanics simulations for benzene clusters and molecular dynamics simulations for methane liquids. (4) We are performing molecular mechanics and kinetics analysis of the interactions between biomoleculaes involved in the biosensors. We expect these works to be finished in the following year.

Acknowledgements

Start-up funding from both the National Taiwan University and the College of Engineering is appreciated. We would like to thank the National Center for High-performance Computing for providing the computing resources. We thank J. S. Moore and L. S. Huang for useful discussions on their experiments. We thank J. C. Jiang and M. Hayashi for useful discussions on computational details.

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