

Exploration

Catalyst Theory, Entropy Decrease in Isolated System and Transformation of Internal Energy

Yi-Fang Chang

Department of Physics, Yunnan University, Kunming, 650091, China

E-Mail: yifangchang1030@hotmail.com.

Article history: Received 10 March 2014, Received in revised form 5 May 2014, Accepted 10 May 2014, Published 13 May 2014.

Abstract: Catalyst as substance remained constant in the reaction may regard as an isolated system. When internal interaction exists, for example, the kinetic energy is transformed to the potential energy, order of this isolated system increases, and entropy decrease. The adsorption, fluctuations, self-assembly and the coarse-grained method etc, are discussed. Further, entropy decrease of macroscopic thermodynamics may be probably obtained in chemistry from the microscopic atomic, molecular and nano-theories, and entropy decrease in thermodynamics of microstructure is calculated quantitatively. Moreover, enzyme as biological catalyst and membrane, and general entropy decrease in biology are researched. The change of entropy should be a testable science.

Keywords: chemistry, entropy, catalyst, internal interaction, enzyme, microstructure.

1. Introduction

A catalyst is a substance that speeds up the rate of a chemical reaction without itself being consumed in the reaction, and may control direction of reactions. The mass of the catalyst remains a constant [1].

Using density-functional theory Reuter, et al., calculated the Gibbs free energy to determine the lowest-energy structure of a $RuO_2(110)$ surface in thermodynamic equilibrium with an oxygen-rich

environment [2], and researched composition and structure of the $RuO_2(110)$ surface in an O_2 and CO environment, which imply the catalytic formation of CO_2 [3]. By extensive density functional theory Wang, et al., calculated a model system, CO oxidation on Au/ZrO_2 , which demonstrates that the oxidation reaction is very sensitive to the oxide structure. This shows that CO oxidation on typical Au/ZrO_2 catalysts could be dominated by minority sites [4]. Liu, et al., discussed the origin and activity of oxidized gold in water-gas-shift catalysis [5]. The rate of ammonia synthesis over a nanoparticle ruthenium catalyst can be calculated directly on the basis of a quantum chemical treatment of the problem using density functional theory. Honkala, et al., compared the results to measured rates over a ruthenium catalyst supported on magnesium aluminum spinel [6].

Present investigations of catalyst theory include: thermodynamic calculations by first principle [7,8], and which may combines statistical mechanics [9] and the kinetic Monte Carlo method [10], etc. Recently, Lu, et al., researched first principles nuclear magnetic resonance signatures of graphene oxide [11]. In this paper, we discuss catalyst theory, entropy decrease in isolated system from transformation of internal energy, and some quantitative calculations in thermodynamics of microstructure.

2. Chemistry and Entropy Decrease

The second law of thermodynamics is based on an isolated system and statistical independence. If fluctuations are magnified due to internal interactions in the system, or various internal complex mechanism and interactions cannot be neglected, a state with smaller entropy (for example, self-organized structure) will be able to appear under some conditions. In these cases, the statistics and the second law of thermodynamics should be different [12-15]. Because internal interactions bring about inapplicability of the statistical independence, entropy decrease in an isolated system is possible for physics [13,16], chemistry [17], biology [18], astronomy [19] and social sciences [20]. In particular, it has a possibility for attractive process, internal energy, system entropy and so on. Therefore, we proposed that a necessary condition of entropy decrease in isolated system is existence of internal interactions [15]. The internal interactions often are related with nonlinearity [13].

The chemical reactions are very complex, and include oscillation, condensation, catalyst and self-organization, etc. In these cases changes of entropy may increase or decrease. In chemical reactions there are various internal interactions, so that some ordering processes with entropy decrease are possible on an isolated system. Moreover, a simplifying Fokker-Planck equation is solved, and we discussed the hysteresis as limit cycle, oscillation and catalyst, etc [17].

For the systems with internal interactions, we proposed that the total entropy should be extended to [14]

$$dS = dS^a + dS^i, \quad (1)$$

where dS^a is an additive part of entropy, and dS^i is an interacting part of entropy. Further, we proposed quantitatively the sufficient and necessary condition of in isolated system [15]:

$$0 > dS^i > -dS^a, \text{ i.e., } |dS^i| > dS^a \text{ (for negative } dS^i \text{)}. \quad (2)$$

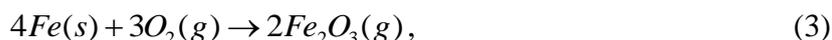
The first law of thermodynamics point out that the total internal energy A of an isolated system is a constant, and there is $A=K(\text{kinetic energy})+V(\text{potential energy})$. It uses the internal energy to identify permissible changes. Present the second law of thermodynamics uses the entropy S to identify the spontaneous changes [21]. S is a measure of the molecular disorder of a system. Usual molecular kinetic energy increases, then disorder and entropy increase. But, when internal interaction in an isolated system exists, i.e., the kinetic energy is transformed to the potential energy, then order increases, and the kinetic energy and entropy decrease.

Various internal energies in isolated systems may be the gravitational interaction, which forms order stars and various celestial bodies from the kinetic energy of nebula motion; the attractive electromagnetic interaction may form some order states; and the strong interaction forms various nuclei. These can derive order states of entropy decrease. Of course, the weak interaction derives disorder and entropy increase. Therefore, entropy decrease of macroscopic thermodynamics may be obtained in chemistry from the microscopic atomic, molecular and nano-theories.

3. Catalyst and Adsorption

A catalyst increases the rate of a reaction by lowering the activation energy [1]. The substance that melts or evaporates goes from a lower energy state to a higher energy state and ΔH is positive, but this is accompanied by increase in disorder and entropy. When we increase the temperature of any substance—solid, liquid, or gas—molecular motions increase and so does entropy. But, conversely, if the temperature of a substance is lowered, molecular motions decrease, and entropy decreases [1].

For iron rusts



there are gas molecules as reactants and none as products, therefore the products are more ordered than reactants, and ΔS is negative [1].

A principle is: when a catalyst is present, the energy of activation is lowered because the catalyst changes the path of the reaction [1]. Catalyst provides a path of alternative reaction, which has lower activation energy E' [21] and corresponds to higher reaction rate according to Arrhenius law.

It is known

$$dS = S' - S = (E'/T') - (E/T). \quad (4)$$

Usual reaction temperature is invariant $T'=T$, so $dS = (E' - E)/T$. When $E' < E$, $dS < 0$

Oxidation and reduction are increase and decrease in oxidation number, respectively. Both are just opposite processes, and may not be always entropy increase. The adsorption heat may be of the endothermic process or exothermic process [22]. The adsorption is that molecules and atoms attach to surfaces in two ways. In the physical adsorption (physisorption), there is van der Waals forces are the interactions between the closed-shell molecules and between adsorbate and the substrate. They have a long range but are weak. In the chemical adsorption (chemisorption), the molecules or atoms stick to the surface by forming a chemical (usually covalent) bond. Both adsorptions are all internal interactions. The physisorption are always the exothermic adsorption, usual chemisorptions are also the exothermic adsorption.

$$\Delta S = (\Delta H - \Delta G)/T. \quad (5)$$

The spontaneous process should be $\Delta G < 0$, so $\Delta S > 0$. Since the adsorption forms a more order structure at the surface, $\Delta S < 0$, and ΔH should be a more negative value, and the adsorption should be exothermic process. It is a usual case.

At least, some catalysts and catalytic reactions may derive entropy decrease in a macroscopic isolated system. Further, catalyst may be extended to some more general processes in which there are middle reactant and keep invariant, and to some cycled reactions. It includes possibly that we proposed the physical-chemical-nuclear multistage chain reaction theory of cold fusion based on the standard quantum mechanics [23]. Since cold fusion is an open system, synergetics and laser theory can be applied, and the Fokker-Planck equation is obtained. Using the corresponding Schrödinger equation and the nonlinear Dirac equation, and combining the multistage chain reaction theory, our quantitative calculations agree completely with some experiments on cold fusion. Moreover, we discussed some new researches, for example, the nonlinear quantum theory, catalyzer and nanomaterial, etc., and proposed the three laws of cold fusion: 1).The time accumulate law. 2).The area direct ratio law. 3).The multistage chain reaction law [23].

A developed direction of thermodynamics is stochastic thermodynamics. Jarzynski proposed nonequilibrium equality for free energy differences [24]. Gammaitoni, et al., investigated stochastic resonance [25]. Liphardt, et al. researched the equilibrium information from nonequilibrium measurements in an experimental test of Jarzynski's equality [26].

Evans and Searles proposed fluctuation theorem [27]. Seifert researched entropy production along a stochastic trajectory and an integral fluctuation theorem [28], and proposed principles and perspectives of stochastic thermodynamics [29]. Tietz, et al., discussed measurement of stochastic entropy production [30]. Carberry, et al., stated that the transient fluctuation theorem (TFT) is a

generalized, second-law-like theorem that bridges the microscopic and macroscopic domains and links the time-reversible and irreversible descriptions. They applied this theorem to a colloidal particle in an optical trap, and demonstrated the TFT in an experiment and show quantitative agreement with Langevin dynamics [31].

Fluctuations often take up some positive roles, for example, noise induced phase transition and stochastic resonance [25], etc. Usual small probability of violation of second law of thermodynamics attenuates rapidly to zero [24,26]. But, we proposed that fluctuations may be magnified due to internal interactions in the system under some conditions, then entropy decrease in isolated system is possible [14].

4. Coarse-Grained Method and Quantitative Calculations of Entropy Decrease in Thermodynamics of Microstructure

The coarse-grained (CG) method [32,33] includes the CG molecular dynamics, the dissipative particle dynamics (DPD), etc. The perspective focuses on the use of classical molecular dynamics and CG models to explore phenomena involving self-assembly in complex fluids and biological systems. Hoogerbrugge and Koelman proposed DPD that presented a novel method for simulating hydrodynamic phenomena [34]. This particle-based method combines features from molecular dynamics and lattice-gas automata. It is shown theoretically simulations that a quantitative description of isothermal Navier-Stokes flow is obtained with relatively few particles. Computationally, the method is much faster than molecular dynamics, and at same time it is much more flexible than lattice-gas automata schemes [34]. They studied the flow of suspensions of solid spheres under steady shear using a newly developed flow simulator. Viscosities have been obtained that are in excellent agreement with experiments reported [35].

Flekkoy and Coveney discussed molecular dynamics and DPD [36]. Tominaga, et al., studied thermodynamic interactions in double-network hydrogels [37]. Mesoscopic-particle-based fluid models as DPD are usually assumed to be CG representations of an underlying microscopic fluid. A fundamental question is whether there exists a map from microscopic particles in these systems to the corresponding CG particles, such that the CG system has the same bulk and transport properties as the underlying system. Espanol, et al., investigated CG of microscopic fluids using a Voronoi-type projection that has been suggested in several studies. The simulations show that the projection fails in defining CG particles that have a physically meaningful connection to the microscopic fluid [38]. Shao, et al., used molecular dynamics simulations to investigate alcohols with varied hydrophobicity and different numbers of hydrophilic groups exert effects on the structure of the model polypeptide and alcohol/protein interactions [39].

The key of the mesoscopic statistics is a role of fluctuations, which bring various thermodynamic quantities (work, heat and entropy, etc.) become stochastic variables.

The CG models provide a computationally efficient method for rapidly investigating the long time- and length-scale processes that play a critical role in many important biological and soft matter processes. Izvekov and Voth (2005) introduced a new multiscale CG (MS-CG) method that employs a variational principle to determine an interaction potential for a CG model from simulations of an atomically detailed model of the same system. The mesoscopic statistics may combine the CG method, which may be the parametrizing CG molecular dynamics (CG-MD), DPD and the multiscale CGMD (MS-CGMD), etc.

Noid, et al., applied the MS-CG variational principle for parametrizing molecular CG force fields and derives a linear least squares problem for the parameter set determining the optimal approximation to this many-body potential of mean force. Linear systems of equations for these CG force field parameters are derived and analyzed in terms of equilibrium structural correlation functions. Further, they developed a formal statistical mechanical framework for the MS-CG method and demonstrates that the variational principle underlying the method may, in principle, be employed to determine the many-body potential of mean force (PMF) that governs the equilibrium distribution of positions of the CG sites for the MS-CG models [40,41].

The key is that the CG particles are defined, and obtain the corresponding effective force field among these molecules. The CG method is analogue with the extensive quantum theory [42-46]. It may probably obtain some new macroscopic effects, for example, the spillover effect and the macroscopic quantum tunneling effect, which is namely a magic internal interaction.

Self-assembly is the autonomous organization of components into patterns or structures without human intervention. Self-assembling processes are common throughout nature and technology [47]. They involve components from the molecular (crystals) to the planetary (weather systems) scale and many different kinds of interactions. The concept of self-assembly is used increasingly in many disciplines, with a different flavor and emphasis in each.

The molecular self-assembly is determined on some weak interactions among molecules, for example, the van der Waalse force, etc. Self-assembly structures of general chain molecular are formed from the nanoporous networks [48].

In the ordering phenomena and nucleation of thermodynamics of microstructure, we may calculate quantitatively entropy decrease. Ordering is essentially one of the cooperative phenomena and has the feature that once an ordered arrangement appears locally, it spreads to surroundings and promotes ordering of an entire crystal. Therefore, the order parameter ought to change greatly in the neighborhood of a specific critical temperature T_c [49]. In the ordering phenomena entropy becomes

smaller. The CuZn ordering can be analysed by Bragg-Williams-Gorsky (B-W-G) long-rang ordering model, the change in entropy for ordering is [49]

$$S = k \ln W \approx (S)_{\varphi=0} - \frac{R}{2} [(1 + \varphi) \ln(1 + \varphi) + (1 - \varphi) \ln(1 - \varphi)]. \quad (6)$$

Here $(S)_{\varphi=0} = R \ln 2$ is the entropy in the disordered state, and φ is an order parameter. Such the change of entropy in the order-disorder transition should be

$$\Delta S = S - (S)_{\varphi=0} = -\frac{R}{2} [(1 + \varphi) \ln(1 + \varphi) + (1 - \varphi) \ln(1 - \varphi)]. \quad (7)$$

For a short-range ordering $\varphi = 1/6$ [16], entropy decreases,

$$\Delta S = -\frac{R}{2} \left[\frac{7}{6} \ln \frac{7}{6} + \frac{5}{6} \ln \frac{5}{6} \right] = -0.0139538R < 0. \quad (8)$$

For a long-range ordering $\varphi = 1/3$ [49], entropy decreases,

$$\Delta S = -\frac{R}{2} \left[\frac{4}{3} \ln \frac{4}{3} + \frac{2}{3} \ln \frac{2}{3} \right] = -0.056633R < 0. \quad (9)$$

Ordering must exist with internal interactions [12-14], in particular, for spontaneous ordering. When φ is bigger, entropy decrease is also bigger. The feature of the long-range ordering is that ordering occurs rapidly in the temperature region near the critical temperature T_c [49].

In analysis of Cu_3Au ordering by B-W-G model, according to the formula [49]

$$\Delta S = -\frac{R}{16} \left[9 \left(1 + \frac{\varphi}{3} \right) \ln \left(1 + \frac{\varphi}{3} \right) + 6(1 - \varphi) \ln(1 - \varphi) + (1 + 3\varphi) \ln(1 + 3\varphi) \right], \quad (10)$$

the critical order parameter $\varphi = 0.46$ [49], and entropy decreases, $\Delta S = -0.09654R < 0$.

In the spontaneous nucleation of thermodynamics, once the radius goes beyond the critical radius r_c the change in free energy becomes downward, the new phase particles (i.e., embryos) will go on growing. A new phase particle of radius r_c is called the critical nucleus [49]. In the spontaneous nucleation there must be internal interactions [12,13]. In Volmer-Weber-Becker-Doring (VWBD) theory of critical nucleus, if a globular particle of a new phase is produced in a supercooled phase, the change in free energy per particle can be expressed by [49]

$$\Delta g = -\frac{\Delta G}{V} \frac{4\pi}{3} r^3 + 4\pi r^2 \sigma. \quad (11)$$

Here V is the molar volume, σ is the interface energy, and the change in free energy according to the phase transformation is

$$\Delta G = \frac{\Delta H}{T_c} \Delta T. \quad (12)$$

Here ΔT is the degree of supercooling. If the change of entropy in nucleation is

$$\Delta S = -\frac{\Delta g}{T}, \quad (13)$$

there will be

$$\Delta S = -\frac{4\pi}{T} r^2 \left(-\frac{\Delta G}{V} \frac{r}{3} + \sigma \right). \quad (14)$$

For a supercooling state of H_2O , there have $\Delta H = 6000\text{J/mol}$, $\Delta T = 40\text{K}$, $T_c = 273\text{K}$, so $\Delta G = (240/273) \times 10^3 \text{J/mol}$, $r = 1.02 \times 10^{-9} \text{m}$, $V = 18 \times 10^{-6} \text{m}^3/\text{mol}$, $\sigma = 0.025 \text{J/m}^2$ [49], then

$$\Delta S = -\frac{4\pi}{T} r^2 (0.0084 \text{J/m}^2) < 0. \quad (15)$$

In fact, the catalysts are just to promote (strengthen) internal interactions in an isolated system. The catalyst in chemical reactions possesses some character of the auto-control mechanism in an isolated system. If it does not need the input energy, at least in a given time interval, the self-catalyst is similar with auto-control like a type of Maxwell demon, which is namely a type of internal interactions. The demon may be a permeable membrane. For the isolated system, this is possible that the catalyst and other substance are mixed to produce new order substance with smaller entropy. Ordering is the formation of structure through the self-organization from a disordered state. Moreover, there are the mesoporous molecular sieves [50] and membrane catalyst, etc.

5. Enzyme and Biochemistry

Catalysts are more essential to the biochemical reactions that occur in living organisms where reactions are carried out at a constant temperature of 37°C . Certain proteins called enzymes act as biological catalysts; they catalyze virtually every chemical reaction that takes place in living systems [1]. Gammaitoni, et al., applied stochastic resonance to neuronal systems [25].

In biology, many enzymes and membranes are all internal interactions. Enzymes as special catalysts are manufactured and used by the human body for each and every reaction that occurs during metabolism [1,3].

Collin, et al., shown that the Crooks fluctuation theorem can be used to determine folding free energies for folding and unfolding processes occurring in weak and strong nonequilibrium regimes, and used optical tweezers to measure repeatedly the mechanical work associated with the unfolding and refolding of a small RNA hairpin and an RNA three-helix junction, and determined the difference in folding free energy between an RNA molecule and a mutant differing only by one base pair, and the thermodynamic stabilizing effect of magnesium ions on the RNA structure [51].

Molecular dynamics (MD) simulations are widely used to study protein motions at an atomic level of detail, but they have been limited to time scales shorter than those of many biologically critical

conformational changes. Shaw, et al., examined two fundamental processes in protein dynamics—protein folding and conformational change within the folded state—by means of extremely long all-atom MD simulations conducted on a special-purpose machine [52].

For the continuous elastic model of the biological membrane, Brannigan, et al., presented an elastic Hamiltonian for membrane energetics. The model implies continuous functional forms for thermal undulation and peristaltic amplitudes as a function of wavelength and predicts previously overlooked relationships between these curves. Undulation and peristaltic spectra display excellent agreement with data from both atomistic and coarse-grained models over all simulated length scales. Applied to thermal membrane fluctuations, this model predicts continuous functional forms for both undulation and peristaltic amplitudes over all wavelengths [53].

West, et al., studied the membrane-protein interactions and membrane-mediated protein-protein interactions by Monte Carlo simulations of a generic CG model for lipid bilayers with cylindrical hydrophobic inclusions. The results are compared with analytical predictions of two popular analytical theories: The Landau-de Gennes theory and the elastic theory. The elastic theory provides an excellent description of the fluctuation spectra of pure membranes and successfully reproduces the deformation profiles of membranes around single proteins. The mechanisms leading to hydrophobic mismatch interactions are critically analyzed [54].

Nano-catalyst is a type of new catalyst [6]. Bell discussed the impact of nanoscience on heterogeneous catalysis [55]. Catalysts are of great importance in the chemical industry and in automobile exhaust catalytic converters [1].

We researched possible entropy decrease due to internal interactions in some isolated systems in biology, in which the neuroscience, the permeable membrane, the molecular motor, etc., are all some internal interactions. Brain, consciousness and neuroscience are some internal interactions, which even possible take a key role for decrease entropy in isolated system. Dormancy of living body is an order state, whose entropy pass through adjustment and decrease to smaller. For the typical instance, the hibernation of animal, and the dormancy of Madagascar's lemur and of various hexapods all show obviously the entropy decrease in isolated system. Further, Qigong and various practices are often related to these order states with entropy decrease. We proposed entropy decrease as an index of therapeutics in biophysics, and life lies in a combination between motion and rest, etc [18].

5. Conclusions

Catalyst is very important in chemistry [56,57], and is also one of kernels in green chemistry [58]. The self-organized order of any organism in isolated system is inevitably a process of entropy decrease, it may hold at least in a certain time. Various chemical and biological systems possess very

rich and colorful internal interactions, we believe that the chemistry and biology may make with great contribution for the test of development on the thermodynamics of entropy decrease in isolated system.

In a word, the change of entropy is a testable science, and should not be a fideism.

References

- [1] Burns, R.A. *Fundamentals of Chemistry*. 4 Ed. Beijing: Higher Education Press. **2003**.
- [2] Reuter, K.; Scheffler, M. Composition, structure, and stability of $RuO_2(110)$ as a function of oxygen pressure. *Phys.Rev.* **2001**, B65:035406.
- [3] Reuter, K.; Scheffler, M. Composition and structure of the $RuO_2(110)$ surface in an O_2 and CO environment: implications for the catalytic formation of CO_2 . *Phys.Rev.* **2003**, B68:045407.
- [4] Wang, C.M.; Fan, K.N.; Liu, Z.P. Origin of oxide sensitivity in gold-based catalysts: a first principle study of CO oxidation over Au supported on monoclinic and tetragonal ZrO_2 . *J.Am.Chem.Soc.* **2007**, 129(9): 2642-2647.
- [5] Liu, Z.P.; Jenkins, S.J.; King, D.A. Origin and activity of oxidized gold in water-gas-shift catalysis. *Phys.Rev.Lett.* **2005**, 94:196102.
- [6] Honkala, K.; Hellman, A.; Remediakis, I.N.; Logadottir, A.; Carlsson, A.; Dahl, .S; Christensen, C.H.; Norskov, J.K. Ammonia synthesis from first-principles calculations. *Science.* **2005**, 307:555-558.
- [7] Reuter, K.; Scheffler, M. First-principles atomistic thermodynamics for oxidation catalysis: surface phase diagrams and catalytically interesting regions. *Phys.Rev.Lett.* **2003**; 90:046103.
- [8] Liu, Z.P.; Gong, X.W.; Kohanoff, J.; Sanchez, C.; Hu, P. Catalytic role of metal oxides in gold based catalyst: a first principles study of CO oxidation on TiO_2 supported. *Phys.Rev.Lett.* **2003**, 91:266102.
- [9] Reuter, K.; Frenkel, D.; Scheffler, M. The steady state of heterogeneous catalysis studied by first-principles statistical mechanics. *Phys.Rev.Lett.* **2004**, 93:116105.
- [10] Rogal, J.; Reuter, K.; Scheffler, M. CO oxidation on Pd (100) at technologically relevant pressure conditions: first-principles kinetic Monte Carlo study. *Phys.Rev.* **2008**, B77:155410.
- [11] Lu, N.; Huang, Y.; Li, H.; Li, Z.; Yang, J. First principles nuclear magnetic resonance signatures of graphene oxide. *J.Chem.Phys.* **2010**, 133:034502.
- [12] Chang Yi-Fang. Internal mechanism of isolated systems and new research on limitations of second law of thermodynamics. In *Entropy, Information and Intersecting Science*. Yu C.Z. et al., Ed. Yunnan Univ. Press. **1994**. p53-60.
- [13] Chang Yi-Fang. Possible decrease of entropy due to internal interactions in isolated systems.

Apeiron. **1997**, 4: 97-99.

- [14] Chang Yi-Fang. Entropy, fluctuation magnified and internal interactions. *Entropy*. **2005**, 7: 190-198.
- [15] Chang Yi-Fang. "Negative temperature" fallacy, sufficient-necessary condition on entropy decrease in isolated systems and some possible tests in physics, chemistry and biology. *Int.Rev.Phys.* **2012**, 6: 469-475.
- [16] Chang Yi-Fang. Unified quantum statistics, possible violation of Pauli exclusion principle, nonlinear equations and some basic problems of entropy. *Int.Rev.Phys.* **2013**, 7:299-306.
- [17] Chang Yi-Fang. Chemical reactions and possible entropy decrease in isolated system. *International Journal of Modern Chemistry*. **2013**, 4(3):126-136.
- [18] Chang Yi-Fang. Possible entropy decrease in biology and some new research of biothermodynamics. *NeuroQuantology*. **2013**, 11(2):189-196.
- [19] Chang Yi-Fang. Grand unified theory applied to gravitational collapse, entropy decrease in astronomy, singularity and quantum fluctuation. *International Journal of Modern Applied Physics*. **2013**, 3(1):8-25.
- [20] Chang Yi-Fang. Social thermodynamics, social hydrodynamics and some mathematical applications in social sciences. *International Journal of Modern Social Science*. **2013**, 2(2):94-108.
- [21] Atkins, P.; de Paula, J. *Atkins' Physical Chemistry*. 7 Ed. Oxford University Press. **2002**.
- [22] Clark, A. *The Theory of Adsorption and Catalysis*. New York: Academic Press. **1970**.
- [23] Chang Yi-Fang. Potential exploration of cold fusion and its quantitative theory of physical-chemical-nuclear multistage chain reaction mechanism. *International Journal of Modern Chemistry*. **2013**, 5(1):29-43.
- [24] Jarzynski, C. Nonequilibrium equality for free energy differences. *Phys.Rev.Lett.* **1997**, 78:2690-2693.
- [25] Gammaitoni, L.; Hanggi, P.; Jung, P.; Marchesoni, F. Stochastic resonance. *Rev.Mod.Phys.* **1998**, 70(1):223-287.
- [26] Liphardt, J.; Dumont, S.; Smith, S.B.; Tinoco Jr. I.; Bustamante, C. Equilibrium information from nonequilibrium measurements in an experimental test of Jarzynski's equality. *Science*. **2001**, 296:1832-1839.
- [27] Evans, D.J.; Searles, D.J. The fluctuation theorem. *Adv.Phys.* **2002**, 51:1529.
- [28] Seifert, U. Entropy production along a stochastic trajectory and an integral fluctuation theorem. *Phys.Rev.Lett.* **2005**, 95:040602.

- [29] Seifert, U. Stochastic thermodynamics: principles and perspectives. *Eur.Phys.J.* **2008**, B64:423-431.
- [30] Tietz, C.; Schuler, S.; Speak, T.; Seifert, U.; Wrachtrup, J. Measurement of stochastic entropy production. *Phys.Rev.Lett.* **2006**, 97:050602.
- [31] Carberry, D.M.; Reid, J.C.; Wang, G.M.; Sevick, E.M.; Searles, D.J.; Evans, D.J. Fluctuations and irreversibility: an experimental demonstration of a second-law-like theorem using a colloidal particle held in an optical trap. *Phys.Rev.Lett.* **2004**, 92:140601.
- [32] Leach, A.R. *Molecular Modelling, Principles and Applications*. Singapore: World Scientific Publishing Company. **1996**.
- [33] Klein, M.L.; Shinoda, W. Large-scale molecular dynamics simulations of self-assembling systems. *Science*. **2008**, 321:798-800.
- [34] Hoogerbrugge, P.J.; Koelman, J. Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics. *Europhys.Lett.* **1992**, 19(3):155-160.
- [35] Koelman, J.; Hoogerbrugge, P.J. Dynamic simulations of hard-sphere suspensions under steady shear. *Europhys. Lett.* **1993**, 21(3):363-368.
- [36] Flekkoy, E.G.; Coveney, P.V. From molecular dynamics to dissipative particle dynamics. *Phys.Rev.Lett.* **1999**, 83:1775-1778.
- [37] Tominaga, T.; Tirumala, V.R.; Lee, S.; Lin, E.K.; Gong, J.P.; Wu, W.L. Thermodynamic interactions in double-network hydrogels. *J.Phys.Chem*, **2008**, B112(13):3903-3909.
- [38] Eriksson, A.; Jacabi, M.L.; Nyström, J.; Tunstrom, K. On the microscopic foundation of dissipative particle dynamics. *Europhys.Lett.* **2009**, 86:4401.
- [39] Shao, Q.; Fan, Y.; Yang, L.; Gao, Y.Q. From protein denaturant to protectant: comparative molecular dynamics study of alcohol/protein interactions. *J.Chem.Phys.* **2012**, 136:115101.
- [40] Noid, W.G.; Chu, J.W.; Ayton, G.S.; Krishna, V.; Izvekov, S.; Voth, G.A.; Das, A.; Andersen, H.C. The multiscale coarse-graining method. I. A rigorous bridge between atomistic and coarse-grained models. *J.Chem.Phys.* **2008**, 128:244114.
- [41] Noid, W.G.; Liu, P.; Wang, Y.; Chu, J.W.; Ayton, G.S.; Izvekov, S.; Andersen, H.C.; Voth, G.A. The multiscale coarse-graining method. II. Numerical implementation for coarse-grained molecular models. *J.Chem.Phys.* **2008**, 128:244115.
- [42] Chang Yi-Fang. Development of Titius-Bode law and the astronomic quantum theory. *J.Yunnan Univ.* **1993**, 16(4):297-203.
- [43] Chang Yi-Fang. Development of Titius-Bode law and the extensive quantum theory. *Phys.Essays.* **2002**, 15(2):133-137.
- [44] Chang Yi-Fang. Development of the extensive quantum theory and its applications in biology,

- chemistry and physics. *J.Jishou Univ.* **2006**, 27(5):34-38.
- [45] Chang Yi-Fang. Extensive quantum biology, applications of nonlinear biology and nonlinear mechanism of memory. *NeuroQuantology*. **2012**, 10(2):183-189.
- [46] Chang Yi-Fang. Nanophysics, macroscopic quantum phenomena and extensive quantum theory. *International Journal of Nano and Material Sciences*. **2013**, 2:9-24.
- [47] Whitesides, G.M.; Grzybowski, B. Self-assembly at all scales. *Science*. **2002**, 295:2418-2421.
- [48] Kudernac, T.; Lei, S.; Elemans, J.A.A.W.; De Feyter, S. Two-dimensional supramolecular self-assembly: nanoporous networks on surfaces. *Chem.Soc.Rev.* **2009**, 38:402-421.
- [49] Nishizawa T. *Thermodynamics of Microstructure*. ASM International. **2008**.
- [50] Kresge, C.T.; Leonowicz, M.E.; Roth, W.J.; Vartuli, J.C.; Beck, J.S. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature*. **1992**, 359:710-712.
- [51] Collin, D.; Ritort, F.; Jarzynsk, C.; Smith, S.B.; Tinoco, Jr. J.; Bustamante, C. Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies. *Nature*. **2005**, 437:231-234.
- [52] Shaw, D.E.; Maragakis, P.; Lindorff-Larson, K.; Piana, S.; Dror, R.O.; Eastwood, M.P.; Bank, J.A.; Jumper, J.M.; Salmon, J.K.; Shan, Y.; Wriggers, W. Atomic-level characterization of the structural dynamics of proteins. *Science*. **2010**, 330:341-346.
- [53] Brannigan, G.; Brown, F.L.H. A consistent model for thermal fluctuations and protein-induced deformations in lipid bilayers. *Biophys.J.* **2006**, 90(5):1501-1520.
- [54] West, B.; Brown, F.L.H.; Schmid, F. Membrane-protein interactions in a generic coarse-grained model for lipid bilayers. *Biophys.J.* **2009**, 96(1):101-115.
- [55] Bell, A. T. The impact of nanoscience on heterogeneous catalysis. *Science*. **2003**, 299: 1688-1691.
- [56] Satterfield, C.N. *Hetrogeneous Catalysis in Practice*. Mcgraw Hill Book Company. **1980**.
- [57] Pearce, R.; Patterson, W.R. *Catalysis and Chemical Processes*. Leonard Hill. **1981**.
- [58] Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice*. Oxford University Press. **1998**.