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Green Chemistry Considerations in Entropic Control of Materials and Processes

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1. Introduction

Materials Science and Green Chemistry are concerned with the design of new chemicals and processes. Thus it is crucial for the materials scientist who is practicing Green Chemistry to be able to determine which chemical processes would occur spontaneously. It is well known that it is the Second Law of Thermodynamics that specifies the direction of spontaneous change. The way the direction of spontaneous change is determined is as follows. Although the First Law of Thermodynamics states that internal energy of an isolated system is conserved in any type of process, the manner in which the internal energy of that system is dispersed may change. If as a result of a specific process the dispersal of the total energy of the isolated system becomes more disorderly, such processes are postulated to occur spontaneously.[1]

Since the change in the extent of disorder in the dispersal of energy is determined by the amount of energy transferred as heat, a thermodynamic function of state named entropy, S, was introduced in a following way. The change of entropy, $\Delta S = S_{\text{final}} - S_{\text{initial}}$, as the system undergoes transfer between the initial and final states is equal to the amount of energy transferred as heat, Δq, divided by the temperature, T, at which the heat is transferred, integrated along the reversible reaction pathway

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \frac{\mathrm{d}q_{\text{rev}}}{T} \qquad (1)$$

The Second Law of Thermodynamics states that for spontaneous processes the entropy of an isolated system never decreases, that is, $\Delta S \geq 0$; thus the sign of the entropy change indicates whether a given process occurs spontaneously.

The term entropy was originally coined by Rudolf Julius Emanuel Clausius in 1865. In his book *The Mechanical Theory of Heat*,[2] he wrote “We might call S the *transformational content* of the body, just as we termed the magnitude U its *thermal and ergonal content*. But as I hold it to be better to borrow terms for important magnitudes from the ancient languages, so that they may be adopted unchanged in all modern languages, I propose to call the magnitude S the *entropy* of the body, from the Greek word *τροπη*, *transformation*. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable.”

Subsequent development of statistical thermodynamics allowed entropy to be defined in a manner different from the classical one described above. The Boltzmann equation (eq 2) establishes the connection between classical entropy, a macroscopic thermodynamic function of state, and the “thermodynamical probability”, W, which is defined as the number of equally probable microstates resulting in the same macroscopic state.[3]

$$S = k_{\mathrm{B}} \ln W \qquad (2)$$

where k_{B} is referred to as the Boltzmann constant. In case of unequally probable microstates, the probabilities of each microstate should be taken into account; entropy is referred to as Gibbs entropy and is calculated as

$$S = -k_{\mathrm{B}} \sum_i p_i \ln p_i \qquad (3)$$

where p_i is the probability associated with the ith microstate.[4]

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Later John von Neumann further extended the concept of entropy into the field of quantum mechanics. Von Neumann derived the well-known entropy formula

$$S = -k_B Tr\rho \ln \rho \tag{4}$$

where ρ is the density matrix operator.[5,6]

Von Neumann was also reported to be indirectly responsible for even further generalization of the entropy concept. When Claude Shannon was going to publish his seminal work on information theory "A Mathematical Theory of Communication",[7] he used the function

$$H(X) = -K\sum_i p_i \log p_i \tag{5}$$

as a quantitative measure of the information that is contained in the random variable X, or alternatively of the uncertainty that is removed after the actual value of X is revealed. Here p_i is the probability of $X = X_i$, where $\{X_i\}$ is the set of all possible outcomes, and K is a constant. According to Shannon, it was von Neumann who advised him to call the function $H(X)$ entropy "... for two reasons. In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, no one knows what entropy really is, so in a debate you will always have the advantage."[8]

The attractiveness of the entropy as an umbrella concept combining such notions as energy dissipated as heat, disorder, or even "mixed-up-ness" of a system, uncertainty, and information resulted in extensive use of the term in areas even farther removed from classical thermodynamics where it originated. For example, entropy is used to describe various phenomena in ecology,[9] economics,[10] and social sciences[11] just to name a few.

2. Entropic Control and Green Chemistry

2.1. Entropy and Sustainability Metrics

The universal applicability and interdisciplinary nature of entropy is common with another term upon which much attention has been recently focused: sustainability. While the concept of sustainable development is rather straightforward, which is to provide for the needs of the current generation without undermining the ability of the future generations to meet their needs as well,[12] it is rather hard to quantify.[13] A number of different metrics were proposed to measure sustainability of national economies in general or that of specific industrial processes and practices in particular.[14−16] Usually they are based on energetic characteristics of the system investigated, such as "emergy"[17] or "exergy".[18] One of the proposed sustainability metrics is, however, based solely on entropy or rather on the rate of entropy production.[19] In this work, the distinction is made between the increase of "material entropy" and "energetic entropy", where the former results from dispersion or mixing the matter in the course of an industrial process, and the latter results from energy being dissipated as heat. Full material sustainability could be achieved if in the end of the useful life of the product, all atoms and molecules used to create this product in the industrial cycle would return to their original degree of purity and order that they had as part of raw materials, thus avoiding the increase of material entropy. This, however, would require energy input. If this energy is obtained by combustion of fossil fuels, CO_2 would be released into the atmosphere, increasing the material entropy, and part of the energy would dissipate as heat, increasing the energetic entropy. In order to achieve full sustainability, the energy should be coming from extraterrestrial sources. Thus relative sustainability (dimensionless) of a given process, σ, is defined as the ratio between the initial and final entropies (where initial entropy is defined as sum of initial entropies of the raw materials subsequently used in the process)

$$\sigma = \frac{S_{\text{initial}}}{S_{\text{final}}} \tag{6}$$

According to the Second Law of thermodynamics, $0 < \sigma < 1$. Processes in which entropy production, ΔS, is minimized correspond to higher relative sustainability, $\sigma \approx 1$, while processes in which excessive amounts of entropy are created have low sustainability, $\sigma \rightarrow 0$. Absolute sustainability, σ_a, is defined as the inverse of the entropy increase as result of the industrial cycle

$$\sigma_a = (\Delta S)^{-1} \tag{7}$$

and is measured in units of K J^{-1}.

2.2. Green Chemistry as Sustainability on the Molecular Level

Green Chemistry can be described as sustainability on the molecular level. Incorporating the Principles of Green Chemistry[20] into design results in processes that do not cause creation of excessive amounts of entropy and thus have high sustainability values. For example, following Principle One, waste prevention, allows one to avoid increase of entropy caused by emissions of waste (and its subsequent dilution) into atmosphere or ocean. Following Principles Six, design for energy efficiency, and Nine, catalysis, allows one to reduce the use of fossil fuels and avoid the associated entropy production described above. Following Principle Seven, renewable feedstocks, allows one to utilize extraterrestrial energy through photosynthesis. Also sequestration of CO_2 during photosynthesis allows one to compensate for CO_2 release into the atmosphere. Finally, Principle Twelve, accident prevention, emphasizes the necessity of avoiding accidents, including releases, explosions, and fires, that is, unwanted spontaneous processes characterized by associated considerable increase of entropy.

2.3. Entropy vs Enthalpy in Chemical Synthesis

Although the Second Law of Thermodynamics allows prediction of the direction of spontaneous change in isolated systems by evaluating the change in its entropy, such systems are rare in synthetic organic chemistry and in materials science. Reaction systems usually exchange energy with their surroundings and therefore cannot be considered isolated. While the state of the reaction system itself can generally be assessed, determining the state of the surroundings, such as changes in their entropy, is less straightforward. Therefore it is useful to be able to determine the direction of the spontaneous change, that is, the sign of entropy change of the large isolated system formed by the reaction system and its surrounding, without actually evaluating the entropy of the surroundings, from the state functions of the reaction system only. Since it is convenient to carry out reactions at constant temperature and pressure, the most useful parameter to evaluate is Gibbs free energy, $G = H - TS$. It can be demonstrated[1] that reactions occur spontaneously if $\Delta G = \Delta H - T\Delta S < 0$, where ΔG is the change in free energy of the reaction system, which is held at constant pressure at thermal equilibrium with its surroundings.

Since, according to the First Law of Thermodynamics, the energy of a closed system, such as that formed by the reaction system and its surroundings, is conserved, both contributions into ΔG can be considered entropic, namely, $T\Delta S$ is due to the changing entropy of the reaction system and ΔH is due to the changing entropy of the surroundings resulting from exchange of energy (heat) between the reaction system and the surroundings. However, it is more convenient to refer to ΔH as the "enthalpic" or "energetic" contribution and to $T\Delta S$ as the "entropic" contribution into ΔG. The magnitude of ΔH is typically defined by the number and nature of bonds created or broken in course of the reaction. The magnitude of $T\Delta S$ (at constant temperature) is defined by changes in entropy, that is, dispersal of energy.

The object of synthetic chemistry historically was to make molecules. In the nearly two centuries that passed since 1828 when urea was first obtained from cyanic acid and ammonia,[21] the science and art of organic synthesis reached the state when any molecule that can exist can be synthesized. Since molecules consist of atoms connected by covalent bonds, in order to synthesize a molecule a number of covalent bonds need to be created or broken. The strength of a covalent bond, such as C−C or C−O, is on the order of magnitude of $100k_BT$;[22] therefore ΔG in covalent synthesis is typically dominated by the enthalpic contribution ΔH the magnitude of which is significantly larger than that of $T\Delta S$.[23] In these cases, the changes in entropy are negligible and they do not determine the outcome (or lack thereof) of the reaction.

2.4. Entropic Control in Organic Chemistry

Contrary to the general trend described above, there exist systems where chemical reactivity is entropically controlled. One such system was reported in 1973.[24] The rate constants of photochemical γ-hydrogen intramolecular abstraction in a series of alkyl phenyl ketones, R(CO)Ph, were found to depend strongly on the structure of the alkyl substituent R, varying by nearly 2 orders of magnitude. This dependence could not be explained without considering entropic contributions to the transition state. The ketones in the series had similar strengths of γ C−H bonds and similar n,π^* triplet energies. A kinetic isotope effect study demonstrated that the differences in photoreactivity could not be attributed to any possible differences in the geometries of the respective transition states. The Arrhenius parameters were evaluated for two members of the series, namely, for valerophenone and *endo*-2-benzoylnorbornane. The structures of the two compounds are presented in the Figure 1. While the activation energies for both substances were essentially the same (3.5 ± 0.5 and 3.7 ± 0.9 kcal/mol, respectively) the rate of γ-hydrogen abstraction was about 60 times lower for valerophenone than that for *endo*-2-benzoylnorbornane (1.2×10^8 and 70×10^8 s^{-1}, respectively). This observation could

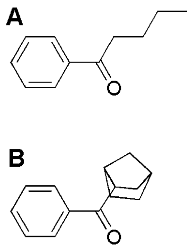

Figure 1. Structures of (A) valerophenone (**1**) and (B) *endo*-2-benzoylnorbornane (**2**).

only be explained by taking into account the activation entropies. The activation entropy for valerophenone was significantly more negative than that for *endo*-2-benzoylnorbornane (-12.5 ± 1.5 eu and -4.0 ± 2.8 eu, respectively). This is due to the contribution of internal rotational degrees of freedom, which are "frozen out" in the transition state. For a six-membered transition state, each such rotation decreases the reaction rate by a factor of 5−8. Thus the difference between the reaction rate for valerophenone and that for *endo*-2-benzoylnorbornane results primarily from the former having two more rotational degrees of freedom, which had to be frozen out in the transition state.

2.5. Intermolecular Interactions and Entropic Control

Traditionally intermolecular interactions are not of primary concern for a synthetic organic chemist due to their low strength compared to that of covalent bonding. However, as the paradigms shift toward Green Chemistry, the role of intermolecular interactions has to be reassessed. Since intermolecular interactions govern such phenomena as diffusion, volatilization, solvation, and phase transfer, they cannot be ignored while designing new substances and materials when the bioavailability or environmental fate of the new molecules is considered. It is clear that neglecting the intermolecular interactions leads to toxicity.

Consequently, as the focus shifts toward the weak intermolecular interactions with lower magnitude of ΔH, the entropic contribution to ΔG becomes non-negligible, since in that case ΔH and $T\Delta S$ are often comparable.[23] In many cases, some of which are described in detail below, the entropic contribution to the free energy of the intermolecular interaction is even more significant than the enthalpic contribution.

Since a large number of biological phenomena are governed by intermolecular interactions, the concept of entropic control is well developed in biochemistry. However, to the authors' knowledge, there is currently no definition of entropic control that is applicable to materials science. Thus the following definition is proposed: a process is referred to as entropically controlled when the entropic contribution $T\Delta S$ to ΔG is at least of the same magnitude as the enthalpic contribution ΔH.

3. Entropic Control of Materials and Processes

As can be seen from the above discussion, entropically controlled processes should be considered by materials scientists looking for elegant solutions to problems posed to them by increasing societal demands for new goods on one hand and increasing societal environmental awareness on the other hand. Since the field of materials science is rather broad, the following collection of topics should be taken as a sparse review that to some extent reflects particular interests of the authors.

3.1. Supramolecular Aggregates and Noncovalent Derivatization

Design of supramolecular aggregates in which molecules are held together by weak, that is, noncovalent, interactions focused much attention of materials scientists turning to biological macromolecules as a source of inspiration.[25] Considering, for example, oligomeric proteins consisting of individual protein subunits, that is, polypeptide chains, assembled into quaternary structure by intermolecular forces such as hydrophobic interactions, while the shape of each subunit (secondary and tertiary structures) is defined largely by a variety of weak intramolecular interactions, allows one to appreciate the endless possibilities of this approach to creating complex structures, which is often preferred by nature over the contemporary synthetic organic chemistry approach based on making and breaking covalent bonds. Whitesides et al.[23] emphasized the significance of entropic considerations under the new paradigm referred to as *noncovalent synthesis*[23] or *intermolecular synthesis*.[26] While in traditional covalent synthesis kinetically stable products are formed, and it is the enthalpies of the bonds that play the primary role in the reaction energetics, the products of noncovalent synthesis are equilibrating structures reflecting the balance between the enthalpy and entropy.

A wide variety of systems forming noncovalently bonded aggregates either in solution or in solid state was studied by various research groups.[26−28] Stability of these aggregates is typically due to strong intermolecular hydrogen bonds, but in many cases those are weaker interactions, such as van der Waals,[27] aromatic−aromatic interactions,[29] or weak C−H···O hydrogen bonds,[30] which determine the shape of the resulting supramolecular structure.

Use of the noncovalently bonded aggregates on the industrial scale was successfully demonstrated to be viable.[31−33] Polaroid Instant Photography relies on hydroquinone as a developer participating in the photoinduced redox chemistry of silver ions. The conflicting requirements of shelf stability and product performance could be satisfied by a hydroquinone, which is stable, that is, insoluble and immobile at neutral pH, but rapidly becomes soluble and mobile when pH is raised to a certain value. The main problems that had to be solved in order to design such material are autoxidation, namely, oxidation of hydroquinone with vagrant oxygen present in the system prior to reaction with silver ions, and premature diffusion, namely, undesired mobility of hydroquinone at neutral pH. The approach traditionally used in the photographic industry is to fine-tune hydroquinone reactivity, aqueous solubility, and diffusivity by covalent derivatization, that is, blocking hydroquinone oxygens by base-labile protecting groups to prevent autoxidation and also render it more hydrophobic at neutral pH. The hydrophobicity and diffusivity of the hydroquinone could be further controlled if desired by substituting one or more aromatic hydrogens with an alkyl group. As the pH increases, the base-labile protecting groups leave, rendering hydroquinone water-soluble, mobile, and prone to oxidation by the silver ions. The derivatized hydroquinone would have to be prepared through multistep synthesis. The disadvantages of this approach become evident when one considers the multitude of traditional covalent transformations required (and their associated costs, both material and environmental). Research aimed to overcome these difficulties lead to development of the concept of *noncovalent derivatization* (NCD).[34] Modification of hydroquinone properties was achieved by employing the bioinspired techniques of molecular recognition and self-assembly rather than the traditional techniques of synthetic organic chemistry. It was demonstrated that cocrystallization of hydroquinone with bis-(*N*,*N*-dialkyl)terephthalamides rendered hydroquinone stable with respect to oxidation, less water-soluble, and relatively immobile at neutral pH. At elevated pH, the hydroquinone becomes deprotonated, which disrupts the networks of hydrogen bonds

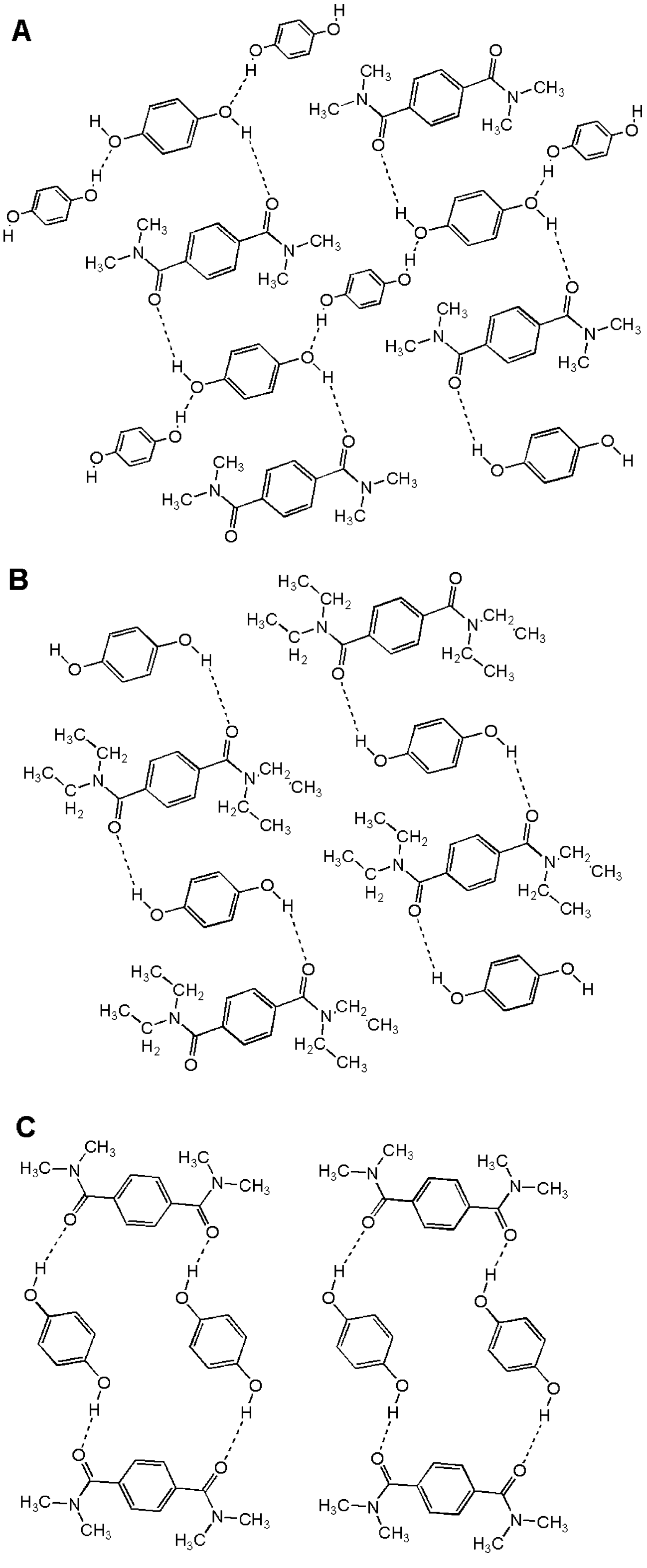

Figure 2. Terephthalamide−hydroquinone motifs: (A) network, 1:2 bis[*N*,*N*-dimethyl]terephthalamide/hydroquinone; (B) chains, 1:1 bis[*N*,*N*-diethyl]terephthalamide/hydroquinone; (C) isolated rings, 1:1 bis[*N*,*N*-dimethyl]terephthalamide/hydroquinone.

maintaining the structural integrity of the cocrystals, and the hydroquinone is being released. Varying the terephthalamide complexing agents and hydroquinone to terephthalamide ratios affects the weak interactions (van der Waals and π-stacking) between the molecules in the cocrystal, which results in a variety of crystal structures exhibiting different motifs of hydrogen bond networks as shown in Figure 2, thus allowing fine control over the hydroquinone properties.[35−37] The entropic contribution into the energetics of the noncovalent derivatization process can be visualized if one considers phase diagrams of binary mixtures of substances A and B that do not cocrystallize but form eutectic mixture (Figure 3a) and that do cocrystallize (Figure 3b). In the former case, the maxima represent the pure crystalline compounds, which are enthalpically favorable due to attractive interaction between the like molecules but entropically unfavorable, and the minimum represents the eutectic mixture where entropy is maximized at the expense of enthalpy. In the latter case, the local maximum representing the cocrystal state corresponds to the balance between entalpic and entropic contributions.[38]

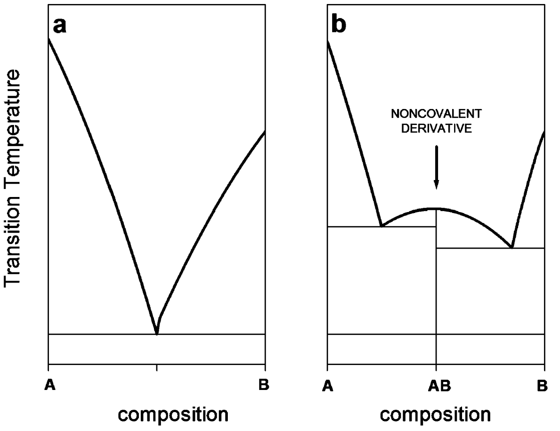

Figure 3. Phase diagrams of binary mixtures of substances A and B, which (a) form a eutectic mixture or (b) cocrystallize.

The environmental and economic benefits of the new approach to hydroquinone derivatization were significant. Noncovalent derivatization of hydroquinone was performed in one step by either solventless grinding, aqueous attriting, or simply adding terephthalamide to the recrystallization liquor of crude hydroquinone, thus avoiding the need for organic solvents, purification procedures, energy inputs, and waste disposal associated with traditional covalent derivatization.[39] Because of these considerations noncovalent derivatization was described as an example of Green Chemistry.[20]

3.2. Entropic Control of Colloidal Stability and Self-Organization

Another area of materials design where entropic control plays an important role is colloids. The ability to control properties of colloidal suspensions is essential in a wide range of applications including but not limited to high strength ceramics, pharmaceuticals, construction materials, personal care products, food industry, coatings, and electronic components.[40] Aqueous colloidal dispersions consist of charged particles and counterions in aqueous media. The counterions' concentration is not uniform; rather, it is higher in the vicinity of the particles and decreases as the distance from the particle surface increases. Thus, two interacting particles interact through an "electric double layer" formed by the counterions. This interaction is repulsive (which is intuitive) and entropic in origin (which is counterintuitive).[22] Indeed, the purely electrostatic (enthalpic) interaction in an overall neutral system consisting of like charged particles separated by oppositely charged counterions is attractive, as in an ionic crystal. However, the most enthalpically favorable state is least favorable entropically. As the particles approach each other, the counterions are “forced” back to the particle surface, thus decreasing their configurational entropy. This entropic repulsive interaction can be controlled by altering the chemical composition of the medium, namely, pH and ionic strength. Stability of the colloidal system is defined by the balance between the attractive van der Waals force, enthalpic in nature, pulling the particles together and the repulsive entropic “electric double layer” force pushing them apart. At short range, the van der Waals forces always prevail over the “electric double layer” forces; however, it is the balance between these forces at long range that defines the time scale required to reach the equilibrium state at adhesive contact. By fine-tuning the strength of the “electric double layer”, entropic, interaction, the colloidal system can be made stable, slowly flocculating, or unstable. In the most stable colloids, the “electric double layer” interaction prevails over the van der Waals interaction, resulting in a long-range repulsion between the particles and a high-energy barrier preventing flocculation of the colloid. As the “electric double layer” repulsion becomes weaker due to higher electrolyte concentration or lower surface potential, the energy barrier becomes lower, and a weak secondary potential minimum appears. The particles may either stay dispersed, in which case the colloid is referred to as kinetically stable, or, if the surface charge is high enough, occupy the weak secondary minimum, which corresponds to reversible flocculation of the colloid. If the strength of “electric double layer” repulsion is decreased further, the energy barrier preventing the particle getting into adhesive contact becomes comparable to k_BT, which results in slow flocculation of the colloid. Eventually the energy barrier becomes so low that it cannot prevent rapid coagulation of the colloid, which in this case is referred to as being unstable.

“Electric double layer” repulsion is not the only entropic effect used to control colloidal stability. Unstable colloidal dispersion can be stabilized by adding polymer, which would adsorb on the particle surface. When two particles approach each other, they experience repulsion due to entropically unfavorable interaction between the adsorbed polymer chains, which are forced into confined space between the two particles and thus lose configurational entropy.[41] This interaction is referred to as steric or overlap repulsion.

Entropic effects do not always result in repulsive interactions between the colloidal particles. If a polymer added to the colloidal dispersion does not adsorb on the particle surfaces, the particles approaching each other experience attraction as the interparticle distance becomes comparable to the polymers’ radius of gyration. Since no polymer coil can approach a particle to a distance closer than its gyration radius (where the distance is measured between the center of the polymer coil and the particle surface), each particle is surrounded by a so-called depletion zone into which the center of a polymer coil cannot enter. When two particles approach each other, the depletion zones overlap thus increasing the total volume available to the polymer and therefore increasing the entropy of the polymer. Since the overlap of the depletion zones is entropically favorable, it results in an attractive interaction, which is referred to as depletion attraction or depletion force.

Depletion attraction is not limited to polymer additives to colloids; it may manifest itself in other phenomena observed in colloidal systems. Depletion effect is the direct cause of the entropy-driven order−disorder phase transitions.[42] Although entropy is usually perceived as the measure of “mixed-up-ness”, the entropic effects in a number of systems can lead to self-organization, that is, increased ordering. It is entropically favorable that monodisperse hard-sphere colloids form crystals as the volume fraction of colloidal particles increases.[43−45] The formation of a higher density ordered crystalline phase in coexistence with the lower density disordered fluid phase in high-density colloids was compared by Forsyth et al.[44] to a traffic jam. If all the cars are on the road, they cannot move, and the entropy is zero. If enough of the cars are parked (crystalline phase), the traffic flows freely (fluid phase), and the overall entropy of the system increases. Crystallization of the high-density colloidal suspensions of monodisperse spherical latex particles was observed experimentally[46] at volume fractions predicted by computer simulations.[47] Fine-tuning the strength of “electric double layer” repulsion between the particles by varying the electrolyte concentration allows ordering of the colloidal particles to be achieved at a desired volume fraction.[48]

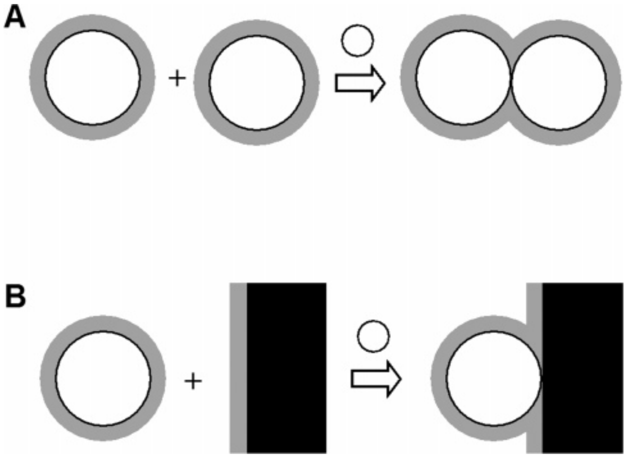

Figure 4. Overlap of the depletion zones of (A) the two approaching particles and (B) the wall and the adsorbed particle.

The entropy-induced phase transitions were observed also in binary colloids consisting of spherical particles of different sizes.[49] These phase transitions generally occurred at lower particle volume fraction than in monodisperse systems. Also, crystallization was occurring on the surface of the vessel containing the colloid rather than in the bulk. To explain these phenomena, it must be considered that the depletion forces can arise not only between two colloidal particles but also between a particle and the wall, as shown schematically in the Figure 4. While each larger particle is surrounded by a depletion zone with the thickness equal to the radius of the smaller particle, a similar depletion zone exists along the wall of the vessel containing the colloid. Adsorption of the larger particle on the wall surface leads to the overlap of their depletion zones thus increasing the volume available for the smaller particles and therefore the entropy of the system.[50] Moreover adsorption of a larger particle on the wall is likely to be more favorable entropically than association of two larger molecules since the increase of the volume available to the smaller particles due to the overlap of depletion zones is twice as large in the former case than in the latter. In the subsequent study, bulk crystallization of the larger particles was also observed at a particle volume fraction significantly lower than that required for freezing of a monodisperse colloid.[51] Strong entropic attraction between colloidal particles and walls in polydisperse colloidal systems as well as wall-induced organization of the adsorbed particles should be taken into account when paints and coatings are designed.

The entropic drive for the larger particles to adsorb on the walls in order to maximize the overlap between the depletion zones can be harnessed in order to control particle flow using engineered surfaces with a variety of features. It was demonstrated[52] that the larger particles adsorbed on the surface are repelled by the edges but are attracted by the corners. Similar arguments allow prediction of particle drift along surfaces with changing curvatures, either in the direction of increase of the radius of curvature on convex surfaces or in the direction of decrease of the radius of curvature on concave surfaces.

Additional interesting phenomena were observed in colloids containing either nonspherical particles or mixtures of spherical and nonspherical particles. Increase of particle volume fraction causes monodisperse colloids containing anisotropic particles, such as rods or disks, to undergo an entropy-driven phase transition from disordered isotropic fluid to anisotropic nematic fluid.[53] Colloidal mixtures of spherical and rod-like particles were found to exhibit an unusually complex phase behavior.[42] Varying the volume fractions of both polystyrene spheres and rod-like viruses produced a variety of ordered phases as a result of entropy maximization. These phases include a columnar phase, where the spheres are self-assembled into columns, which are aligned perpendicular to the rods, and lamellar phase, where layers of spheres are alternating with layers of rods.

The anisotropic shape of the rod-like particles also results in more complex depletion interactions with the wall than was the case for spherical particles. The effect of so-called entropic torque was described recently.[54] Rod-like particles in a binary mixture with small spherical particles are attracted to the wall, and as they approach the wall they experience increasingly strong torque orienting the rod parallel to the wall. This effect was successfully used by Zhou et al.[55] in order to control the orientation of porphyrin adsorbed on silver substrate. While porphyrin molecules adsorbed from ethanol solution are oriented randomly, adding poly(ethylene oxide) oligomers facilitates depletion attraction between the porphyrin molecules and the substrate, which results in adsorbed porphyrin molecules being oriented parallel to the surface of the substrate.

3.3. Self-Assembly of Amphiphiles

Entropy-driven organization is not limited to colloids. Amphiphilic molecules in water tend to self-assemble into ordered structures, such as micelles, vesicles, or bilayers, when their concentration is above a certain threshold referred to as a critical micelle concentration (CMC).[22] Formation of these aggregates results from the conflicting forces: force of attraction between the tails of the amphiphilic molecules and force of repulsion between the headgroups. Balance between these forces defines the optimal headgroup area, that is, the interfacial area per molecule, while the optimal headgroup area along with the tail volume and critical length define the size and shape of the aggregates. While the latter force is complex in nature and results from a variety of interactions, namely, steric repulsion, hydrophilic repulsion, and, in case of ionic headgroup, electrostatic repulsion, the former force is mainly due to hydrophobic interaction between the alkyl chains forming the tails of the amphiphilic molecules.[22]

Hydrophobic interaction, that is, strong attraction between hydrophobic species in aqueous medium, which is stronger than their attraction in vacuum, is believed to be of mainly entropic origin[56] and results from the highly entropically unfavorable solvation (hydration) of these species. Since the alkyl (and other hydrophobic) moieties are unable to form strong hydrogen bonds with neighboring water molecules, the latter have to be oriented so as to minimize disruption of the hydrogen bond network. This places restrictions on the possible orientations of the water molecules in the vicinity of the hydrophobic solutes and decreases their entropy. Aggregation of the hydrophobic tails results in overlapping of their hydration zones and is therefore entropically favorable. An additional entropic effect contributing to the micelle formation, namely, limiting the micelle size, arises from the reduction of allowed configuration of the amphiphilic molecules caused by the limiting of possible headgroup locations to the micelle−water interface.[57,58]

3.4. Entropic Control of Transport and Sorption in Porous Materials

Design of molecular sieves, heterogeneous catalysts, and other highly porous materials requires understanding of factors controlling transport through the pores as well as sorption on the pores' surfaces. It was demonstrated recently that entropic effects play important roles in both of these phenomena.

The model for entropic transport through quasi-one-dimensional structures was applied to diffusion in porous systems by Reguera et al.[59] The origin of entropic control in these systems lies in the irregular geometry of the porous channels. The variations of the channel cross-section and curvature along the transport direction cause changes in the number of states accessible for the particles or molecules being transported. Thus the entropy of the system is varying along the channels and so-called entropic barriers arise, which control the diffusion in the material.[60] It was demonstrated[59] that particle current through entropic barriers decreases with temperature. This is because the strength of the entropic potential is being controlled by temperature and increases as the temperature increases, thus reducing the current. This scenario is different from that where the barriers are energetic in nature, since in the latter case increasing temperature provides the activation energy necessary to overcome the barrier and results in increased particle current. Moreover, the entropic nature of the barriers results in the effective diffusion coefficient exhibiting temperature dependence different from that expected in a system with energetic barriers. The dependence of the effective diffusion coefficient on temperature is predicted to be non-monotonic, exhibiting a maximum at the optimal temperature. These results are in good agreement with molecular simulation of diffusion of small alkanes in zeolites.[61]

Three different types of entropic effects were demonstrated to govern the sorption of alkanes on zeolites, an important system for the petroleum industry where zeolites are used for the separation of alkane mixtures,[62,63] namely, size entropy, configurational entropy, and length entropy. All these effects become most pronounced at high pressures, that is, loadings. Size entropy effect favors sorption of lower molecular weight alkanes over that of higher molecular weight alkanes. This is because at high surface coverage it is easier to fill the gaps with small rather than with large molecules. Separation of alkane isomers with different degrees of branching in zeolites with narrow channels is governed by the configurational entropy effect, namely, sorption of linear alkanes is more efficient than that of branched ones, since the former can be packed efficiently inside the channels while the latter would preferentially reside at channel intersections. The situation is opposite in zeolites with channels that are large enough to adsorb bulkier branched molecules. In that case, it is the branched molecules that can be packed more efficiently, since their linear dimensions are smaller than those of linear alkanes of same molecular weight. Taking the entropic effects into account allows the design of membranes for efficient separation of any given mixture of alkanes.

3.5. Smart Adhesives

Another rapidly expanding area of materials design is adhesive coatings.[64] Contemporary research on adhesives is not limited to assuring that the new adhesives are adequately serving their primary purpose, that is, to hold two surfaces together. A wide variety of so-called “smart adhesives” were developed recently. Smart adhesives, in addition to their main “adhesive” function, have one or more secondary “smart” functions, desirable for specific applications. Examples of such functions include thermal or electrical conductivity, fire resistance, and vibration absorption.

An important smart property of an adhesive is the ability to disbond on demand. It is useful in a variety of applications such as 3M’s Post-it notes, where surfaces are attached to each other temporarily and can be separated without damage to either of them. This ability is also important from the environmental standpoint, since it allows for easy disassembly of a product at the end of its lifetime for the purpose of recycling or reuse of its individual components.

A system in which adhesive properties are entropically controlled was developed recently.[65] A polymer/metal adhesive joint was shown to have strong adhesion at room temperature and reduced adhesion at elevated temperature. When cooled down again, the adhesion on the interface resumed its initial high values, and such reversible behavior persisted through multiple heating/cooling cycles. The mechanism of adhesion dependence on temperature was proposed based on entropic effect. At low temperature, the polymer, 1,4-polybutadiene, cross-linked and oxidized, adheres to the aluminum surface with carboxylic acid functional groups, formed as a result of the polymer oxidation. This enthalpically favorable interaction causes migration of carboxylic acid groups to the interface, which in turn causes entropically unfavorable extension of the polymer chains out of entropically preferable random-coil conformations. At elevated temperatures, the entropic effect becomes dominating, the polymer chains restore their random-coil shape, the surface concentration of carboxylic acid groups decreases, and the polymer−metal adhesion decreases dramatically. The degree of cross-linking of the polymer determines the elasticity of the polymer, thus affecting the balance between enthalpic and entropic forces.

3.6. Entropy-Driven Designer Molecules

Molecular machines, both natural and artificial, recently became the focus of much attention due to their potential to allow for further miniaturization in electronics, beyond the level achievable via the traditional “top-down” approach.[66] These supramolecular structures convert energy into mechanical motion, where the energy can be supplied from a variety of sources—chemical reaction, light, etc. The system moves between local minima on a potential energy surface via low-energy pathways by stochastic motion.[67] Coupling between the mechanical movement and chemistry of the system determines the incline of the potential energy surface. Thus, the behavior of these molecular machines is essentially energy-controlled.

An alternative class of entropy-driven molecular machines was proposed recently.[68] These high molecular weight systems minimize their free energy by acquiring conformations corresponding to maximal entropy, while the bonding energies remain constant. The principle of operation would be based on movable parts, which can be externally activated. Initially, the movable parts, such as sliding rings, are immobilized. After activation, such as heating, the system acquires enough energy for the movable part to escape the potential well where it was immobilized and to move freely. Thus, to minimize free energy, entropy of the system should be maximized, which involves changes of the conformation to allow for an increased number of locations available to the movable parts. Examples of such controlled, externally triggered conformation changes include, but are not limited to, swelling/deswelling transformations in polymers, contraction of “molecular muscles”, switching in rotaxane-like molecules, and transitions between linear polymeric chains and ring structures.

4. Conclusions

As materials design incorporates the principles of Green Chemistry, it places more emphasis on intermolecular interactions, and the entropic contribution into the energetics of the process becomes non-negligible. Deriving inspiration from entropically controlled chemistry by which nature creates an endless variety of materials without resorting to high temperatures, hazardous reagents, extreme pHs, and non-renewable feedstocks will allow the design of alternative, environmentally benign materials and processes.

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6. References

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