

Paper Reading Notes 1

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12/19/19

1) Paper (1) (Published) Anisotropic chemical strain in cubic ceria due to oxygen-vacancy-induced elastic dipoles

1.1 “*Chemical Strain*” --- In chemistry, a molecule experiences strain when its chemical structure undergoes some stress which raises its internal energy in comparison to a strain-free reference compound. The internal energy of a molecule consists of all the energy stored within it. A strained molecule has an additional amount of internal energy which an unstrained molecule does not. This extra internal energy, or strain energy, can be likened to a compressed spring. Much like a compressed spring must be held in place to prevent release of its potential energy, a molecule can be held in an energetically unfavorable conformation by the bonds within that molecule. Without the bonds holding the conformation in place, the strain energy would be released.

1.2 Ceria: CeO₂

1.3 Elastic dipole: The elastic dipole tensor is a fundamental quantity relating the elastic field and atomic structure of a point defect (<https://journals.aps.org/prb/pdf/10.1103/PhysRevB.94.241112>).

12/20/19

1) Paper (9) How Solid-Electrolyte Interphase Forms in Aqueous Electrolytes

1.1 Key component: Aqueous SEI; A model for the durability and aging of aqueous SEI was also proposed.

2) Basic Terminology refresh:

2.1 “*Electrolyte*” (Wiki) --- Electrolytes dissociate in water because water molecules are dipoles and dipoles orient in an energetically favorable manner to solvate the ions.

2.2 “Cell Potential”:

[https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_\(Analytical_Chemistry\)/Electrochemistry/Voltaic_Cells/The_Cell_Potential/Standard_Cell_Potential](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Voltaic_Cells/The_Cell_Potential/Standard_Cell_Potential)

The standard cell potential (E_{cell}^o) is the difference of the two electrodes, which forms the voltage of that cell. To find the difference of the two half cells, the following equation is used:

$$E_{cell}^o = E_{Red,Cathode}^o - E_{Red,Anode}^o \quad (1a)$$

with

- E_{cell}^o is the standard cell potential (under 1M, 1 Barr and 298 K).
- $E_{Red,Cathode}^o$ is the standard reduction potential for the reduction half reaction occurring at the cathode
- $E_{Red,Anode}^o$ is the standard reduction potential for the oxidation half reaction occurring at the anode

12/23/19

1) Basic Terminology refresh:

1.1 “*Electrolysis*” (Wiki) --- The main components required to achieve electrolysis are: (a) An electrolyte; (b) A direct current (DC).

Reduction Reaction: +H, -O, gain of e-

Oxidation Reaction: -H, +O, loss of e-

1.2 “*Fuel Cell*” (Wiki)

@Anode, a catalyst causes the fuel to undergo oxidation reactions that generate ions (often positively charged hydrogen ions) and electrons. The ions move from the anode to the cathode

through the electrolyte. @Cathode, another catalyst causes ions, electrons, and oxygen to react, forming water and possibly other products.

Fuel cells are classified by the type of electrolyte they use and by the difference in startup time: (A) proton exchange membrane fuel cells (The operating temperature range: 60–100 °C); (B) solid oxide fuel cells, etc.

1.2 “Solid oxide fuel cell” (Wiki)

- Solid oxide fuel cells (SOFCs) use a solid material, most commonly a ceramic material (solid, nonporous metal oxide) called yttria-stabilized zirconia (YSZ), as the electrolyte. They require high operating temperatures (800–1000 °C) and can be run on a variety of fuels including natural gas.
- SOFCs are unique since in those, negatively charged oxygen ions travel from the cathode (positive side of the fuel cell) to the anode (negative side of the fuel cell) instead of positively charged hydrogen ions travelling from the anode to the cathode, as is the case in all other types of fuel cells.
- Disadvantages for SOFC: High temperature is required. ---> slow start-up time, making SOFCs less useful for mobile applications
- Advantages: A high operating temperature ---> removing the need for a precious metal catalyst like platinum, thereby reducing cost.
- Why high T is needed? High T ensures the good ionic conductivity of YSZ. (The ceramics used in SOFCs do not become electrically and ionically active until they reach very high temperature).
- Typical operating temperature: 800–1,000 °C.
- A solid oxide fuel cell is made up of four layers, three of which are ceramics. (Note: Coefficient of Thermal Expansion (CTE) issues):

(A) Anode: The ceramic anode layer must be very porous to allow the fuel to flow towards the electrolyte. The most common material used is a cermet made up of nickel mixed with the ceramic material that is used for the electrolyte in that particular cell, typically YSZ nanomaterial-based catalysts, this YSZ part helps stop the grain growth of nickel. Larger grains of nickel would reduce the contact area that ions can be conducted through, which would lower the cells efficiency. The anode is commonly the thickest and strongest layer in each individual cell, because it has the smallest polarization losses, and is often the layer that provides the mechanical support. Electrochemically speaking, the anode's job is to use the oxygen ions that diffuse through the electrolyte to oxidize the hydrogen fuel.

(B) The electrolyte is a dense layer of ceramic that conducts oxygen ions. Its electronic conductivity must be kept as low as possible to prevent losses from leakage currents.

(C) The cathode is a thin porous layer on the electrolyte where oxygen reduction takes place. Cathode materials must be, at a minimum, electrically conductive. Currently, lanthanum strontium manganite (LSM) is the cathode material of choice for commercial use because of its compatibility with doped zirconia electrolytes. Mechanically, it has a similar coefficient of thermal expansion to YSZ and thus limits stress buildup because of CTE mismatch. Also, LSM has low levels of chemical reactivity with YSZ which extends the lifetime of the materials.

(D) Interconnect: The interconnect can be either a metallic or ceramic layer that sits between each individual cell. Its purpose is to connect each cell in series, so that the electricity each cell generates can be combined. Requirement: thermal stability at high temperatures and excellent electrical conductivity.

- Polarizations: Polarizations, or overpotentials, are losses in voltage due to imperfections in materials, microstructure, and design of the fuel cell. Polarizations result from (A) ohmic resistance of oxygen ions conducting through the electrolyte ($iR\Omega$), (B) electrochemical activation barriers at the anode and cathode, and finally (C) concentration polarizations due to inability of gases to diffuse at high rates through the porous anode and cathode (shown as η_A for the anode and η_C for cathode). The cell voltage can be calculated using the following equation:

$$V = E_0 - iR\omega - \eta_{cathode} - \eta_{anode}$$

where: E_0 = Nernst potential of the reactants; R = Thévenin equivalent resistance value of the electrically conducting portions of the cell; $\eta_{cathode}$ = polarization losses in the cathode; η_{Anode} = polarization losses in the anode:

(A) Ohmic polarization: Ohmic losses in an SOFC result from ionic conductivity through the electrolyte. This is inherently a materials property of the crystal structure and atoms involved. However, to maximize the ionic conductivity, several methods can be done. Firstly, operating at higher temperatures can significantly decrease these ohmic losses. Substitutional doping methods to further refine the crystal structure and control defect concentrations can also play a significant role in increasing the conductivity. Another way to decrease ohmic resistance is to decrease the thickness of the electrolyte layer.

(B) Concentration polarization: It is the result of practical limitations on mass transport within the cell and represents the voltage loss due to spatial variations in reactant concentration at the chemically active sites. This situation can be caused when the reactants are consumed by the electrochemical reaction faster than they can diffuse into the porous electrode, and can also be caused by variation in bulk flow composition. The latter is due to the fact that the consumption of reacting species in the reactant flows causes a drop in reactant concentration as it travels along the cell, which causes a drop in the local potential near the tail end of the cell.

(C) Activation polarization: The activation polarization is the result of the kinetics involved with the electrochemical reactions. Each reaction has a certain activation barrier that must be overcome in order to proceed and this barrier leads to the polarization. The activation barrier is the result of many complex electrochemical reaction steps where typically the rate limiting step is responsible for the polarization.

12/24/19

1) Basic Terminology refresh:

1.1 “Electrochemistry of Cell Potential”:

([https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_\(Analytical_Chemistry\)/Electrochemistry/Basics_of_Electrochemistry](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Basics_of_Electrochemistry))

(A) Red Cat and An Ox --- Reduction Cathode and Anode Oxidation

(B) Cell Potentials: Electrons move from areas of higher potential energy to areas of lower potential energy. In this case, the anode has a higher potential energy; electrons therefore move from anode to cathode. Their potential difference is called the cell potential, E_{cell} . For a spontaneous reaction, E_{cell} is positive and ΔG is negative: $\Delta G = -nFE_{cell}$. The standard cell potential is denoted E_{ocell} . $E_{ocell} = E_{ocathode} - E_{oAnode}$.

Note: For a reaction to occur, ΔG needs to be < 0 , and thus E needs to be positive.

1.2 “Reduction potential” (Wiki) --- E_0 (standard reduction potential).

Redox potential (aka oxidation / reduction potential): The more positive the reduction potential, the greater the species' affinity for electrons and tendency to be reduced.

A higher E° means there is a greater tendency for reduction to occur, while a lower one means there is a greater tendency for oxidation to occur.

2) Paper (5) Review on Modeling of the Solid Electrolyte Interphase (SEI) for Lithium-Ion Batteries

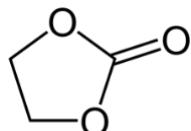
2.1 Lithium hexafluorophosphate, **LiPF₆**, Wiki

- A white crystalline powder has a high solubility in non-aqueous, polar solvents.
- Specifically, solutions of LiPF₆ in carbonate blends of ethylene carbonate, dimethyl carbonate, diethyl carbonate and/or ethyl methyl carbonate, with a small amount of one or many additives like vinylene carbonate, serve as state-of-the-art electrolytes in lithium-ion batteries.
- The inertness of the hexafluorophosphate anion toward strong reducing agents, such as lithium metal.



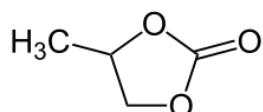
2.2 Ethylene carbonate (**EC**), (CH₂O)₂CO. Wiki

- It is classified as the carbonate ester of ethylene glycol and carbonic acid. At room temperature (25 °C) ethylene carbonate is a transparent crystalline solid, practically odorless and colorless, and somewhat soluble in water. In the liquid state (melting point 34-37 °C) it is a colorless odorless liquid.
- Ethylene carbonate is used as a polar solvent with a molecular dipole moment of 4.9 D, only 0.1 D lower than that of propylene carbonate (PC).
- It can be used as a high permittivity component of electrolytes in lithium batteries and lithium-ion batteries. Other components like diethyl carbonate, ethyl methyl carbonate, dimethyl carbonate and methyl acetate can be added to those electrolytes in order to decrease the viscosity and melting point.

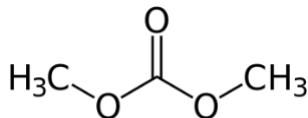


2.3 Propylene carbonate (PC) Wiki

- PC is used as a polar, aprotic solvent. Due to its high dielectric constant of 64, it is frequently used as a high-permittivity component of electrolytes in lithium batteries, usually together with a low-viscosity solvent (e.g. dimethoxyethane). Its high polarity allows it to create an effective solvation shell around lithium ions, thereby creating a conductive electrolyte. However, it is not used in lithium-ion batteries due to its destructive effect on graphite.

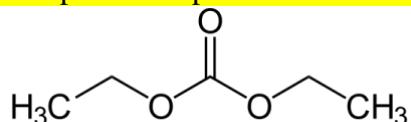


2.4 Dimethyl carbonate (**DMC**) is an organic compound with the formula OC(OCH₃)₂. Wiki

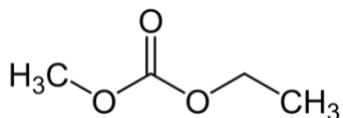


2.5 Diethyl carbonate (DEC), OC(OCH₂CH₃)₂. Wiki

It can be used as a component of electrolytes in lithium batteries. It has been proposed as a fuel additive to support cleaner diesel fuel combustion because its high boiling point might reduce blended fuels' volatility, minimize vapor buildup in warm weather that can block fuel lines.



2.6 Ethyl Methyl Carbonate (EMC), WikiData



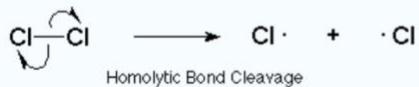
2.7 Homolytic cleavage <https://socratic.org/organic-chemistry-1/radical-reactions/homolytic-v-heterolytic-cleavage>

What is bond cleavage?

Bond cleavage is the splitting of a chemical bond.

There are two types of bond cleavage: **homolytic** and **heterolytic**.

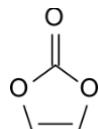
In homolytic cleavage, the two electrons in the bond are divided equally between the products.



In heterolytic cleavage, one atom gets both of the shared electrons.

2.8 Vinylene Carbonate (VC), Wiki

VC is used widely as an electrolyte additive for lithium-ion batteries where it promotes the formation of an insoluble film between the electrolyte and the negative electrode: the SEI (solid-electrolyte-interface). This polymer film allows ionic conduction, but prevents the reduction of the electrolyte at the negative (graphite) electrode and contributes significantly to the long-term stability of lithium-ion batteries.



12/26/19

1) Basic Terminology refresh:

1.1 “*Force Field*”: Wiki

- A force field refers to the functional form and parameter sets used to calculate the potential energy of a system of atoms or coarse-grained particles in molecular dynamics simulations. The parameters of the energy functions may be derived from experiments in physics or chemistry, calculations in quantum mechanics, or both.
- The basic functional form of potential energy includes A) bonded terms for interactions of atoms that are linked by covalent bonds, and nonbonded (also termed noncovalent) terms that describe the long-range electrostatic and van der Waals forces.
- Type: (a) *All-atom* force fields provide parameters for every type of atom in a system, including hydrogen; (b) *United-atom interatomic potentials* treat the hydrogen and carbon atoms in each methyl group (terminal methyl) and each methylene bridge as one interaction center; (c) *Coarse-grained potentials*, which are often used in long-time simulations of macromolecules such as proteins, nucleic acids, and multi-component complexes, provide even cruder representations for higher computing efficiency.

1.2 “AMBER force field”: Wiki

The functional form of the AMBER force field is^[2]

$$V(r^N) = \sum_{\text{bonds}} k_b(l - l_0)^2 + \sum_{\text{angles}} k_a(\theta - \theta_0)^2$$

$$+ \sum_{\text{torsions}} \sum_n \frac{1}{2} V_n [1 + \cos(n\omega - \gamma)] + \sum_{j=1}^{N-1} \sum_{i=j+1}^N f_{ij} \left\{ \epsilon_{ij} \left[\left(\frac{r_{0ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{r_{0ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

- Bond & Angle energy: Harmonic Oscillator model;
- Torsional energy: Fourier series;
- Non-bonded energy: (a) Van Der Waals --- Lennard-Jones Potential; (b) Electrostatic Potential --- Coulomb Potential

1.3 “Morse Potential”: Wiki

- The Morse potential is a convenient interatomic interaction model for the potential energy of a diatomic molecule. It is a better approximation for the vibrational structure of the molecule than the QHO (quantum harmonic oscillator) because it explicitly includes the effects of bond breaking, such as the existence of unbound states. It also accounts for the anharmonicity of real bonds and the non-zero transition probability for overtone and combination bands.
- The Morse potential energy function has the following form, where r is the distance between the atoms, r_e is the equilibrium bond distance, D_e is the well depth (defined relative to the dissociated atoms), and a controls the 'width' of the potential (the smaller a is, the larger the well).

$$V'(r) = D_e (1 - e^{-a(r-r_e)})^2$$

1.4 “CHARMM Force Field”: Wiki

1.5 “Implicit solvation”: Wiki

Implicit solvation (sometimes termed continuum solvation) is a method to represent solvent as a continuous medium instead of individual “explicit” solvent molecules. The method is often applied to estimate free energy of solute-solvent interactions in structural and chemical processes, such as folding or conformational transitions of proteins, DNA, RNA, and polysaccharides, association of biological macromolecules with ligands, or transport of drugs across biological membranes.

1.6 “GROMOS”: Wiki

The united atom force field was optimized with respect to the condensed phase properties of alkanes.

1.7 “Molecular Dynamics”: Wiki

- During a classical MD simulation, the most CPU intensive task is the evaluation of the potential as a function of the particles' internal coordinates. Within that energy evaluation, the most expensive one is the non-bonded or non-covalent part. In Big O notation, common molecular dynamics simulations scale by $O(n^2)$ if all pair-wise electrostatic and van der Waals interactions must be accounted for explicitly. This computational cost can be reduced by employing electrostatics methods such as particle mesh Ewald summation $O(n \log(n))$, particle-particle-particle-mesh (P3M), or good spherical cutoff methods $O(n)$.
- For simulating molecules in a solvent, a choice should be made between explicit and implicit solvent. Explicit solvent particles (such as the TIP3P, SPC/E and SPC-f water models) must be calculated expensively by the force field, while implicit solvents use a mean-field approach. But the granularity and viscosity of explicit solvent is essential to reproduce certain properties of the solute molecules. This is especially important to reproduce chemical kinetics.
- The time evolution of $X(t)$ (Position) and $V(t)$ (Velocity) is called a trajectory. Given the initial positions (e.g., from theoretical knowledge) and velocities (e.g., randomized Gaussian), we can calculate all future (or past) positions and velocities.
- Potentials in MD simulations --- Interatomic potential/Force field: When finer levels of detail are needed, potentials based on quantum mechanics are used; some methods attempt to create hybrid classical/quantum potentials where the bulk of the system is treated classically but a small region is treated as a quantum system, usually undergoing a chemical transformation.
- Because of the non-local nature of non-bonded interactions, they involve at least weak interactions between all particles in the system. Its calculation is normally the bottleneck in the speed of MD simulations. To lower the computational cost, force fields employ numerical approximations such as shifted cutoff radii, reaction field algorithms, particle mesh Ewald summation, or the newer particle-particle-particle-mesh (P3M).
- Potentials in MD simulations: (A) Empirical potentials; (B) Pair potentials versus many-body potentials; (C) Semi-empirical potentials (There are a wide variety of semi-empirical potentials, termed tight-binding potentials(TB), which vary according to the atoms being modeled); (D) Polarizable potentials; (E) Potentials in ab initio methods; (F) Hybrid QM/MM (Quantum Mechanics/ Molecular Mechanics; (G) Coarse-graining and reduced representations;
- Classical MD vs. Quantum Mechanical Method (Including DFT, Ab Initio Molecular Dynamics (AIMD)): In classical MD, one potential energy surface (usually the ground state) is represented in the force field. This is a consequence of the Born–Oppenheimer approximation. In excited states, chemical reactions or when a more accurate representation is needed, electronic behavior can be obtained from first principles by using a quantum mechanical method, such as density functional theory. This is named Ab Initio Molecular Dynamics (AIMD). A significant advantage of using ab initio methods is the ability to study reactions that involve breaking or formation of covalent bonds, which correspond to multiple electronic states.
- Hybrid QM/MM (Quantum Mechanics/ Classical or Molecular Mechanics) Basic ideology: To balance to limits of QM (expensive computing cost) and MM (require extensive parameterization; energy estimates obtained are not very accurate; cannot be used to simulate reactions where covalent bonds are broken/formed; and are limited in their abilities for providing accurate details regarding the chemical environment), a small part of the system is treated quantum-mechanically (typically active-site of an enzyme or reactive part of a molecule) and the remaining system is treated classically.

- Coarse-grained (CG) models: Instead of explicitly representing every atom of the system, one uses "pseudo-atoms" to represent groups of atoms.

12/28/19

1) Basic Terminology refresh:

1.1 “*LAMMPS*”: Wiki

1.2 “*Potential of mean force (PMF)*”: Wiki

1.3 “*Linear combination of atomic orbitals (LCAO)*”: Wiki

1.4 “*Tight binding (TB)*”: Wiki

- The name "tight binding" of this electronic band structure model suggests that this quantum mechanical model describes the properties of tightly bound electrons in solids. The electrons in this model should be tightly bound to the atom to which they belong and they should have limited interaction with states and potentials on surrounding atoms of the solid. As a result, the wave function of the electron will be rather similar to the atomic orbital of the free atom to which it belongs. The energy of the electron will also be rather close to the ionization energy of the electron in the free atom or ion because the interaction with potentials and states on neighboring atoms is limited.
- **Interatomic Matrix Element** between the atomic orbitals m and l on adjacent atoms: It is also called the bond energy or two center integral and it is the most important element in the tight binding model.

12/30/19

1) Basic Terminology refresh:

1.1 “*Monte Carlo method*”: Wiki

1.2 “*Markov chain*”: Wiki

A Markov chain is a stochastic model describing a sequence of possible events in which the probability of each event depends only on the state attained in the previous event.

1.3 “*Deterministic algorithm*”: Wiki vs. “*non-deterministic approach*”

- In computer science, a deterministic algorithm is an algorithm which, given a particular input, will always produce the same output, with the underlying machine always passing through the same sequence of states.
- non-deterministic approach: each realization provides a different outcome, for example, Monte Carlo method

1.4 “*Monte Carlo integration*”: Wiki + <https://www.youtube.com/watch?v=q6gJ2T0NSwM>

1.5 “*ReaxFF (reactive force field)*”: Wiki

- Whereas traditional force fields are unable to model chemical reactions because of the requirement of breaking and forming bonds (a force field's functional form depends on having all bonds defined explicitly), ReaxFF eschews explicit bonds in favor of bond orders, which allows for continuous bond formation/breaking.
- From Paper (23): ReaxFF is a highly transferable empirical reactive potential, constructed based on bond-order/bond distance notion, [44,45], which allows for bond formation and bond dissociation during molecular statics/ dynamics (MS/D) simulation. It is capable of describing

a smooth transition between the nonbonded states and single, double or triple bonded systems. The total interaction energy in ReaxFF is divided in to several energy contributions given by the following equation,

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{val}} + E_{\text{tor}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{vdw}} \\ + E_{\text{coulombic}} \quad (1)$$

- The energy terms in eq 1 comprise the bond energy (E_{bond}), valence-angle (E_{val}), torsion-angle energy (E_{tor}) and lone pair (E_{lp}), overcoordinate (E_{over}) and under coordinate (E_{under}) energy penalty terms as well as nonbonded interactions i.e. van der Waals (E_{vdw}) and coloumbic energy (E_{coulomb}). **All the connectivity dependent energy terms (e.g., valence and torsion angles) are bond-order dependent and updated at every MD or energy minimization step.**
- Thus, the energy and forces related to these components approaches to zero upon bond dissociation. Furthermore, nonbonded interactions such as van der Waals and Columbic terms are calculated for the entire system between each pair of atoms. ReaxFF is a polarizable force field in which electronegativity equalization method (EEM) [46], and [47] is employed to account for the charge distribution based on the geometry changes of atoms. All the aforementioned features enable ReaxFF to simulate the chemical reactions occur between elements at extreme dynamic environment with a comparable accuracy of DFT simulations. ReaxFF potential has been successfully used to model the materials behavior under extreme conditions of loading, temperature and pressure. [50,51]

1.6 “Protic vs. Aprotic solvent”: Wiki

- A protic solvent is a solvent that has a H atom bound to an O, a N or a F atom. In general terms, any solvent that contains a labile H⁺ is called a protic solvent. The molecules of such solvents readily donate protons (H⁺) to reagents. Conversely, aprotic solvents cannot donate hydrogen.

01/03/20

1) Basic Terminology refresh:

1.1 “Space Charge”: Wiki

2) Paper (5) Review on Modeling of the Solid Electrolyte Interphase (SEI) for Lithium-Ion Batteries

Summary:

2.1 SEI --- Allows Li⁺ transport and blocks electrons leakage.

2.2 Challenges of designing SEI: (A) The electrolyte reduction reactions are unclear. (B) SEI has a complicated structure, and the structure-property relationships are largely unknown.

2.3 SEI failure mechanism --- Fig 3

2.4 Modeling of electrolyte reduction mechanisms

- LIB electrolyte common contents: **(A) Li salt (LiPF₆)** dissolved in **(B) organic solvents** which contains **(B-1) high dielectric ingredients**, like Ethylene Carbonate (EC) or Propylene Carbonate ($\epsilon_r = 64$, wiki) (Reason: It's easier for organic solvents with high dielectric constant to dissolve the Li salt into Li⁺ and PF₆⁻. As a comparison, ϵ_r (H₂O) = 80); **(B-2) some low**

viscosity ingredients, like DMC, DEC, EMC; **(B-3) some additives** to improve the SEI, like VC, FEC.

- EC solvent decomposition mechanism ---> reduction kinetics of EC (one electron and two electron reduction mechanism, Table 1) ---> reduction potential of each solvent component --> effect of Li-salt anion, solvation structure, anode surface state ---> buildup of SEI layer (initial formation)

2.5 In vivo modification of SEI: (A) Effect of VC on SEI formation (graphite anode); (B) effect of FEC on SEI formation (Si and Sn electrode); (C) ES to avoid PC co-intercalation into graphite anode.

2.6 SEI properties, battery performance: (A) Electron insulating properties of inorganic components in SEI; (B) Li-ion diffusion through SEI --- a porous (organic) outer layer permeable to Li⁺, salt anions (dissolved in the electrolyte), and even solvent molecules, and a dense (inorganic) inner layer facilitating only Li-ion transport. Ionic conductivity of the SEI components. Li-ion de-solvation at the SEI/electrolyte interface. (C) Mechanical properties of SEI: modulus and adhesion; (D) Chemical stability of SEI: solubility and reactivity (chemical and electrochemical) (E)SEI growth mechanisms

2.7 In vitro design of SEI --- designing a surface coating layer to achieve the multi-functionality of the SEI: (A) ALD (Atomic layer deposition) and MLD (molecular layer deposition); (B) fully lithiated and non-fully lithiated materials; (C) Evolving properties ---> design of coating geometry, equation 6.

01/04/20

1) Paper (2) Computational study of lithium nucleation tendency in Li₇La₃Zr₂O₁₂ (LLZO) and rational design of interlayer materials to prevent lithium dendrites

1.1 Methodology about how to start a simulation

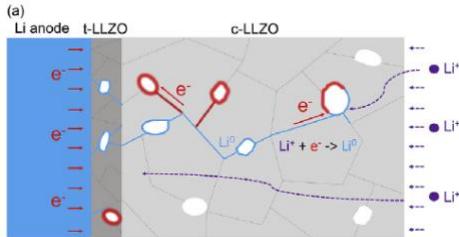
"The unit cell of c-LLZO contains 192 atoms that include eight formula units of Li₇La₃Zr₂O₁₂. The Li atoms were assigned on the partially occupied 24d and 96h sites in c-LLZO via the distribution principle proposed by Cussen and O'Callaghan [44,45] and Xie et al. [43], which minimizes the energy by avoiding the electrostatically unfavorable Li⁺ configurations. Through this guided distribution principle, the energy deviation among different Li configurations can be reduced to ~0.1 eV/unit cell, which is much smaller than the entirely random Li distribution, which leads to an energy deviation as high as ~3 eV/unit cell. The structure with the lowest energy was taken for further study, and the number of Li atoms in 24d and 96h sites is 13 and 43, respectively, which is similar to the measured occupancies."

Small summary: (1) Looking for related literature for the needed parameters to start modeling the crystal structure. (2) With some guided distribution principle, run the simulation to obtain different atoms configuration. (3) Find the structures with comparatively low energy, and compared their structure or some calculated properties with experiment values. If they agree well with each other or their difference is acceptable, then this structure could be taken for further study.

1.2 Summary:

- In lithium solid electrolyte battery (c-LLZO), metallic Li is found inside the solid electrolyte area. This paper basically talks about how metallic Li forms in this area.
- TDOS were calculated for 4 materials. (1) Stoichiometric c-LLZO slab; (2) Nonstoichiometric c-LLZO slab; (3) Nonstoichiometric t-LLZO slab; (4) Li₂PO₂N slab.

- Additional states in the bandgap on the surface of c-LLZO and t-LLZO (but not in the bulk) -> Excess electrons are trapped ---> Excess e- tend to disperse on the surfaces of c-LLZO and t-LLZO, and even localize around the La atoms of c-LLZO ---> Metallic Li forms along the pore surfaces in LLZO
- Computation method: It was performed by the Vienna Ab initio Simulation Package (VASP) based on plane-wave DFT.
- One picture to describe the paper: Fig 5a



2) Paper (3) Transferable Self-Consistent Charge Density Functional Tight-Binding Parameters for Li–Metal and Li–Ions in Inorganic Compounds and Organic Solvents

2.1 Training set & Validation set

2.2 Summary:

- Training data set <---> an iterative SCC-DFTB parametrization workflow Fig 1
- Validation <---> (1) Surface Energy and Li Adsorption on the Li–Metal; (2) Surface Energy for Li₂O and Li₂CO₃.
- Use the validated parameters to simulate the (1) Li/Li₂CO₃ interface; (2) EC solvent; and then (3) Li⁺ ion dissolved in EC (solvation energy & mean square displacement (MSD)).
- Use the SCC-DFTB method to investigate the effect of SEI thickness on SEI electron blocking properties (PDOS ---> bandgap).

3) Paper (4) Computational design of metal oxides to enhance the wetting and adhesion of silver-based brazes on yttria-stabilized-zirconia (YSZ)

3.1 Brazing: (Wiki)

Brazing is a metal-joining process in which two or more metal items are joined together by melting and flowing a filler metal into the joint, the filler metal having a lower melting point than the adjoining metal.

3.2 Work of adhesion: (Handbook of Adhesives and Surface Preparation, 2011)

The work of adhesion is defined as the reversible thermodynamic work that is needed to separate the interface from the equilibrium state of two phases to a separation distance of infinity.

3.3 Reactive Air Brazing (RAB): <https://availabletechnologies.pnnl.gov/technology.asp?id=112>

RAB technique, developed at PNNL, utilizes a novel copper oxide-silver single phase liquid as the basis for joining electrochemically active ceramics such as yttria stabilized zirconia and lanthanum strontium cobalt ferrite to oxidation resistant materials such as FeCrAlY. Materials of this type are commonly employed in the oxygen generators used in syngas production, solid oxide fuel cells, etc.

3.3 Summary:

- Core question: Adhesion of Ag-based brazes on YSZ.

- 2 mechanisms: (1) Oxygen atoms dissolved on Ag liquid drop surface can hop into the YSZ oxygen vacancy sites, which increases the W_{adh} by providing additional sites for Ag-O bonding across the interface. (Part 3.1) (2) CuO interlayer promotes adhesion of Ag/CuO and CuO/YSZ.
- Eqn 1 W_{adh} :

$$W_{\text{adh}} \equiv (\gamma_{1V} + \gamma_{2V}) - \gamma_{12} = (E_1 + E_2 - E_{12})/2A$$

Where γ_{1V} and γ_{2V} represent of materials 1 and 2, γ_{12} represents the solid1-solid2 interface energy. In Eqn 1, γ_{1V} and γ_{2V} could be easily calculated from DFT. The challenging part to calculate is γ_{12} - It is time consuming to calculate this value by DFT for large amounts of material combinations. In this case, a descriptor X_{MO} is formulated to calculate γ_{12} and thus W_{adh} :

$$\chi_{\text{MO}} = \frac{f((N_M + N_O) \times |E_{M-O}|) - (N_O \times |E_{Ag-O}|)}{A_{\text{MO}}}$$

In this case, by calculating X_{MO} and establishing the γ_{12} - X_{MO} relationship, γ_{12} value and thus W_{adh} could be quickly calculated.

- As a result, the adhesion of Ag on various oxides (Single cation oxides and complex oxides) could be predicted by comparing W_{adh} with the help of PDOS analysis.

01/08/20

1) Paper (6) From Microparticles to Nanowires and Back: Radical Transformations in Plated Li Metal Morphology Revealed via in Situ Scanning Electron Microscopy

1.1 Lithium plating:

https://www.nasa.gov/sites/default/files/atoms/files/1-lithium_plating_azimmerman.pdf

Lithium metal that has been deposited on the surface of the anode, instead of moving into the carbon intercalation sites (like graphite). (Lithium metal deposited more rapidly than intercalation can occur)

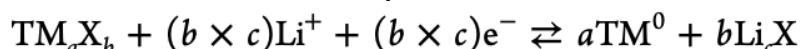
1.2 Calculation part: MD, Figure 3 (g-i).

2) Paper (7) Nanoscale Protection Layers (PL) to Mitigate Degradation in High-Energy Electrochemical Energy Storage Systems

2.1 Terminology: Conversion-type electrode:

<https://pubs.acs.org/doi/full/10.1021/acs.accounts.7b00487>

- Among the candidates to replace current intercalation-type electrode materials, conversion-type electrode materials are very promising because of their high theoretical capacity and low cost.
- conversion reaction materials react during lithiation to form entirely new products, often with dramatically changed structure and chemistry,
- Generally, the conventional/classical concept of a conversion reaction can be expressed as:



where TM denotes a transition metal and X an anionic species. Transition metal compounds such as transition metal oxides, sulfides, fluorides, phosphides, and nitrides can undergo such conversion reactions, yielding high-theoretical-capacity materials.

2.2 Summary:

- This article talks mostly about experiments, with the last part discussing the MD simulation.

- Degradation mechanisms: (1) Suffering large volume changes upon lithiation/delithiation, inviting stress as well as fracture; (2) Dendrite Growth; (3) For highly reactive electrodes (i.e. Li metal), mobile chemical species in the liquid electrolyte can attack the electrode, suppressing its redox activity and thus degrading the battery.
- **Experimental part:** (1) Protection layers (PL) to stabilize reactive Li metal anodes; (2) PLs to promote reversibility of conversion-type electrodes in 2 ways: (A) maintaining structural integrity; (B) extending reversible Li insertion and delaying irreversible conversion reactions (Questions: Are these conversion reactions are Unfavored? If so, why do we still want such conversion-type electrode if such conversion reactions are irreversible?)
- **Computation part:** Using reactive MD simulations. It discusses the different performance of SiO₂ and Al₂O₃ on the stress distribution of the core-shell structured electrodes.

01/10/20

1) Paper (8) Polaron size and shape effects on oxygen vacancy interactions in lanthanum strontium ferrite

1.1 Terminology:

1.1.1 Lanthanum Strontium Ferrite (LSF, La_{1-x}Sr_xFeO_{3-δ})

<https://www.americanelements.com/lanthanum-strontium-ferrite-lsf>

LSF is used for fuel cell cathode applications. Upon firing, LSF will partially sinter to form well-defined necks and open gas paths to permit simultaneous gas and electrical transfer. LSF has an excellent thermal expansion match with Yttria Stabilized Zirconia (YSZ) electrolytes. It is highly electronically conductive and has proven long term stability. LSF belongs to a class of "A" site and "B" site doped perovskite structures with these properties.

1.1.2 Polaron:

(A) Wiki

A polaron is a fermionic quasiparticle used in condensed matter physics to understand the interactions between electrons and atoms in a solid material.

(B) <http://nanoscale.blogspot.com/2009/01/what-is-polaron.html>

- When a charge carrier (an e- or h+) is placed into a solid, the surrounding ions can interact with it (e.g., positive ions will be slightly attracted to a negatively charged carrier). The ions can adjust their positions slightly, balancing their interactions with the charge carrier and the forces that hold the ions in their regular places. This adjustment of positions leads to a polarization locally centered on the charge carrier. The combo of the carrier & the surrounding polarization is a polaron. There are "large" and "small" polarons, defined by whether or not the polarization cloud is much larger than the atomic spacing in the material. Polarons are a useful way of thinking about carriers in ionic crystals, materials with "soft" vibrational modes (such as the manganites), and organic semiconductors.
- Analogy for understanding: ball-rolling-on-a-rubber-sheet analogy:
- The ball is the charge carrier; the deformation of the rubber sheet is the polarization "cloud". Consider tilting the rubber sheet - this is analogous to applying an electric field to the material. The ball will roll in response to the tilt, but it will be slowed down compared to how it would roll on a hard tilted surface, since it has to put energy into deforming the sheet. In real materials, this shows up as a correction to the effective mass of the charge carrier. All other things being equal, polarons are heavy compared to bare quasiparticles.
- A very crude way of thinking about the attractive pairing interaction between electrons in low temperature superconductors --- Imagine a ball rolling in some direction, leaving behind itself

- a little groove in the sheet that "fills in" at some rate. This would lower the energy of some other ball if that other ball were traveling in, say, the exact opposite direction of the first ball.
- Self-trap polaron: Imagine a ball dropping on the sheet will pull the sheet down so far that it'll look like a little punching bag. Now if you try to tilt the sheet, the sheet will have stretched so tightly that the ball won't want to roll at all. Instead, the little punching bag will hang there at an angle relative to the sheet. Something analogous to this can happen in real materials, too - polarons can self-trap. That is, the charge carrier deforms the local environment so much that it basically digs itself such a deep potential well that it can't move anymore.

1.1.3 Perovskite Structure: Wiki

- A perovskite is any material with the same type of crystal structure as CaTiO₃, known as the perovskite structure, or $\text{xA}_{2+\text{v}}\text{B}_{4-\text{v}}\text{X}_{2-\text{v}}$, where '**A**' and '**B**' are two cations of very different sizes, and X is an anion that bonds to both. **The 'A' atoms are larger than the 'B' atoms.** The ideal cubic structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold cuboctahedral coordination.

1.1.4 Paramagnetism: Wiki

- Paramagnetism is a form of magnetism whereby some materials are weakly attracted by an externally applied magnetic field, and form internal, induced magnetic fields in the direction of the applied magnetic field.

1.1.5 Antiferromagnetism: Wiki

- In materials that exhibit antiferromagnetism, the magnetic moments of atoms or molecules, usually related to the spins of electrons, align in a regular pattern with neighboring spins (on different sublattices) pointing in opposite directions.

1.1.6 Néel temperature: Wiki

- The Néel temperature or magnetic ordering temperature, T_N, is the temperature above which an antiferromagnetic material becomes paramagnetic—that is, the thermal energy becomes large enough to destroy the microscopic magnetic ordering within the material.

1.1.7 Degenerate orbitals: <https://www.quora.com/What-is-the-meaning-of-degenerate-orbitals>

- Orbitals refer to the wave function of the electron around a nucleus. Each orbital is associated to an energy value depending on its quantum parameters. Degenerate orbitals are orbitals that have the same energy. They are different (they may display differently in space around the nucleus) but they are associated to the same energy. You can break this degeneracy by applying a suitable external field on the system (electric or magnetic field, for example). Some orbitals then will have a higher energy, others lower energy (\Rightarrow CFT). They are no longer degenerated.

1.1.8 Crystal Field Theory (CFT), see pictures below.

Crystal Field Theory (CFT)

1. YouTube : Electronic Structure of Coordinated Complexes

Transition Metals :

- (I) • Bare Metal orbitals.
(5-fold degenerate) $\begin{array}{c} \uparrow \\ d_{xy} \\ \uparrow \\ d_{yz} \\ \uparrow \\ d_{zx} \\ \uparrow \\ d_{z^2} \\ - \\ d_{x^2-y^2} \end{array}$

- Transition Metal Complex (with some ligands)

- (1) (a) Octahedral complexes. (6 ligands)
— weak field ligands
(high-spin config) $\begin{array}{c} e_g \\ \uparrow \\ t_{2g} \\ \uparrow \\ \uparrow \\ \uparrow \end{array} \quad \Delta_o (W)$

have relatively weak ligand bonds ; have a small splitting (Δ_o) compared with the amount of energy that's required to pair 2 electrons in a single orbital)

- strong field ligands
(low-spin config) $\begin{array}{c} e_g \\ - \\ - \\ t_{2g} \\ \uparrow \downarrow \\ \uparrow \quad \uparrow \end{array} \quad \Delta_o (S)$



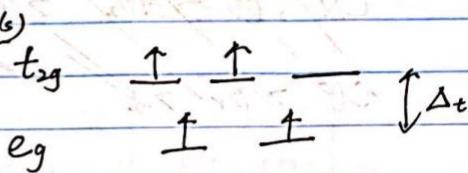
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Electron Pairing Energy: Repulsion between paired electrons in a single orbital.

$\Delta_o(W) < E$ required to put $2 e^-$ into 1 orbital

$\Delta_o(S) > E$ required to put $2 e^-$ into 1 orbital.

(2) Tetrahedral structures (4 ligands)
(high-spin config only)

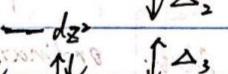
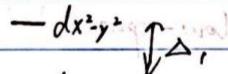


(3) Square planar complexes (4 ligands)

- important for d^8 metal complexes

($Cu^{2+}, Pt^{2+}, Pd^{2+}, Ir^+, Au^{3+}$)

- nearly always low-spin config



d_{yz}, d_{zx} lowest

(II). Spectrochemical Series.

- The magnitude of the crystal field splitting depends on the binding strength of the ligand

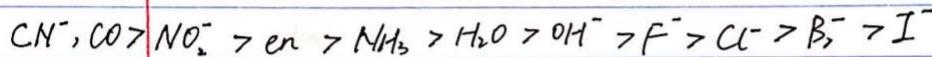
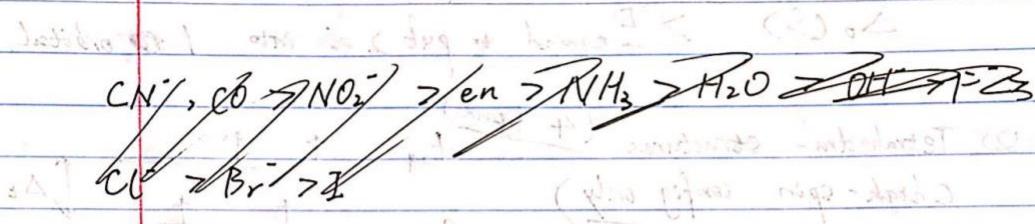
Strong field ligands produce large energy splittings & absorb short wavelength (~~long wavelength~~).

CS

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- Weak field ligands have small splitting.



Strong field, ethylene diamine weak field,
 large Δ , $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ small Δ ,
 low-spin high spin

(III) Magnetic Properties.

- Most ordinary materials have all

e^- paired. Zero spin = diamagnetic

(slight repulsion)

$\Rightarrow e_g \quad - \quad -$

d^6 octahedral field

$t_{2g} \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$

low-spin diamagnetic

- Unpaired e^- have magnetic fields.

so are attracted by an external field.

(paramagnetic)

$\Rightarrow e_g \quad I \quad I$

$t_{2g} \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$

high-spin paramagnetic



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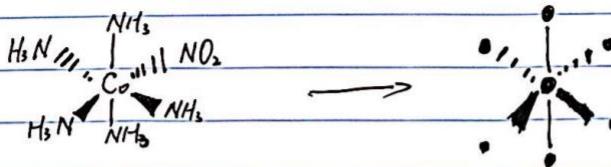
Permanently oriented spins are ferromagnetic.

(IV) Ligand Field Theory

- Takes into account that metal-ligand bonds cannot be fully ionic.
- Orbitals on the metal ($3d$, $4s$, $4p$) interact with valence orbitals of the ligands to form:
 - bonding orbitals (mostly ligand character, mostly occupied)
 - antibonding orbitals (mostly metal character, sometimes occupied)
 - non-bonding orbitals (usually $3d$ orbitals).

2. YouTube : Crystal Field Theory (Author: Professor Dave Explains)
(CFT)

- ↳ • CFT is based on the premise that metal ions & ligands can be treated as point charges.



- Ligands : all have excess e^- that can donate to metal ions
This electron density will repel the existing electron density on the metal ion.

- Due to this repulsion, the energy of certain d orbitals will be increased, and not in an equal manner.

↓
orbital energy splitting

Crystal Field Splitting energy will be determined by
the strength of ligands / oxidation state / coordination number



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(1)

(2)

(3)

1.2 Summary

1.2.1 Materials: Lanthanum Strontium Ferrite (LSF, $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$), ($0 \leq x \leq 1$)), where δ represents the overall oxygen non-stoichiometry. δ can impact the mobile oxygen vacancy site fraction, X, and hence the ionic conductivity; In this paper, 4 kinds of composition of LSF were studied: (a) Orthorhombic LaFeO_3 ; (b) Rhombohedral $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$; (c) Cubic $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$; (d) Cubic SrFeO_3 .

1.2.2 Methods: DFT with a Hubbard-U approach (DFT + U) was used to address the on-site electronic interactions of the 3d orbitals in the multivalent Fe atoms. (Using the spin-polarized density functional theory (DFT)-predicted magnetic moments on Fe to determine the Fe charge state distribution)

1.2.3 General knowledge of the theory about Polaron and Crystal-Field-Splitting (CFT) is required to understand this paper.

1.2.4

(A) **LFO**: Oxygen-vacancy-adjacent Fe atoms \longleftrightarrow Square Pyramidal (SP) coordinated \longleftrightarrow excess electrons produced during oxygen vacancy formation remained localized at the first nearest neighbor Fe atoms \Longrightarrow Small oxygen vacancy polarons \Longrightarrow Dilute polaron models (little polaron-polaron interactions)

(B) **LSF55, SFO**: Oxygen-vacancy-distant-Fe atoms \longleftrightarrow Octahedrally-coordinated (Oh) \longleftrightarrow excess electrons produced during oxygen vacancy formation were distributed to the second-nearest-neighbor Fe atoms \Longrightarrow Large oxygen vacancy polarons \Longrightarrow Stronger polaron-polaron interactions with increasing δ and X. \Longrightarrow Highly oxygen deficient compositions (high δ) of LSF55 and SFO are prone to oxygen-vacancy-ordering-induced phase transformations.

01/16/20

- 1) Paper (11) In situ stress measurements during electrochemical cycling of lithium-rich cathodes.
- 2) Paper (16) Long-range charge transfer and oxygen vacancy interactions in strontium ferrite.

2.1 Summary

- This Paper (16) is a predecessor paper of Paper (8).
- Methods: Refer to Paper (8). DFT+U calculations.
- Materials: (a) cubic SrFeO_3 , (b) tetragonal $\text{SrFeO}_{2.875}$, (c) orthorhombic $\text{SrFeO}_{2.75}$, and (d) brownmillerite $\text{SrFeO}_{2.5}$.
- Fe charge state distribution is determined: The charge on Fe in square pyramidal (SP) was shown to always remain +4 while the Fe in distorted octahedral (Oh) varied from +4 to +3 with δ .
- The “long-range charge transfer” mechanism is explained by the CFT theory and computation results.
- ΔG_{vac} , ΔE_{fvac} vs. oxygen nonstoichiometry δ are calculated and plotted. Temperature vs. oxygen vacancy site fraction X is also calculated and plotted.
- Oxygen vacancy formation site: O₂ vacancies are always formed at the site shared by the two highest charged octahedral Fe (except brownmillerite).
- Selection of parameter U is also discussed.

3) Paper (10) Integrated Computation and Experimental Investigation on the Adsorption Mechanisms of Anti-Wear and 010 Anti-Corrosion Additives on Copper

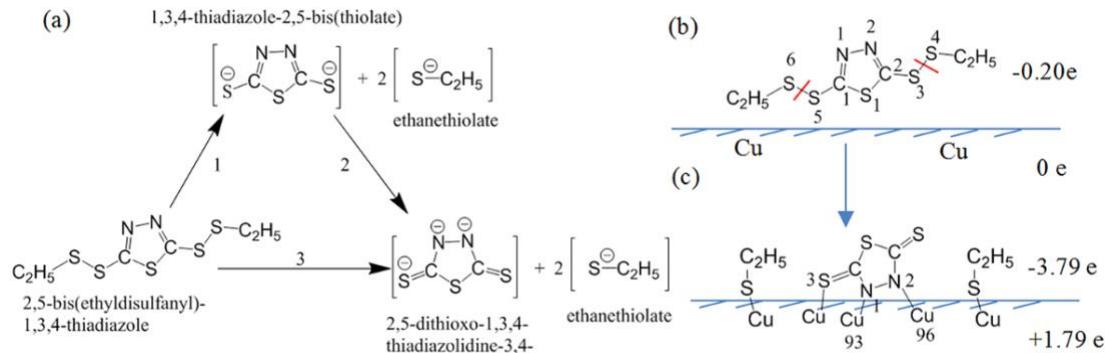
3.1 Terminology

3.1.1 “Bader Charge Analysis”: <https://theory.cm.utexas.edu/henkelman/research/bader/>

- Richard Bader developed an intuitive way of dividing molecules into atoms called the Quantum Theory of Atoms in Molecules (QTAIM). His definition of an atom is based purely on the electronic charge density. Bader uses what are called zero flux surfaces to divide atoms. A zero flux surface is a 2-D surface on which the charge density is a minimum perpendicular to the surface. Typically, in molecular systems, the charge density reaches a minimum between atoms and this is a natural place to separate atoms from each other. Bader's theory of atoms in molecules is often useful for charge analysis. For example, the charge enclosed within the Bader volume is a good approximation to the total electronic charge of an atom. Click link for pictures.

3.2 Summary

- Materials: Antiwear --- EAK; Anticorrosion --- DTA
- Methods: Using plane-wave DFT implemented in VASP. (A) (6×4) simulation cell is employed instead of (6×2) simulation cell, to exclude self-interaction between the molecule and its images due to the periodic boundary condition. (B) It's proven that 5 Cu layers are thick enough to represent the surface properties of Cu. (C) A simplified model with 1 Cu atomic layer to select the initial configurations of molecules and the initial adsorbed site to reduce the computational cost.
- Various types of Cu–Cu bond distances change due to adsorption was calculated. “Bader Charge Analysis” method was used to analyze the charge change of specific atoms (S, N and some C atoms) after adsorption.
- DTA adsorption on Cu (110) surface. 1 picture --- Fig 4.



3.3 Personal Comment

- In page 7, there is a point of view --- “The sum of the absolute values of the three parts is larger than the adsorption energy of DTA onto the Cu (110) surface and the excess energy comes from the intermolecular interactions of the three portions.” I personally think that this might need a further explanation and discussion to support the point.
- In addition, I have been thinking about whether there is a surface characterization method that can directly probe the existence of the decomposed molecular moieties like $\text{C}_2\text{H}_5-\text{S}$ and $\text{C}_2\text{S}_3\text{N}_2$, but have not gotten an answer. I once considered the method --- “electron induced neutral desorption” (EIND), but it seems that it will introduce new issues, for example, even if the detector could detect the existence of the molecular moiety $\text{C}_2\text{H}_5-\text{S}$ detached from the Cu

surface, it still could not rule out the possibility that the molecular moiety C₂H₅-S is generated from the bombarding of the incoming probing electrons.

01/19/20

1) Paper (12) Computationally Driven Two-Dimensional Materials Design: What Is Next?

1.1 Terminology

1.1.1 Various types of magnetism: Wiki

In general, the magnetic properties of materials are mainly due to the magnetic moments of their atoms' orbiting electrons. Sometimes, either spontaneously, or owing to an applied external magnetic field—each of the electron magnetic moments will be, on average, lined up. --- magnetic properties appear.

(1) Diamagnetism (i.e. Cu, Carbon)

Diamagnetism appears in all materials and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. An applied magnetic field creates an induced magnetic field in materials in the opposite direction, causing a repulsive force. Despite its universal occurrence, diamagnetic behavior is trivial compared to other kinds of magnetism and is observed only in a purely diamagnetic material. In a diamagnetic material, there are no unpaired electrons, so the intrinsic electron magnetic moments cannot produce any bulk effect.

(2) Paramagnetism (i.e. Al, O₂, Ti, FeO)

Paramagnetism is a form of magnetism whereby some materials are weakly attracted by an externally applied magnetic field, and form internal, induced magnetic fields in the direction of the applied magnetic field. It's due to the presence of unpaired electrons in the material, so most atoms with incompletely filled atomic orbitals are paramagnetic. Due to their spin, unpaired electrons have a magnetic dipole moment and act like tiny magnets. An external magnetic field causes the electrons' spins to align parallel to the field, causing a net attraction. However, paramagnets do not retain any magnetization in the absence of an externally applied magnetic field because thermal motion randomizes the spin orientations.

(3) Ferromagnetism (i.e. Fe, Co, Ni and their alloys)

Ferromagnetism is the basic mechanism by which certain materials form permanent magnets, or are attracted to magnets. A ferromagnet has unpaired electrons. However, in addition to the electrons' intrinsic magnetic moment's tendency to be parallel to an applied field, there is also in these materials a tendency for these magnetic moments to orient parallel to each other to maintain a lowered-energy state. Thus, even in the absence of an applied field, the magnetic moments of the electrons in the material spontaneously line up parallel to one another.

(4) Antiferromagnetism (i.e. Cr, Spin glasses)

In an antiferromagnet, unlike a ferromagnet, there is a tendency for the intrinsic magnetic moments of neighboring valence electrons to point in opposite directions. When all atoms are arranged in a substance so that each neighbor is anti-parallel, the substance is antiferromagnetic. Antiferromagnets have a zero net magnetic moment, meaning that no field is produced by them.

(5) Ferrimagnetism (i.e. Yttrium Iron Garnet (YIG))

Like ferromagnetism, ferrimagnets retain their magnetization in the absence of a field. However, like antiferromagnets, neighboring pairs of electron spins tend to point in opposite directions. In the geometrical arrangement, there is more magnetic moment from the sublattice of electrons that point in one direction, than from the sublattice that points in the opposite direction.

Note: For (3) Ferromagnetism, (4) Antiferromagnetism, and (5) Ferrimagnetism, they are all the manifestation of ordered magnetism.

1.1.2 Two important temperatures that are related to magnetism: Wiki

(1) Curie temperature (T_c): Wiki

- It's the temperature above which certain materials lose their permanent magnetic properties, which can (in most cases) be replaced by induced magnetism (paramagnetism).
- In most cases: **T_c @ Ferromagnetism ---> Paramagnetism**

(2) Néel temperature (T_N): Wiki (already listed in previous discussion in this note)

- T_N is the temperature above which an antiferromagnetic material becomes paramagnetic—that is, the thermal energy becomes large enough to destroy the microscopic magnetic ordering within the material.
- **T_N @ Antiferromagnetism ---> Paramagnetism**

1.1.3 Spintronic Device (<https://www.youtube.com/watch?v=q3-S5hM-3QY>)

- See the short video to get an idea.
- It has the potential to be used as computer memory device.

1.2 Summary

- Materials: MXenes (Two-dimensional transition metal carbides, carbonitrides, and nitrides)
- Target: Looking for 2D materials with ferromagnetic properties ---> needed for spintronic devices
- This paper is an introductory guide paper for various paper regarding with the computation assisted 2D materials design for an issue of ACS Nano.

2) Paper (13) Atomistic Simulation Derived Insight on the Irreversible Structural Changes of Si Electrode during Fast and Slow Delithiation

2.1 Summary

- Target to be studied: the structural change of the Al_2O_3 -coated Si anode in LIB during the fast/slow delithiation
- Methods: (A) ReaxFF-MD simulations. (B) The driving force for delithiation in this method: Li concentration gradient. (C) Fast and slow diffusion rates mimic: To mimic the “natural” diffusion of Li out of Si at different delithiation rates ($\Delta N/\Delta t$), Δt was varied. Δt is the time for Li to diffuse and for the a-LixSi to relax in response to the concentration gradient caused by Li removal. And $\Delta t = 0.1$ ps and $\Delta t = 1.0$ ps were chosen to represent delithiation at fast and slow rates.
- **Higher peaks** of the radial distribution function of Si-Si ($g(r)_{\text{Si-Si}}$) **at the first and second nearest neighbor** ---> a smaller number of first and second nearest Si-Si bonds in the

- delithiated a-LixSi structures ---> loss of directly bonded Si-Si pairs ---> excess volume in the delithiated a-LixSi structures ---> faster re-lithiation rate compared to the equilibrium a-Si
- For the slow delithiation rate, the surface delamination did not occur before Li_{1.0}Si ---> If the coated Si-thin-film electrode can be cycled between a-Li_{1.0}Si and a-Li_{3.75}Si, coating delamination can be prevented.

01/21/20

1) Paper (14) Simulation of the Effect of Contact Area Loss in All-Solid-State Li-Ion Batteries

1.1 Terminology

1.1.1 “*Ion association*”: (Wiki)

In chemistry, ion association is a chemical reaction whereby ions of opposite electrical charge come together in solution to form a distinct chemical entity.

1.1.2 “*Overpotential*”: Wiki

In electrochemistry, overpotential is the potential difference (voltage) between a half-reaction's thermodynamically determined reduction potential and the potential at which the redox event is experimentally observed. In an electrolytic cell the existence of overpotential implies the cell requires more energy than thermodynamically expected to drive a reaction. In a galvanic cell the existence of overpotential means less energy is recovered than thermodynamics predicts. In each case the extra/missing energy is lost as heat. The measured overpotential represents the required extra energy to sustain the electrode reaction rate, and this energy will be transferred into heat.

1.1.3 “*Charge transfer coefficient*”: Wiki

Charge transfer coefficient, and symmetry factor (symbols α and β , respectively) are two related parameters used in description of the kinetics of electrochemical reactions. They appear in the Butler–Volmer equation and related expressions. Charge transfer coefficient is the parameter that signifies the fraction of overpotential that affects the current density. Or in other words, it signifies the fraction of the interfacial potential at an electrode-electrolyte interface that helps in lowering the free energy barrier for the electrochemical reaction. The electroactive ion present in the interfacial region experiences the interfacial potential and electrostatic work is done on the ion by a part of the interfacial electric field. It is charge transfer coefficient that signifies this part that is utilized in activating the ion to the top of the free energy barrier.

1.1.4 “*Transference number (or Ion transport number)*”: Wiki

It is the fraction of the total electrical current carried in an electrolyte by a given ionic species i, $t_i = \frac{I_i}{I_{tot}}$. Differences in transport number arise from differences in electrical mobility. For example, in an aqueous solution of NaCl, less than half of the current is carried by the positively charged Na⁺ ions (cations) and more than half is carried by the negatively charged Cl⁻ ions (anions) because the Cl⁻ ions are able to move faster, i.e., Cl⁻ ions have higher mobility than Na⁺ ions. The sum of the transport numbers for all of the ions in solution always equals unity.

1.1.2 “*Butler-Volmer Equation*”

Please see the pictures below.

01

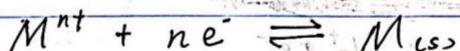
Butler - Volmer Equation.

Youtube: "kinetics of electrode reaction | Butler Volmer & TAFEL equations." — Advanced Chemistry

(I) Reactions (or processes) that happened @ the electrode.

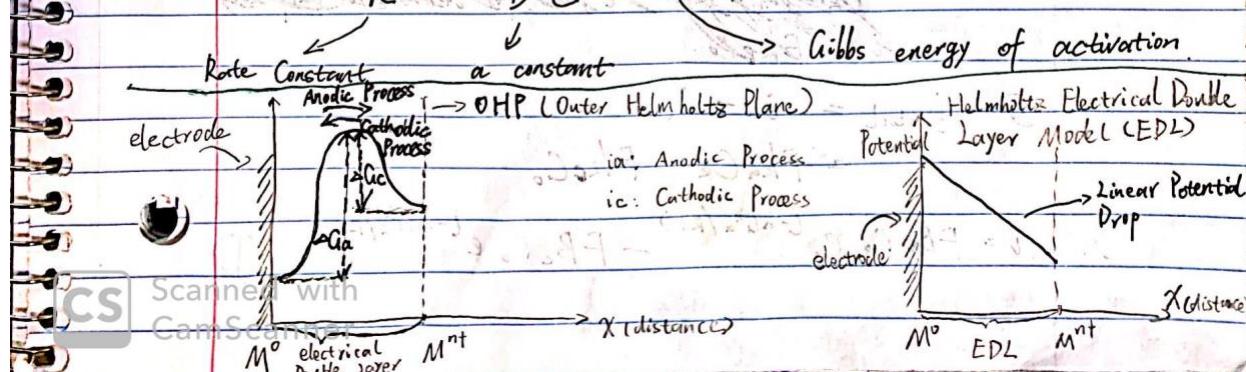
- ① Diffusion of the reactant to the electrode.
- ② Absorption of the reactant on the electrode.
- ③ Transfer of e^- to or from the absorbed reactant species
- ④ Desorption of the product from the electrode
- ⑤ Diffusion of the product away from the electrode surface.

(II) Example:



Eyring equation (Eyring-Polanyi equation) \rightarrow Arrhenius Equation:

$$k = B e^{-\Delta G^*/RT}$$



If we are considering that only a single electron transfer is taking place, and the transfer of electron is the rate determining step.

C_o & C_R

concentration oxidized & reduced form of the species outside the double layer

rates for cathodic & Anodic

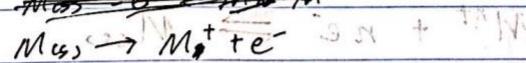
$$k_a C_o \text{ & } k_c C_R$$

Magnitude of the charge transfer is

$$F = e N_A \rightarrow \text{Avogadro constant}$$

Faraday's constant $\rightarrow 1.6 \times 10^{-19} C$

① Anodic:



$$i_a = F k_a C_o$$

② Cathodic: $M_o^{+} + e^{-} \rightarrow M_{ss}$

$$i_c = F k_c C_o$$

(for convenience purposes)

$$\textcircled{3} \quad i_{\text{total}} = i_a - i_c$$

$$= F k_a C_o - F k_c C_o$$

$$\therefore i = F B_a C_o e^{(-\Delta G_a^*/RT)} - F B_c C_o e^{(-\Delta G_c^*/RT)}$$



If $i_a > i_c$, $i > 0$, it will be anodic current

If $i_a < i_c$, $i < 0$, it will be cathodic current

If reduction is taking place, $M^+ + e^- \rightarrow M_s$

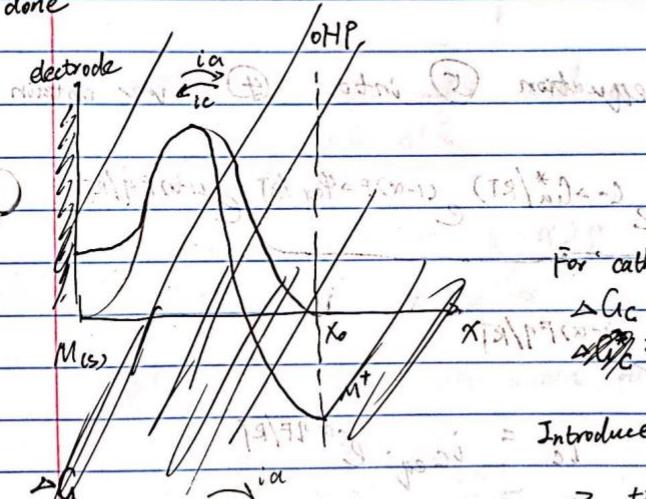
$$W = e \Delta \varphi$$

↑ potential difference

electrical work
done

The electrical potential at a point is defined as the work done by bringing a unit positive charge from infinity to that point.

$$W = q \times V$$

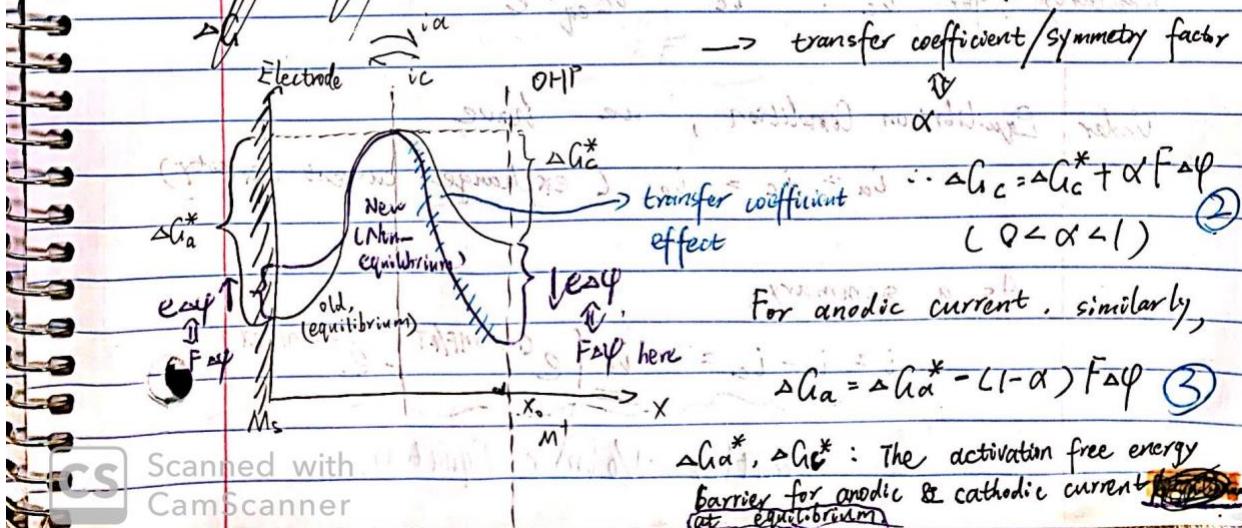


For cathodic current

$$\Delta G_c = \Delta G_c^* + F \Delta \varphi$$

= Introduce one more factor \rightarrow

\rightarrow transfer coefficient/symmetry factor



For anodic current, similarly,

$$\Delta G_a = \Delta G_a^* - (1-\alpha) F \Delta \varphi \quad (3)$$

$\Delta G_a^*, \Delta G_c^*$: The activation free energy barrier for anodic & cathodic current (at equilibrium)

Substituting equation ② & ③ into ①, we obtain

$$i = F \beta_a C_R e^{(-\Delta G_a^*/RT)} e^{(1-\alpha)F\Delta\varphi/RT}$$

$$-F \beta_c C_o e^{(-\Delta G_c^*/RT)} e^{-\alpha F\Delta\varphi/RT}$$

$$\eta = \Delta\varphi - \Delta\varphi_{eq} \quad (5) \Rightarrow \Delta\varphi = \eta + \Delta\varphi_{eq}$$

overpotential

Substituting equation ⑤ into ④, we obtain

$$i_a : i_a = F \beta_a C_R e^{(-\Delta G_a^*/RT)} e^{(1-\alpha)F\Delta\varphi_{eq}/RT} e^{(1-\alpha)F\eta/RT}$$

$$\eta = i_a^* \cdot e^{(1-\alpha)F\eta/RT}$$

$$\text{Similarly, for } i_c : i_c = i_{c_{eq}} \cdot e^{-\alpha F\eta/RT}$$

Under Equilibrium Condition, we have

$$i_a = i_c = i_0 \quad (\text{exchange current density})$$

As a summary,

$$i = i_a - i_c = i_0 \left\{ e^{(1-\alpha)MF/RT} - e^{-\alpha MF/RT} \right\}$$



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CamScanner

Butler-Volmer Equation

$$\text{Ansatz: } e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

if x is very small, $\frac{x^2}{2!}, \frac{x^3}{3!}, \dots$ could be neglected.
Thus, $e^x \approx 1 + x$

3 Scenarios:

(A) If η is very small, $\frac{\eta F}{RT} \ll 1$.

$$\rightarrow i = i_0 \left\{ \left[1 + \frac{(1-\alpha)NF}{RT} \right] - \left[1 - \frac{\alpha NF}{RT} \right] \right\}$$

$$i = i_0 \frac{\eta F}{RT} \quad (\text{A})$$

(B) If $\eta > 0$ and η is very large.

$e^{-\alpha NF/RT}$ is very small and could be neglected

$$\text{if } i = i_0 e^{(1-\alpha)\eta F/RT}$$

$$\ln i = \ln i_0 + (1-\alpha)\eta F/RT \quad (\text{B}) \Rightarrow \text{Tafel Equation}$$

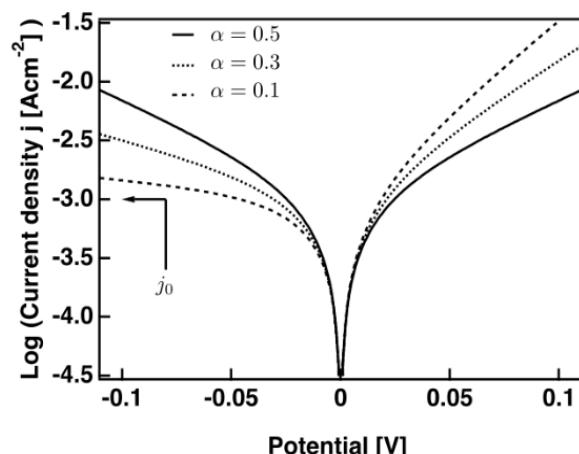
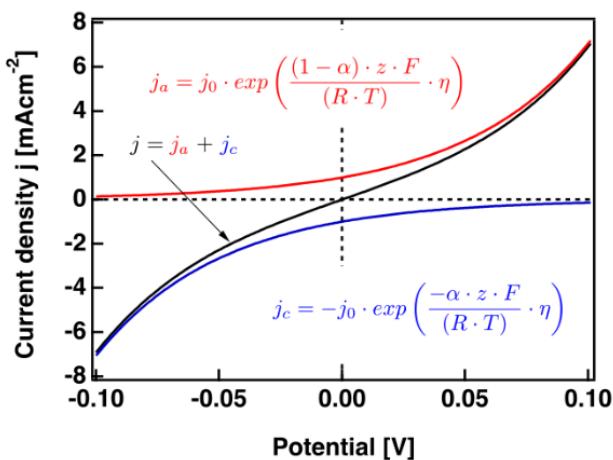
(C) If $\eta < 0$ and η has very large absolute value ↑

$e^{(1-\alpha)\eta F/RT}$ is very small and can be neglected.

$$i = -i_0 e^{-\alpha NF/RT}$$

$$\ln(-i) = \ln(i_0) - \frac{\alpha NF}{RT} \quad (\text{C})$$

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The left graph shows the current density as function of the overpotential η . The anodic and cathodic current densities are shown as j_a and j_c , respectively for $\alpha = \alpha_a = \alpha_c = 0.5$ and $j_0 = 1 \text{ mA cm}^{-2}$ (close to values for platinum and palladium). The lower graph shows the logarithmic plot for different values of α (Tafel plot) Source: https://en.wikipedia.org/wiki/Butler%E2%80%93Volmer_equation

1.1.3 “Newman Battery Model”

Paper: Newman, John, et al. "Modeling of lithium-ion batteries." *Journal of power sources* 119 (2003): 838-843.

- The basic modeling framework consists of (1) porous electrode theory, (2) concentrated solution theory, (3) Ohm's law, (4) kinetic relationships, and (5) charge and material balances.
- (1) Porous electrode theory treats the porous electrode as a superposition of active material, electrolyte, and filler, with each phase having its own volume fraction. (2) Concentrated solution theory provides the relationship between driving forces (such as gradients in chemical potential) and mass flux. (3) Ohm's law describes the potential drop across the electrode and also in the electrolyte. In the electrolyte, Ohm's law is modified to include the diffusion potential. (4) Butler–Volmer equation generally is used to relate the rate of electrochemical reaction to the difference in potential between the electrode and solution, using a rate constant (exchange current density) that depends on the composition of the electrode and the electrolyte.
- Summary:
 - (1) Side reactions at the lithium electrode can change the surface concentration of lithium ions, introducing error into measurements of the cell potential as a function of bulk electrolyte concentration (concentration-cell measurements).
 - (2) Heat generation during relaxation after cessation of the current: Concentration gradients formed during passage of current are associated with a heat-of-mixing effect.
 - (3) MD simulations: (A) Decrease in conductivity with increasing salt concentration in liquid carbonate electrolytes is caused by ion association. (B) Multiple orthogonal fields can act in concert to drive species diffusion in a way which mimics three simultaneous electrochemical experiments. In this case, it is possible to extract a full set of diffusion coefficients for a mixture containing up to six species using only one simulation. (C) External electronic fields, E , which mimic the effect of concentration gradients are used rather than actual concentration gradients.

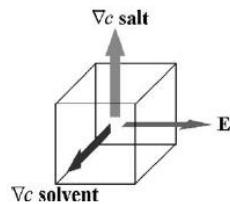
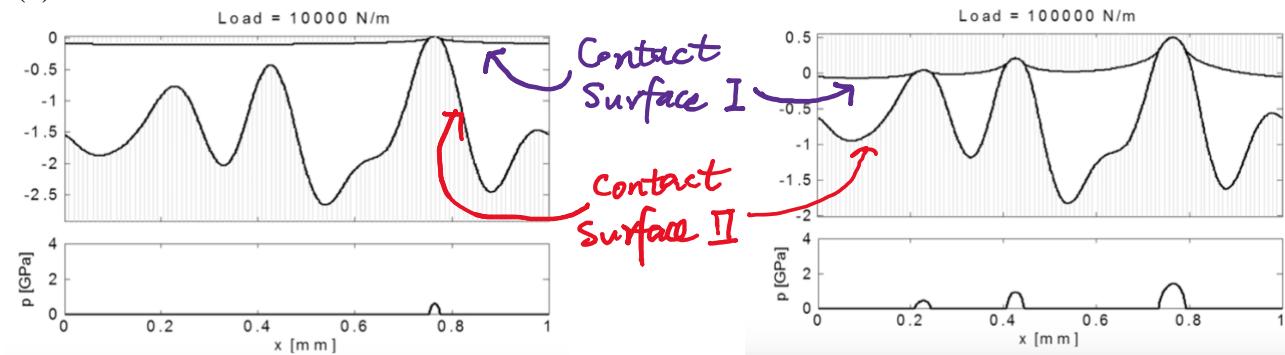


Fig. 3. Orthogonal external driving forces.

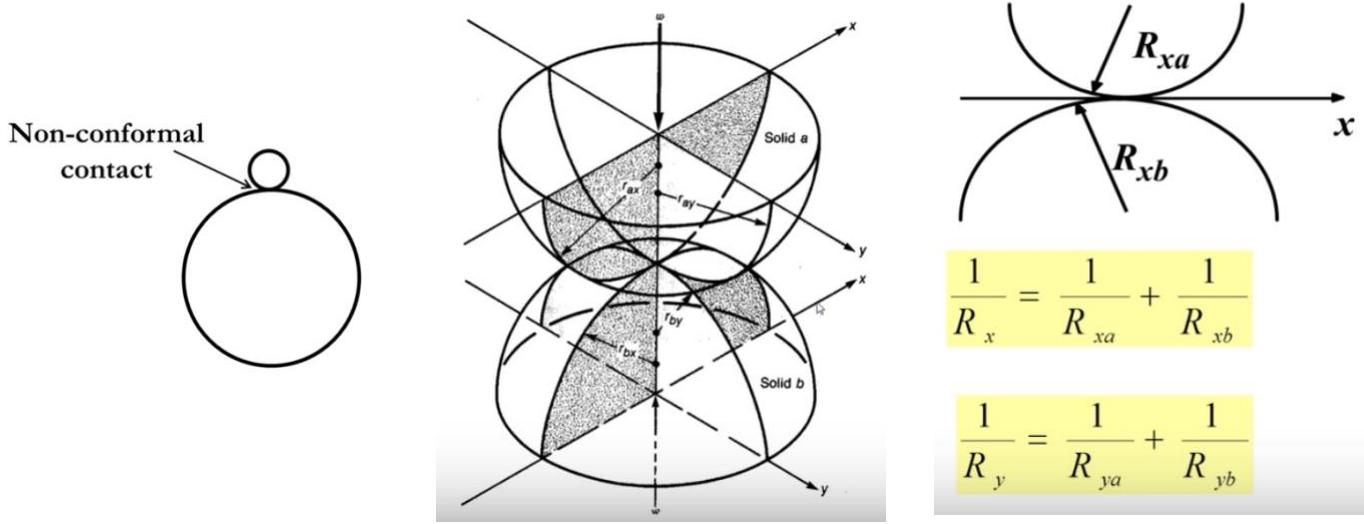
1.1.3 “Contact mechanics theory”: <https://www.youtube.com/watch?v=L5JYdbcBUSE>

Basic Contact Mechanics knowledge background:

- General idea:



(2) Non-conformal contact: Small contact area; High stress; Deformations (Elastic, Plastic)



$$\frac{1}{R_x} = \frac{1}{R_{xa}} + \frac{1}{R_{xb}}$$

$$\frac{1}{R_y} = \frac{1}{R_{ya}} + \frac{1}{R_{yb}}$$

(3) All non-conformal bodies can be approximated as ellipsoids. The surfaces in contact deforms elastically and an elliptical contact area occurs.

(4) The contacting bodies can be approximated by 2 ellipsoids. They have the radii of curvature R_{xa} and R_{xb} in one direction and R_{ya} and R_{yb} in the other. The contact can then be seen one ellipsoid in contact with a plane. The equivalent radii then becomes R_x and R_y , as shown in the picture above.

Some definitions

Characteristic elastic modulus and radius of curvature:

- Effective elastic modulus,

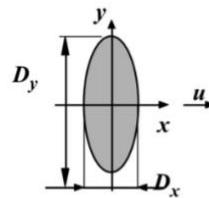
$$E' = 2 \left[\frac{(1 - \nu_1^2)}{E_1} + \frac{(1 - \nu_2^2)}{E_2} \right]^{-1}$$

- Combined radius,

$$R = \left[\frac{1}{R_x} + \frac{1}{R_y} \right]^{-1}$$

- Load and load per unit length, w and w'

Dry contact - Hertzian theory The size of the elastically deformed region



The surfaces are deformed and an elliptical contact occurs

$$D_x = 2 \left(\frac{6 \varepsilon w R}{\pi k E'} \right)^{1/3}, D_y = 2 \left(\frac{6 k^2 \varepsilon w R}{\pi E'} \right)^{1/3}$$

where ε and k are functions of R_x and R_y .

For a line contact $k \rightarrow \infty$ and

$$D_x = 2b = \sqrt{8w'R_x/\pi E'}$$

Multi-asperity contact and real area of contact

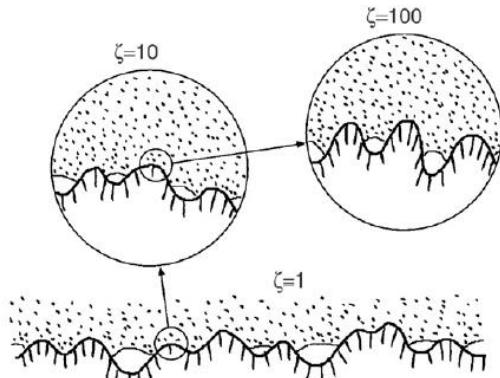
- Surfaces in contact touch each other only in microscopically small asperity contacts ($\text{Ø}10\text{-}100\mu\text{m}$)
- Apparent contact area** = the contact area if surfaces are perfectly smooth
- Real contact area** = the sum of all small asperity contacts, i.e. the true contact area
- The real contact area is only a small fraction of the apparent contact area, say $10^{-6}\text{-}10^{-2}$

1.1.4 “Persson’s contact mechanics theory”:

Paper: Persson, Bo NJ. "Contact mechanics for randomly rough surfaces." Surface science reports 61, no. 4 (2006): 201-227.

(1) Fractal surface: (google translate)

A curve or geometric figure, each part of which has the same statistical character as the whole. Fractals are useful in modeling structures (such as eroded coastlines or snowflakes) in which similar patterns recur at progressively smaller scales, and in describing partly random or chaotic phenomena such as crystal growth, fluid turbulence, and galaxy formation.



An elastic (e.g., rubber) block (dotted area) in adhesive contact with a hard rough substrate (dashed area). **The substrate has roughness on many different length scales** and **the rubber makes partial contact with the substrate on all length scales**. When a contact area is studied at low magnification ($\zeta = 1$) it appears as if complete contact occurs in the macroasperity contact regions, but when the magnification is increased it is observed that in reality only partial contact occurs.

(2) “*The most important property of a rough surface is the **surface roughness power spectrum** which is the Fourier transform of the height–height correlation function:*

$$C(\mathbf{q}) = \frac{1}{(2\pi)^2} \int d^2x \langle h(\mathbf{x})h(\mathbf{0}) \rangle e^{-i\mathbf{q}\cdot\mathbf{x}}$$

Here $z = h(x)$ is the height of the surface at the point $x = (x, y)$ above a flat reference plane chosen so that $\langle h(x) \rangle = 0$. The angular bracket $\langle \cdot \cdot \cdot \rangle$ stands for ensemble averaging. In what follows we consider only surfaces for which the statistical properties are isotropic so that $C(\mathbf{q}) = C(q)$ only depends on the magnitude $|\mathbf{q}|$ of the wavevector \mathbf{q} .”

The power spectrum of a self-affine fractal surface is

$$C(q) \sim q^{-2(H+1)}$$

where the Hurst exponent H is related to the fractal dimension via $D_f = 3 - H$.

(3) Various contact mechanics theories developed

Most contact mechanics theories for randomly rough surfaces approximate the surface asperities with spherical or elliptical “bumps” to which they apply the Hertz contact theory. In most cases the elastic coupling between the asperity contact regions is neglected which is a good approximation only if the (average) distance between nearby contact regions is large enough. A necessary (but not sufficient) condition for this is that the normal (squeezing) force must be so small that **the area of real contact is very small** compared to the nominal contact area. This is the basic strategy both for the Greenwood–Williamson theory and the (more accurate)

theory of Bush et al., and we describe briefly both these theories. **The theory of Persson starts from the opposite limit of complete contact, and the theory is (approximately) valid for all squeezing forces.**

- Hertz theory:

Hertz studied **the frictionless contact between elastic solids with smooth surface profiles which could be approximated as parabolic close to the contact area**. This theory predicts that the contact area A increases non-linearly with the squeezing force F_N as $A \sim F_N^{2/3}$. The simplest model of a randomly rough but nominal flat surface consists of a regular array of spherical bumps (or cups) with equal radius of curvature R and equal height.

- Archard:

Archard showed that in a more realistic model of rough surfaces, where the **roughness is described by a hierarchical model consisting of small spherical bumps on top of larger spherical bumps and so on, the area of real contact is proportional to the load**. This model explains the basic physics in a clear manner, but it cannot be used in practical calculations because real surfaces cannot be represented by the idealized surface roughness assumed by Archard.

- Greenwood-Williamson theory:

They described **the rough surface as consisting of spherical bumps of equal radius of curvature R , but with a Gaussian distribution of heights**. This model **predicts that the area of real contact is nearly proportional to the load**.

- The theory of Bush, Gibson and Thomas:

A more refined theory as compared to Greenwood-Williamson theory. Bush et al. approximated the summits with paraboloids to which they applied the Hertzian contact theory. The height distribution was described by a random process, and they found that at low squeezing force the area of real contact increases linearly with F_N .

- Drawbacks of theories mentioned above:

(A) They neglect the interaction between the different contact regions. That is, if an asperity is squeezed against a flat hard surface it will deform not just locally, but the elastic deformation field will extend some distance away from the asperity and hence influence the deformation of other asperities. (B) The contact mechanics theories can only be applied as long as $A \ll A_0$.

- Persson theory:

Contrarily, Persson's theory starts from the opposite limit of very large contact, and is in fact exact in the limit of complete contact (that is, the pressure distribution at the interface is exact). **It also accounts (in an approximate way) for the elastic coupling between asperity contact regions**. For small squeezing force it predicts that the contact area A is proportional to the load F_N , while as F_N increases A approaches A_0 in a continuous manner. Thus, the theory is (approximately) valid for all squeezing forces.

1.2 Paper Summary

(1) The contact area at the electrode|electrolyte interface inside the all-solid-state batteries would be decreased continuously because of the volume change of the electrodes (during the discharging and charging process).

(2) Simulation:

(A) Effect of contact area loss on the performance of Li battery including (a) accumulation of Li on electrode surface, (b) discharge voltage & capacity: “the imperfect contact is incorporated into a 1-D Newman battery model that simulates the discharging process of an all-solid-state battery with the assumption that the Li concentration will be localized at the reduced contact area”.

(B) The relationship between the applied pressure and the contact area is simulated by applying Persson’s contact mechanics theory (using self-affined surfaces).

(3) The contact area as a function of the applied pressure is calculated for film-type Li/Li₃PO₄/LiCoO₂ and bulk-type Li/LGPS/TiS₂.

02/04/20

1) Paper (15) Atomistic Origin of Deformation Twinning in Biomimetic Aragonite

1.1 Terminology

1.1.1 “Crystal twinning”: <https://www.tulane.edu/~sanelson/eens211/twinning.htm>

- Sometimes during the growth of a crystal, or if the crystal is subjected to stress or temperature/pressure conditions different from those under which it originally formed, two or more intergrown crystals are formed in a symmetrical fashion. These symmetrical intergrowths of crystals are called twinned crystals.

- Origin of Twinning

(1) Growth Twins

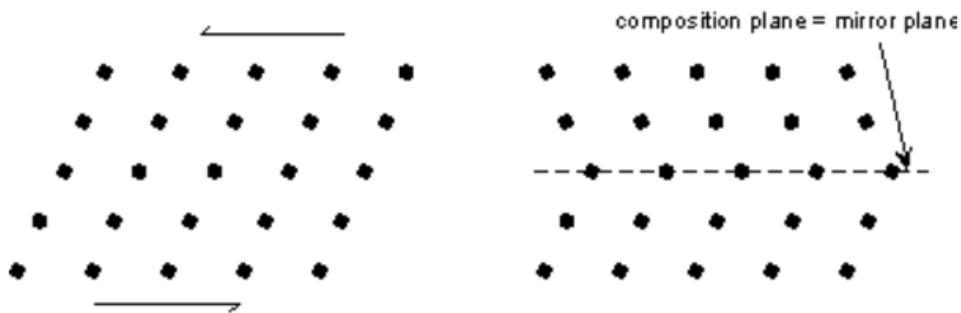
When accidents occur during crystal growth and a new crystal is added to the face of an already existing crystal, twinning can occur if the new crystal shares lattice points on the face of the existing crystal, but has an orientation different from the original crystal. Such growth twins can be contact twins, or can be penetration twins.

(2) Transformation Twins

Transformation twinning occurs when a preexisting crystal undergoes a transformation due to a change in pressure or temperature. This commonly occurs in minerals that have different crystal structures and different symmetry at different temperatures or pressures. When the temperature or pressure is changed to that where a new crystal structure and symmetry is stable, different parts of the crystal become arranged in different symmetrical orientations, and thus form an intergrowth of one or more crystals.

(3) Deformation Twins

During deformation atoms can be pushed out of place. If this happens to produce a symmetrical arrangement, it produces deformation twins. The mineral calcite can be easily twinned in this way, producing polysynthetic twins on {012}.



1.1.2 “Activation Volume”

(1) <https://goldbook.iupac.org/terms/view/V06644> (PAC, 1994, 66, 1077. (Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)) on page 1175)

“A quantity derived from the pressure dependence of the rate constant of a reaction (mainly used for reactions in solution), defined by the equation:

$$\Delta^{\ddagger}V = -R T \left(\frac{\partial(\ln k)}{\partial p} \right)_T$$

providing that the rate constants of all reactions (except first-order reactions) are expressed in pressure-independent concentration units, such as mol dm⁻³ at a fixed temperature and pressure. The volume of activation is interpreted, according to transition state theory, as the difference between the partial molar volumes of the transition state (V) and the sums of the partial volumes of the reactants at the same temperature and pressure, i.e.

$$\Delta^{\ddagger}V = V - \sum (r V_R)$$

where r is the order in the reactant R and V_R its partial molar volume”.

(2) <https://www.sciencedirect.com/topics/engineering/activation-volume>

“Activation volume is an important variable and the deformation mechanism and strain rate sensitivity can be determined using the sample size and activation volume”.

1.2 Summary

(1) Nacre, or the **biomineral aragonite**, is composed of **mineral aragonite (CaCO₃, 95 vol%)** and **biopolymer interlayers (5 vol%)** between the aragonite platelets and the aragonite nanoparticles inside the platelets. **Nacre’s toughness & mechanical strength** is much **higher**, as compared to the **mineral aragonite**. In addition, its **fracture strength** and **toughness** both **increase a lot under impact loading (high strain rate)** as compared to that under **quasi-static loading (low strain rate)**. This paper’s target is to find the atomistic origin of the enhancement of both strength & ductility of the biomineral aragonite.

(2) “Under high strain rate compressions, the typical polymer chain relaxation between aragonite platelets and nanoparticles do **not have time** to participate in deformation. Thus, **strengthening and toughening are primarily carried by the (i) internanoparticle deformation or rotation, in combination with the (ii) emission of partial dislocations and the onset of (iii) deformation twinning within individual aragonite nanoparticles**”.

(3) Methods: “*The generalized-stacking-fault energy (GSFE) curve along the sliding direction is computed from DFT method implemented in VASP*”. ---> A six-layer slab is found thick enough to mimic GSFE.

(4) Notation:

SFE: stacking fault energy

TFE: twin formation energy

USFE: unstable stacking fault energy (The peaks of the GSFE, which represent the energy barriers to form a stacking fault or a twin, something like activation energy barrier in a chemical reaction)

UTFE: unstable twin formation energy

ciNEB: climbing image nudge elastic band method

(4) By comparing the GFSE curves for both rigid sliding situation (no relaxation, corresponding to mineral aragonite) and constrained sliding situation (only allowing layer expansion, corresponding to biomineral aragonite), it is found that the USFE dropped a lot, from the rigid sliding situation (> **the calculated fracture energy**) to the expansion-allowing situation (< **the calculated fracture energy**). ---> In the mineral aragonite, where the layer expansion is **NOT** allowed (**rigid sliding situation**), **fracture will occur before sliding** can be **activated**. In the biomineral aragonite, the existence of soft biopolymer allows the expansion normal to the twinning plane. As a result, sliding in the form of stacking faults or partial dislocations could be activated prior to fracture.

(5) Under high strain rate, the strain energy is high enough to overcome the USFE & UTFE. Therefore, deformation twins, partial dislocations, and stacking faults are observed (instead of full dislocations).

Under low strain rate (quasi-static deformation), the strain energy is insufficient to overcome the USFE & UTFE barrier. Thus, grain boundary sliding is activated & nanograin rotation is observed.

(6) Aragonite has the highest $\gamma_{\text{USFE}} / \gamma_{\text{SFE}}$ ratio. Based on my understanding, it indicates that as long as the strain energy is high enough to help aragonite structure overcome the UFSE, the stacking fault structure of aragonite would be relatively stable because of its comparatively low SFE.

(7) Reasons for aragonite’s high $\gamma_{\text{USFE}} / \gamma_{\text{SFE}}$ ratio: Large number of first nearest Ca-O neighbors - --> the Ca-O ionic bonds are more shared than that in perovskite oxides.

02/06/20

1) Paper (17) Stabilizing high voltage LiCoO₂ cathode in aqueous electrolyte with interphase-forming additive

1.1 Terminology

1.1.1 “Water-in-Salt Electrolyte”

Source: Suo et al. ““Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries.” Science 350, no. 6263 (2015): 938-943.

*“A “water-in-salt” electrolyte is obtained by dissolving lithium bis(trifluoromethane sulfonyl)imide (**LiTFSI**) at extremely high concentrations (molality >20 m) in water. This leads to an anion-containing Li⁺ solvation sheath, which results in the formation of a dense interphase on the anode surface mainly arising from anion reduction. Combined with the substantially reduced electrochemical activity of water at such a high concentration, this highly concentrated water-in-salt electrolyte provides an expanded electrochemical stability window of ~3.0 V.*

LiTFSI was chosen as the salt because of its high solubility in water (>20 m at 25°C) and high stability against hydrolysis. When the LiTFSI concentration is above 5 m, the water-in-salt definition applies, as the salt outnumbers the solvent in this binary system by both weight and volume. In these solutions, the average number of water molecules available to solvate each ion is far below the “solvation numbers” that are well established in conventional electrolytes (~1.0 m). Instead, interionic attractions become more pronounced relative to solvent-ion interactions, incurring unusual physicochemical properties. More important, the interphasial chemistry on electrode surfaces could be altered as a direct consequence of the different cation solvation sheath structure. This “cation solvation–interphase chemistry” correlation has been leveraged to manipulate the electrochemical behavior of nonaqueous electrolytes on both graphitic anode and metal oxide cathodes, but its effect on aqueous electrolytes had remained unexplored”.

2) Paper (18) Computational Exploration of the Li-Electrode_Electrolyte Interface in the Presence of a Nanometer Thick Solid-Electrolyte Interphase Layer

Paper Summary:

<https://drive.google.com/file/d/1NUyDJawlyukqh0LeBOadsl-MQYs9BY4D/view?usp=sharing>

02/09/20

1) Paper (19) Connecting the irreversible capacity loss in Li-ion batteries with the electronic insulating properties of solid electrolyte interphase (SEI) components

Key points in this paper interest me the most:

- The calculation of critical thickness d* and the irreversible capacity loss (C_{ir}).
- The relationship of Bandgap and stress:
 - Assumption form other papers: only focusing on the normal stress rather than shear stress
 - *“Distance between anions rather than the distance between anions and cations is the most important parameter, as the electrons are donated to anions”*. ---> a new structure parameter, η, (normalized average anion distance) is proposed.
 - 4 different stress(strain) situations are considered for calculation.
 - The bandgap decreases linearly with increasing η. (η>1, tension; η<1, compression) ---> Bigger η, ---> Larger distance between anions ---> Smaller bandgap ---> Lower electron tunneling barrier (which is not good for Li battery)

2) Paper (20) Ab initio diffuse-interface model for lithiated electrode interface evolution

2.1 Terminology

2.1.1 “Order parameter”:

(A) Wiki

An order parameter is a measure of the degree of order across the boundaries in a phase transition system; it normally ranges between zero in one phase (usually above the critical point) and nonzero in the other. At the critical point, the order parameter susceptibility will usually diverge.

(B) <https://physics.stackexchange.com/questions/138255/what-is-an-order-parameter>

In a wide variety of phase transitions (both for first order and second order transitions) there exists a quantity which is zero below the transition temperature and becomes nonzero above the transition temperature. For example, in a gas-liquid phase transition as T goes to below the coexistence line at constant pressure, the liquid phase that appears has a much higher density than the gas phase. In this case, we can define $(\rho_l - \rho_g)$ as the order parameter. (*Statistical Mechanics for Chemistry and Material Science* - Biman Bagchi (2018))

2.1.2 Phase-field theory

(A) Wiki:

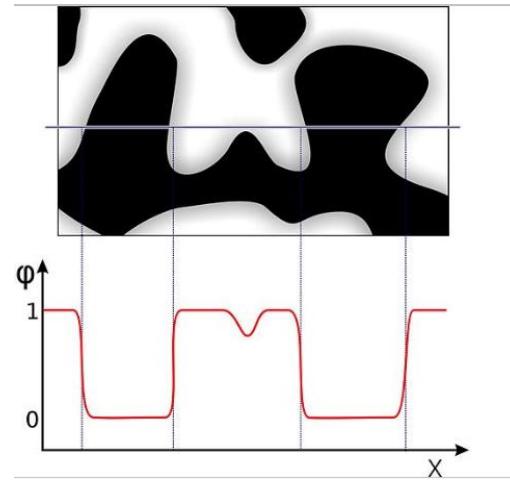
A phase field model is a mathematical model for solving interfacial problems. It has mainly been applied to solidification dynamics, but it has also been applied to other situations. The method substitutes boundary conditions at the interface by a partial differential equation for the evolution of the phase field that takes the role of an order parameter. This phase field takes two distinct values (for instance +1 and -1) in each of the phases, with a smooth change between both values in the zone around the interface, which is then diffuse with a finite width. A discrete location of the interface may be defined as the collection of all points where the phase field takes a certain value (e.g. 0). A phase field model is usually constructed in such a way that in the limit of an infinitesimal interface width (the so-called sharp interface limit) where the correct interfacial dynamics are recovered.

Phase field models are usually constructed in order to reproduce a given interfacial dynamics. A number of formulations of the phase field model are based on a free energy function depending on an order parameter (the phase field) and a diffusive field (variational formulations). Equations of the model are then obtained by using general relations of statistical physics. Such a function is constructed from physical considerations, but contains a parameter or combination of parameters related to the interface width. Parameters of the model are then chosen by studying the limit of the model with this width going to zero, in such a way that one can identify this limit with the intended sharp interface model.

Other formulations start by writing directly the phase field equations, without referring to any thermodynamical functional (non-variational formulations). In this case the only reference is the sharp interface model, in the sense that it should be recovered when performing the small interface width limit of the phase field model.

A good example:

(See Picture below) A two-phase microstructure and the order parameter ϕ profile is shown on a line across the domain. Gradual change of order parameter from one phase to another shows diffuse nature of the interface.



(B) YouTube:

(I) Representative viewpoints:

- (1) (Math) An approach to obtain solutions of Partial Differential Equations (PDEs) that are hard to solve – by introducing artificial regions of continuity where there are discontinuities.
- (2) (Materials Science) PDEs that describe **diffusion** (of **atoms** and **heat**) as well as **phase transformations**.

(II) What are phase field models?

- Models in which the time evolution of order parameters are described as PDEs.
- Order parameters are field variables (They describe the microstructure).
- Order parameters: Constant in bulk and change over small regions (“**interfaces**”)

(III) Cahn-Hilliard (CH) & Allen-Cahn (AC) equations

- 2 canonical phase field models:
 - Cahn-Hilliard equation
(Wiki)
 - The Cahn–Hilliard equation is an equation of mathematical physics which describes the process of phase separation, by which the two components of a binary fluid spontaneously separate and form domains pure in each component. If c is the concentration of the fluid, with $c = \pm 1$ indicating domains, then the equation is written as
- $$\frac{\partial c}{\partial t} = D \nabla^2 (c^3 - c - \gamma \nabla^2 c),$$
- Where D is a diffusion coefficient with units of $\text{Length}^2/\text{Time}$ and $\sqrt{\gamma}$ gives the length of the transition regions between the domains. Here $\partial/\partial t$ is the partial time derivative and ∇^2 is the Laplacian in n dimensions. Additionally, the quantity $\mu = c^3 - c - \gamma \nabla^2 c$ is identified as a chemical potential.

- The Cahn–Hilliard equation has the form of a conservation law, $\frac{\partial c}{\partial t} = \nabla \cdot \mathbf{j}(x)$, with $\mathbf{j}(x) = D\nabla\mu$. Thus, the phase separation process conserves the total concentration $C = \int d^n x c(x, t)$, so that $\frac{dc}{dt} = 0$.

From this YouTube video,
CA Model, 2 Equations:

$$\frac{\partial c}{\partial t} = \nabla \cdot M \nabla \mu_c \quad (1), \quad \mu_c = \left(\frac{1}{N_V}\right) \begin{bmatrix} \delta F \\ \delta c \end{bmatrix} \quad (2),$$

Here, concentration is a conserved order parameter. If you take an integral of the concentration field over the entire domain and if you differentiate it with respect to time, that is going to be 0. Because the integral is going to be 0, $dc/dt = 0$.

- Allen-Cahn equations
(Wiki)
 - The Allen–Cahn equation is a reaction–diffusion equation of mathematical physics which describes the process of phase separation in multi-component alloy systems, including order-disorder transitions.
 - The equation describes the time evolution of a scalar-valued state variable η on a domain Ω during a time interval τ , and is given by:

$$\begin{aligned} \frac{\partial \eta}{\partial t} &= M_\eta [\operatorname{div}(\varepsilon_\eta^2 \nabla \eta) - f'(\eta)] \quad \text{on } \Omega \times \mathcal{T}, \quad \eta = \bar{\eta} \quad \text{on } \partial_\eta \Omega \times \mathcal{T}, \\ &- (\varepsilon_\eta^2 \nabla \eta) \cdot m = q \quad \text{on } \partial_q \Omega \times \mathcal{T}, \quad \eta = \eta_o \quad \text{on } \Omega \times \{0\}, \end{aligned}$$

where M_η is the mobility, f is a double-well potential, $\bar{\eta}$ is the control on the state variable at the portion of the boundary $\partial_\eta \Omega$, q is the source control at $\partial_q \Omega$, η_o is the initial condition, and m is the outward normal to $\partial\Omega$.

From this video,
AC Equations, 2 equations: (It is non-local)

$$\frac{\partial \phi}{\partial t} = -L\mu_\phi \quad (1), \quad \mu_\phi = \frac{\delta F}{\delta \phi} \quad (2)$$

The order parameter does not have to be conserved.

Short Summary, in general, any phase field model can be considered as a combination of these 2 models.

(IV) The Recipe

- Order parameter:** A field variable – continuous and has values for all positions and time; could be conserved or non-conserved; describes the topology (Microstructure)

- **Free energy functional:** To describe the free energy for a given microstructure; a functional of the order parameters (Thermodynamics). (We use free energy functional because in solid phase transformations, where most of the time we are assuming that temperature is a constant. So isothermal problem is a very good thermodynamic description)
- **Variational derivative equated to the chemical potential, which in turn, determines how the order parameter change:** Microstructure evolves in such a way that the free energy keeps decreasing (Kinetics) (The constitutive law: the rate of change of the order parameter is proportional to the gradient in the chemical potential or proportional to the chemical potential itself.)
- **Any other relevant equation:** Elasticity, magnetism (Physics) (Coupled with other Physics).

(V) Characteristics of Phase-Field theory

- Interfaces are not sharp; diffuse interface model
- No tracking of interface: numerical solutions are easier
- Gradient energy coefficient: interfacial energy contributions (Gibbs-Thomson, for example) are automatically accounted for
- Topological singularities (splitting or disappearance of interfaces): naturally take care of
- Elastic stress, magnetic and electric field: can be coupled by adding the relevant free energy term.

(VI) Challenges

- Isotropic issues
 - In the literature, we assumed everything to be isotropic. It is an important problem of how to incorporate the anisotropy.
- Deformation induced microstructure changes (Plastic deformation)
 - Plasticity: Mechanisms
 - Incorporation of mechanisms: appropriate free energy and parameters
 - Interaction between different mechanisms (Competing mechanisms)
 - Translating the mechanistic picture into prediction of mechanical behavior/properties
 - Calculating Cost: Parallel computation

(VII) Summary

- Phase-field Model: non-classical PDEs
- Ideal for the study of microstructure evolution
- Formulations and parameters: yet to be completely mapped out
- Software, data storage and analysis, numerical methods, fitting-in with other models: open

2.2 Key points in this paper interest me the most:

“More generally, the approach that we present here is important for the development of the phase-field (PF) methodology, which has achieved significant progress [1–9] in the simulation of morphological evolution not only in traditional materials science problems (alloy solidification [10], surface growth [11–13], crystal nucleation [14]), but also in prominent electrochemical problems, especially in the field of Li-ion batteries [15–17]”.

“The power of PF methodology essentially pertains to its ability to predict the evolution of arbitrary morphologies and complex microstructures without explicitly tracking the positions of interfaces, while using fundamental information from thermodynamics and kinetics as input [18–21]. The introduction of interface currents and the specific choice of the PF parameters by Karma et al. removed the artifacts due to the diffuse character of the interface and ensured that the convergence of the diffuse interface results in the sharp interface solution [22–24]”.

02/18/20

1) Paper (23) Atomic Insight into the Lithium Storage and Diffusion Mechanism of SiO₂Al₂O₃ Electrodes of Lithium Ion Batteries ReaxFF Reactive Force Field Modeling

(I) Interesting points:

1.1 For LIB, atomically deposited layers of SiO₂ and Al₂O₃ have been recognized as promising **coating materials** to **buffer the volumetric expansion** and **capacity retention** of the nanostructured Si-based electrodes.

1.2 ReaxFF: See --- 12/30/19, 1.5

02/20/20

1) Paper (36) One-to-one spatially matched experiment and atomistic simulations of nanometer-scale indentation

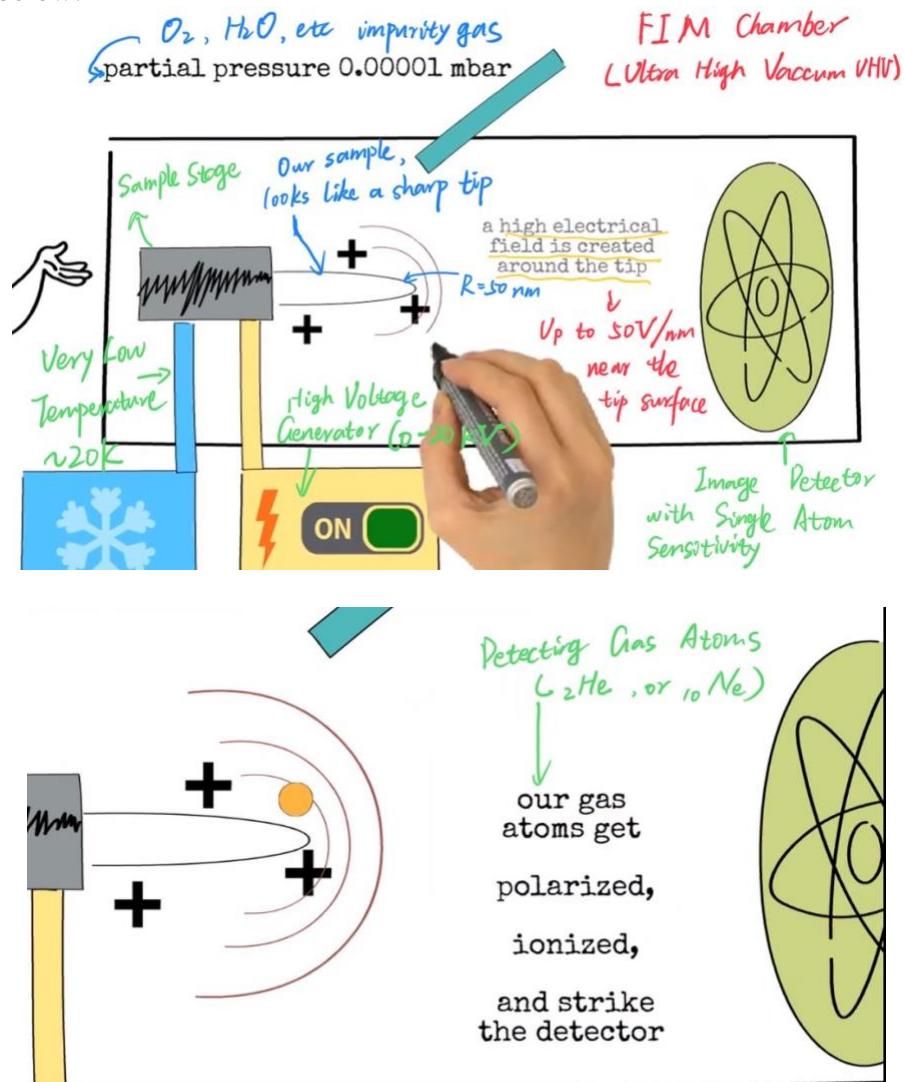
1.1 Terminology

1.1.1 “Field-Ion Microscopy (FIM)”

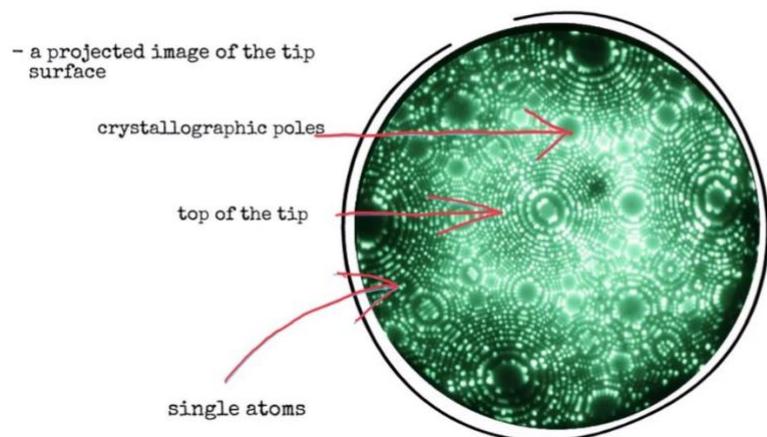
(A) Wiki

“In FIM, a sharp (<50 nm tip radius) metal tip is produced and placed in an ultra-high vacuum chamber, which is backfilled with an imaging gas such as helium or neon. The tip is cooled to cryogenic temperatures (20–100 K). A positive voltage of 5 to 10 kilovolts is applied to the tip. Gas atoms adsorbed on the tip are ionized by the strong electric field in the vicinity of the tip (thus, “field ionization”), becoming positively charged and being repelled from the tip. The curvature of the surface near the tip causes a natural magnification — ions are repelled in a direction roughly perpendicular to the surface (a “point projection” effect). A detector is placed so as to collect these repelled ions; the image formed from all the collected ions can be of sufficient resolution to image individual atoms on the tip surface. Unlike conventional microscopes, where the spatial resolution is limited by the wavelength of the particles which are used for imaging, the FIM is a projection type microscope with atomic resolution and an approximate magnification of a few million times.”

(B) YouTube: <https://www.youtube.com/watch?v=6zBJy1xrppY>
 See pictures below.



What do we see on the detector?



02/25/20

01) Paper (38) Oxidation-assisted ductility of aluminum nanowires

1.1 Terminology

1.1.1 “Homologous temperature”: Wiki

Homologous temperature expresses the thermodynamic temperature of a material as a fraction of the thermodynamic temperature of its melting point (using the Kelvin scale):

$$T_H = T(K)/T_{mp}(K)$$

The homologous temperature of a substance is useful for determining the rate of steady state creep (diffusion dependent deformation). A higher homologous temperature results in an exponentially higher rate of diffusion dependent deformation. Additionally, for a given fixed homologous temperature, two materials with different melting points would have similar diffusion-dependent deformation behavior.

1.1.2 “Superplasticity”: Wiki

In materials science, superplasticity is a state in which solid crystalline material is deformed well beyond its usual breaking point, usually over about 600% during tensile deformation. Such a state is usually achieved at high homologous temperature. Examples of superplastic materials are some fine-grained metals and ceramics. Other non-crystalline materials (amorphous) such as silica glass ("molten glass") and polymers also deform similarly, but are not called superplastic, because they are not crystalline; rather, their deformation is often described as Newtonian fluid. Superplastically deformed material gets thinner in a very uniform manner, rather than forming a "neck" (a local narrowing) that leads to fracture. Also, the formation of microvoids, which is another cause of early fracture, is inhibited.

In metals and ceramics, requirements for it being superplastic include a fine grain size (less than approximately 20 um) and a fine dispersion of thermally stable particles, which act to pin the grain boundaries and maintain the fine grain structure at the high temperatures and existence of two phases required for superplastic deformation. Those materials that meet these parameters must still have a strain rate sensitivity (a measurement of the way the stress on a material reacts to changes in strain rate) of >0.3 to be considered superplastic. The mechanisms of superplasticity in metals are still under debate—many believe it relies on atomic diffusion and the sliding of grains past each other. Also, when metals are cycled around their phase transformation, internal stresses are produced, and superplastic-like behavior develops.

1.1.3 “Hot forming”: <https://www.autoform.com/en/glossary/hot-forming/>

Hot forming is a temperature- and time-dependent process. With this method, parts are formed in their soft state at elevated temperatures and then quenched in the tool.

The hot forming process consists of the following steps: (1) Heat treatment in furnace; (2) Transfer from furnace to press and drawing tool; (3) Plastic hot forming; (4) Quenching in the closed, cooled die.

1.2 Key points in this paper interest me the most:

- This paper is an excellent example of using MD simulations (ReaxFF) to determine the effect of the environment (O_2) on the mechanical properties (yield strength and strain at fracture, more specifically) of the materials (Al nanowires, AlNWs)
- One paragraph to summarize the paper: The very thin oxide layer (Al_2O_3) formed on the surface of the AlNWs can increase the ductility and decrease the yield strength. Under ambient (O_2) environment, while the Al_2O_3 -covered AlNWs are being stretched below the critical strain rate ϵ_c (At this low strain rate, sufficient time was available for diffusing oxygen atoms to repair the broken Al–O bonds, and prevented necking formation; The O_2 diffused to the surface of NW was chemisorbed to the broken Al–O bonds at the surface Al and initially formed an Al–O–O bond. These weak homopolar O–O bonds were then broken at a higher strain with one O atom becoming connected to nearby Al atoms), the Al_2O_3 -covered AlNWs would demonstrate superplasticity. However, if the Al_2O_3 -covered AlNWs are stretched under vacuum condition, the number of large Al–O rings (with 16, 18, 20 and 24 atoms) increased at the expense of smaller rings (with 4, 10, 12 and 14 atoms), leading to the void formation. Check picture 4.

02/27/20

01) Paper (94) Aluminum–silicon interfaces and nanocomposites: A molecular dynamics study

1.1 Terminology

1.1.1 “Creep”: Wiki (Short introduction here)

- Creep (or cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of persistent mechanical stresses. It can occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods and generally increases as they near their melting point.
- Creep is a "time-dependent" deformation. It works on the principle of Hooke's law. The rate of deformation is a function of the material's properties, exposure time, exposure temperature and the applied structural load.

1.1.2 “Griffith Theory of Fracture”:

https://link.springer.com/referenceworkentry/10.1007%2F978-0-387-92897-5_259

The Griffith theory states that a crack will propagate when the reduction in potential energy (that occurs due to crack growth) is greater than or equal to the increase in surface energy (due to the creation of new free surfaces). This theory is applicable to elastic materials that fracture in a brittle fashion.

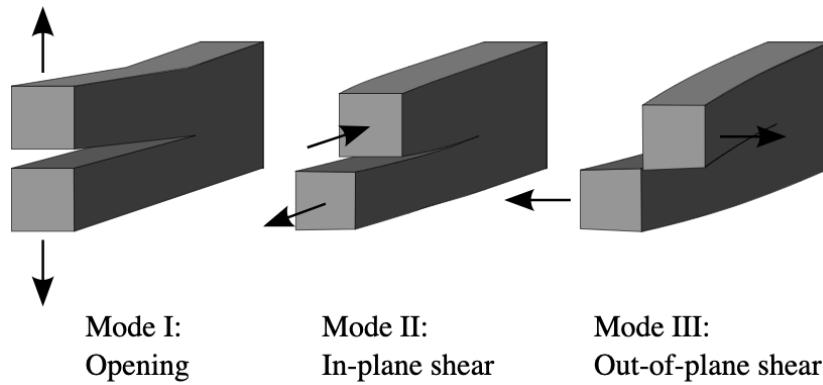
1.1.3 Knowledge related to fracture mechanics: Wiki

(I) General

- Fracture mechanics is the field of mechanics concerned with the study of the propagation of cracks in materials. It uses methods of analytical solid mechanics to calculate the driving force on a crack and those of experimental solid mechanics to characterize the material's resistance to fracture. It applies the physics of stress and strain behavior of materials, in

particular the theories of elasticity and plasticity, to the microscopic crystallographic defects found in real materials in order to predict the macroscopic mechanical behavior of those bodies.

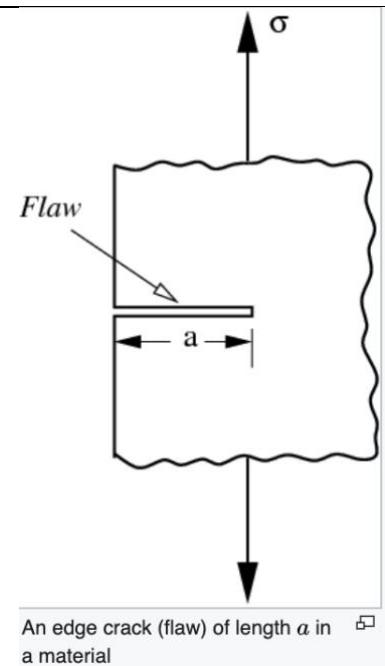
- There are three ways of applying a force to enable a crack to propagate (See pictures below):
 - (A) Mode I fracture – Opening mode (a tensile stress normal to the plane of the crack)
 - (B) Mode II fracture – Sliding mode (a shear stress acting parallel to the plane of the crack and perpendicular to the crack front)
 - (C) Mode III fracture – Tearing mode (a shear stress acting parallel to the plane of the crack and parallel to the crack front).



(II) Griffith's criterion (Applicable for **brittle materials**, i.e. glass)

- Griffith's work was motivated by two contradictory facts: (a) The stress needed to fracture bulk glass is around 100 MPa; (b) The theoretical stress needed for breaking atomic bonds of glass is approximately 10,000 MPa. <== A theory was needed to explain the phenomenon.

- Griffith found that the product of the square root of the flaw length (a) and the stress at fracture (σ_f) was nearly constant, which is expressed by the equation: $\sigma_f \sqrt{a} \approx C$.
- The growth of a crack, the extension of the surfaces on either side of the crack, requires an increase in the surface energy. In the end, Griffith found that $C = \sqrt{\frac{2E\gamma}{\pi}}$.
- Where E is the Young's modulus of the material and γ is the surface energy density of the material.
- Is **NOT** applicable to **ductile/soft** materials.



(III) Irwin's modification (Applicable for **Ductile/Soft materials**, i.e. steel)

- “Griffith's theory provides excellent agreement with experimental data for brittle materials such as glass. For ductile materials such as steel, although the $\sigma_y\sqrt{a} \approx C$ still holds, the surface energy (γ) predicted by Griffith's theory is usually unrealistically high.”
- “In ductile materials, a plastic zone develops at the tip of the crack. As the applied load increases, the plastic zone increases in size until the crack grows and the elastically strained material behind the crack tip unloads. The plastic loading and unloading cycle near the crack tip leads to the dissipation of energy as heat. Hence, a dissipative term has to be added to the energy balance relation devised by Griffith for brittle materials. In physical terms, additional energy is needed for crack growth in ductile materials as compared to brittle materials”.
- “Irwin's strategy was to partition the energy into two parts: (A) the stored elastic strain energy which is released as a crack grows. This is the thermodynamic driving force for fracture. (B) The dissipated energy which includes plastic dissipation and the surface energy (and any other dissipative forces that may be at work). The dissipated energy provides the thermodynamic resistance to fracture. Then the total energy is $G = 2\gamma + G_p$, where γ is the surface energy and G_p is the plastic dissipation (and dissipation from other sources) per unit area of crack growth”.
- “The modified version of Griffith's energy criterion: $\sigma_f\sqrt{a} = \sqrt{\frac{EG}{\pi}}$ ”.

1.1.3 “Embedded Atom Method (EAM)”:

- Wiki
- “EAM is an approximation describing the energy between atoms, an interatomic potential. The energy is a function of a sum of functions of the separation between an atom and its neighbors. In the original model, the latter functions represent the electron density. EAM is related to the second moment approximation to tight binding theory, also known as the Finnis-Sinclair model. These models are particularly appropriate for metallic systems. EAMs are widely used in molecular dynamics simulations”.
 - In a simulation, the potential energy of an atom i , is given by
$$E_i = F_\alpha \left(\sum_{i \neq j} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{\alpha\beta}(r_{ij})$$
 - “where r_{ij} is the distance between atoms i and j , $\phi_{\alpha\beta}$ is a pair-wise potential function, ρ_β is the contribution to the electron charge density from atom j of type β at the location of atom i , and F is an embedding function that represents the energy required to place atom i of type α into the electron cloud”.
 - “Since the electron cloud density is a summation over many atoms, usually limited by a cutoff radius, the EAM potential is a multibody potential. For a single element system of atoms, three

scalar functions must be specified: the embedding function, a pair-wise interaction, and an electron cloud contribution function. For a binary alloy, the EAM potential requires seven functions: three pair-wise interactions (A-A, A-B, B-B), two embedding functions, and two electron cloud contribution functions. Generally, these functions are provided in a tabularized format and interpolated by cubic splines”.

1.2 “Modified Embedded Atom Method (MEAM)” (From this paper)

- Generally, “*the MEAM is used to describe the interatomic interactions between Al-Al, Si-Si, and Al-Si. This potential is similar to the more common EAM potentials but allows for the directional dependence of the Si bonding*”.
- “*MEAM defines the energy E of the system as the sum of energies for each atom i, with each atom having energy contributions from an embedding function F that depends on a local electron density and a pair potential ϕ , so that*”
- “*where A is a constant, E_c is the cohesive energy, and $\bar{\rho}^0$ is a reference electron density. The pair potential only depends on the distance between atoms i and j, $R_{ij} \equiv |\vec{r}_i - \vec{r}_j|$. The actual angular dependence of the potential is buried in the definition of $\bar{\rho}_i$, which represents the electron density at atomic site i. The electron density is determined using*”

$$\bar{\rho}_i = \rho_i^{(o)} \sqrt{1 + \Gamma_i} \text{ with } \Gamma_i = \sum_{h=1}^3 t^{(h)} \left(\frac{\rho_i^{(h)}}{\rho_i^{(o)}} \right)^2 ;$$

- “*where t is an adjustable parameter used to weight the directional dependence, $\rho_0^{(i)}$ is a spherically symmetric term, and the $\rho_i^{(h)}$ represent the angular dependent terms of the electron density as*”

$$(\rho_i^{(o)})^2 = \sum_{j \neq i} \rho_i^{a(o)}(R_{ij}),$$

$$(\rho_i^{(1)})^2 = \sum_{\alpha} \left[\sum_{j \neq i} \rho_i^{a(1)}(R_{ij}) \frac{R_{ij}^{\alpha}}{R_{ij}} \right]^2,$$

$$(\rho_i^{(2)})^2 = \sum_{\alpha, \beta} \left[\sum_{j \neq i} \rho_i^{a(2)}(R_{ij}) \frac{R_{ij}^{\alpha} R_{ij}^{\beta}}{R_{ij}^2} \right]^2 - \frac{1}{3} \sum_{j \neq i} \left[\rho_i^{a(2)}(R_{ij}) \right]^2$$

$$(\rho_i^{(3)})^2 = \sum_{\alpha, \beta, \gamma} \left[\sum_{j \neq i} \rho_i^{a(3)}(R_{ij}) \frac{R_{ij}^{\alpha} R_{ij}^{\beta} R_{ij}^{\gamma}}{r^4} \right]^2 - \frac{3}{5} \sum_{\alpha} \left[\sum_{j \neq i} \frac{R_{ij}^{\alpha}}{R_{ij}} \rho_j^{a(3)}(R_{ij}) \right]^2,$$

where

$$\rho^{a(h)}(R) = \exp[-\beta^{(h)}(R/r_e - 1)]$$

- “*Where $\rho^{a(h)}(R)$ is the electron density from a neighboring atom at a distance R from the atom of interest. The a, b, and c variables are summed over the three directional components of the distance vector between atoms i and j.*”
- “*From the energy, the force on an individual atom is $f_i = -dE/dr_i$. The molecular dynamics method is employed to follow the dynamic evolution of the atomic system under applied load. Newton’s equations of motion are then integrated in the MD*”.

1.3 Key points in this paper interest me the most:

- This paper employs the molecular dynamics method to study the Al-Al & Al-Si interface, the deformation & failure of the interfaces for Al polycrystals and Al-Si nanocomposites (loaded in tension)
- This paper calculates the (A) tensile strength (σ_f) and (B) the interface & fracture energy for various (9 types) Al-Si interfaces. For (A) tensile strength (σ_f), there are 3 important factors: (1) The Al/Si interfacial bonding is mainly determined by the orientation and dangling bonds at the Si surface. (2) The orientation of the Al(1 1 1) planes with respect to the direction of the applied load. (3) How well the Al matches with the Si surface. For (B), the toughness of the interfaces is dominated by the orientation of Al(111) planes relative to the direction of the applied load.
- “The deformation mechanisms in the (a) Al polycrystal and (b) Al-Si nanocomposites are notably different, with the former (a) showing extensive grain boundary deformation and dislocation activity and the latter (b) deforming predominantly by Al-Si interface sliding/shearing, leading to enhanced hardening for higher-Si-content”.
- “The failure modes in the (a) Al polycrystal and (b) Al-Si nanocomposite are notably different, with the former (a) showing void nucleation and then cleavage across Al grains and the latter (b) showing void nucleation and damage accumulation along a selected Al-Si interface, both aided by stress concentrations due to local texture (Al polycrystal) or elastic mismatch (Al-Si nanocomposite)”.

02/28/20

1) Paper (96) Mesoscale simulation of morphology in hydrated perfluorosulfonic acid membranes

1.1 Terminology

1.1.1 “Ionomer”: Wiki

“An ionomer is a polymer composed of repeat units of both electrically neutral repeating units and ionized units covalently bonded to the polymer backbone as pendant group moieties. Usually no more than 15 mole percent are ionized. The ionized units are often carboxylic acid groups.

The classification of a polymer as an ionomer depends on the level of substitution of ionic groups as well as how the ionic groups are incorporated into the polymer structure. For example, (A) polyelectrolytes also have ionic groups covalently bonded to the polymer backbone, but have a much higher ionic group molar substitution level (usually greater than 80%); (B) Ionenes are polymers where ionic groups are part of the actual polymer backbone. These two classes of ionic-group-containing polymers have vastly different morphological and physical properties and are therefore not considered ionomers.

Ionomers have unique physical properties including electrical conductivity and viscosity— increase in ionomer solution viscosity with increasing temperatures (see conducting polymer). Ionomers also have unique morphological properties as the non-polar polymer backbone is

energetically incompatible with the polar ionic groups. As a result, the ionic groups in most ionomers will undergo microphase separation to form ionic-rich domains.”

1.1.2 “Partition function”: Wiki

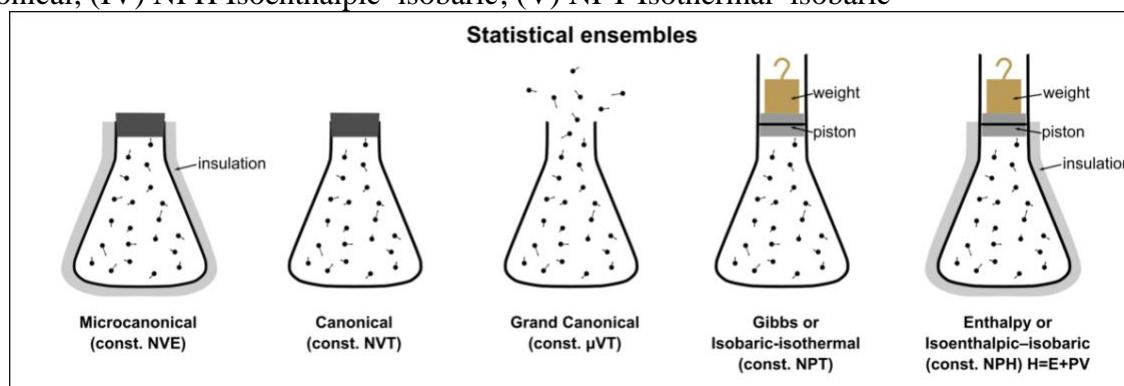
(0) *“In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives. The partition function is dimensionless, it is a pure number. Each partition function is constructed to represent a particular statistical ensemble (which, in turn, corresponds to a particular free energy)”.*

P.S. What is a statistical ensemble? Wiki

“An ensemble is an idealization consisting of a large number of virtual copies (sometimes infinitely many) of a system, considered all at once, each of which represents a possible state that the real system might be in. In other words, **a statistical ensemble is a probability distribution for the state of the system**.

A thermodynamic ensemble is a specific variety of statistical ensemble that, among other properties, is in statistical equilibrium, and is used to derive the properties of thermodynamic systems from the laws of classical or quantum mechanics.

5 thermodynamic ensembles: (I) NVE Microcanonical; (II) NVT Canonical; (III) μ VT Grand canonical; (IV) NPH Isoenthalpic-isobaric; (V) NPT Isothermal-isobaric



(1) <https://www.youtube.com/watch?v=ws3RZCvWCD8&t=190s>

Physical meaning of partition function: For a thermodynamic system, we can calculate every property of the system by using the partition function, including energy entropy, free energy, chemical potential, equilibrium constant, etc.

Study notes from the YouTube video

Partition Function

For an ensemble, for example canonical ensemble, the microscopic states distribution is like the following:

E_3	1	2	3	$g_3=3$
E_2	1			$g_2=1$
E_1	1	2		$g_1=2$

g_i : Degeneracy

$$P_i \propto g_i e^{-E_i/k_B T}$$

↓

$$P_i = C g_i e^{-E_i/k_B T}$$

$$\sum_{i=1}^n P_i = 1 \quad \text{"normalization"}$$

Here, we define a function, "Partition Function", Q

$$Q = \sum_{i=1}^{\text{All microscopic states}} e^{-E_i/k_B T}$$

$$= \sum_{i=1}^{\text{All Energy Levels}} g_i \cdot e^{-E_i/k_B T}$$

"Partition Function", contains all information about the system.

$$P_i = \frac{g_i e^{-\beta E_i}}{\sum_{i=1}^n g_i e^{-\beta E_i}}, \quad \beta = \frac{1}{k_B T}$$

$$P_i = \frac{1}{Q} \cdot g_i e^{-\beta E_i}$$

Microcanonical Ensemble (NVE)

Canonical Ensemble (NVT)

Grand Canonical Ensemble (GVT)

Isoenthalpy-isobaric Ensemble (NPH)

Isothermal-isobaric Ensemble (NPT)

- (2) <https://www.quora.com/What-is-the-partition-function-in-physics-Elementary-statistical-mechanics-texts-seem-to-compute-this-in-trivial-examples-without-ever-defining-it-in-general-and-the-more-advanced-texts-just-assume-you-know-what-it-is-already>

Partition function has the following 2 physical aspects:

(A) Partition function as a probability normalization factor (as shown above)

(B) Partition function as a generating function:

"In reality, what we really want to know are things like the expected energy averaged over all possibilities. This is because experimentally one usually does not characterize a system with sufficient resolution to distinguish between microscopic configurations, rather one measures macroscopic quantities (like the energy). If we can compute the partition function analytically such that we know the functional dependence on β , then the function can give us the expected energy. Specifically, average energy is given by a derivative of the logarithm of the partition function with respect to β ".

$$-\frac{\partial \ln Z}{\partial \beta} = \sum_{\text{All States } i} \frac{E_i e^{-\beta E_i}}{Z} = \sum_{\text{All States } i} E_i p(\text{State } i) = \langle E \rangle$$

"The angled brackets indicate an expectation value".

- (3) <https://www.quora.com/How-you-define-the-partition-function-of-a-system-and-what-is-its-significance>

"The partition function is just what it sounds like; it tells you how many different ways you can partition a system into subsystems have the same Energy, Entropy, etc."

By saying a 'system', we mean something composed of smaller parts, and that we can describe with energies or probabilities (log energies). This could be a gas or even a molecule, a neural network. All we need is a way to write down the system as a collection of different configurations parts, and some way to describe the probability of observing the system in one or more of these individual configurations.

The Canonical Partition Function is the (Boltzmann) weighted sum of the microstates of any system

$$Z = \sum_i e^{-\beta E_i}$$

The partition function is also a combinatorial generating function. The partition function has lots of applications. In particular, we can use it to express the important global variables that describe a system, such as the Total Energy, the Free Energy, the Entropy, the Variance, etc.

Of particular interest are the Free Energy and the Variance

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}.$$

$$\langle (\Delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

The heat capacity (C), entropy (S) and Helmholtz free energy (A , where $A = U - TS$, where $U = \langle E \rangle$) is"

$$\begin{aligned} C_v &= \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2} \langle (\Delta E)^2 \rangle \\ S &\equiv -k_B \sum_s P_s \ln P_s = k_B (\ln Z + \beta \langle E \rangle) = \frac{\partial}{\partial T} (k_B T \ln Z) = -\frac{\partial A}{\partial T} \\ A &= \langle E \rangle - TS = -k_B T \ln Z. \end{aligned}$$

1.1.3 "Mean Field Theory (MFT)": Wiki (English + Chinese)

(1) Wiki

"In physics and probability theory, mean-field theory (aka MFT or rarely self-consistent field theory) studies the behavior of high-dimensional random (stochastic) models by studying a simpler model that approximates the original by averaging over degrees of freedom. Such models consider many individual components that interact with each other. In MFT, the effect of all the other individuals on any given individual is approximated by a single averaged effect, thus reducing a many-body problem to a one-body problem. The main idea of MFT is to replace all interactions to any one body with an average or effective interaction, sometimes called a molecular field. This reduces any multi-body problem into an effective one-body problem."

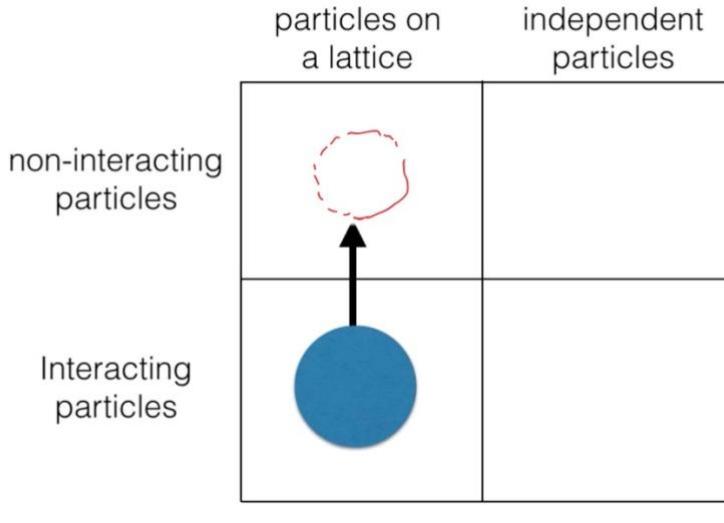
(2) https://www.youtube.com/watch?v=kyfQhlH_0qA

In real world problems, "for many (energy) Hamiltonian (H) of interest, it is impossible to solve for the partition function exactly. This is particularly true for systems of interacting particles".
 ==> In this case, "we are forced to calculate partition functions, average energies and equations of states for these types of systems using approximation techniques".

There are 2 ways of using approximations. “*The most common one used in research involves the use of computers with (brute force simulations?). The other one involves approximating the Hamiltonian (H), which is the **Mean-Field Theory (MFT)**.*”

“*In fact, in research, MFT is often used in combination with computer simulation. First, we usually use a mean field approximation to simplify the Hamiltonian (H). Even when we do this, however, we might still arrive at an expression for the partition function that cannot be solved analytically and must still be solved by brute force simulation.*”

What model Hamiltonians do we look at



(3) <https://www.youtube.com/watch?v=4MjhuY3keaY&t=186s>

“*MFT is useful to explore the qualitative behavior of **phase transitions** and **critical behavior** of any models. MFT can be useful tool to study the behavior of any models in the vicinity of their critical points. MFT makes it possible to convert the model to something we can solve and enables us to explore critical behavior*”.

1.1.4 “Mesoscale Dynamics”:

03/02/20

Study Plan

- 1) Polymer Physics
- 2) 4 papers about Mesoscale Dynamics
- 3) Simulation of polymer nanocomposites

05/02/20

1) Canonical Ensemble and Canonical Partition Function

[https://en.wikipedia.org/wiki/Partition_function_\(statistical_mechanics\)](https://en.wikipedia.org/wiki/Partition_function_(statistical_mechanics))

https://en.wikipedia.org/wiki/Canonical_ensemble

Canonical partition function [edit]

Definition [edit]

Initially, let us assume that a thermodynamically large system is in **thermal contact** with the environment, with a temperature T , and both the volume of the system and the number of constituent particles are fixed. A collection of this kind of systems comprises an ensemble called a **canonical ensemble**. The appropriate **mathematical expression** for the canonical partition function depends on the **degrees of freedom** of the system, whether the context is **classical mechanics** or **quantum mechanics**, and whether the spectrum of states is **discrete** or **continuous**.[citation needed]

Classical discrete system

For a canonical ensemble that is classical and discrete, the canonical partition function is defined as

$$Z = \sum_i e^{-\beta E_i},$$

where

i is the index for the **microstates** of the system,

e is **Euler's number**,

β is the **thermodynamic beta**, defined as $\frac{1}{k_B T}$,

E_i is the total energy of the system in the respective **microstate**.

The exponential factor $e^{-\beta E_i}$ is otherwise known as the **Boltzmann factor**.

Classical continuous system

In **classical mechanics**, the **position** and **momentum** variables of a particle can vary continuously, so the set of microstates is actually **uncountable**. In **classical statistical mechanics**, it is rather inaccurate to express the partition function as a **sum** of discrete terms. In this case we must describe the partition function using an **integral** rather than a sum. For a canonical ensemble that is classical and continuous, the canonical partition function is defined as

$$Z = \frac{1}{h^3} \int e^{-\beta H(q,p)} d^3 q d^3 p,$$

where

h is the **Planck constant**,

β is the **thermodynamic beta**, defined as $\frac{1}{k_B T}$,

$H(q,p)$ is the **Hamiltonian** of the system,

q is the **canonical position**,

p is the **canonical momentum**.

To make it into a dimensionless quantity, we must divide it by h , which is some quantity with units of **action** (usually taken to be **Planck's constant**).

Classical continuous system (multiple identical particles)

For a gas of N identical classical particles in three dimensions, the partition function is

$$Z = \frac{1}{N!h^{3N}} \int \exp\left(-\beta \sum_{a=1}^N H(\mathbf{p}_a, \mathbf{x}_a)\right) d^3 p_1 \cdots d^3 p_N d^3 x_1 \cdots d^3 x_N$$

where

p_i indicate particle momenta,

x_i indicate particle positions,

β is a shorthand notation serving as a reminder that the p_i and x_i are vectors in three-dimensional space,

H is the classical Hamiltonian of a single particle.

The reason for the factorial factor $N!$ is discussed [below](#). The extra constant factor introduced in the denominator was introduced because, unlike the discrete form, the continuous form shown above is not dimensionless. As stated in the previous section, to make it into a dimensionless quantity, we must divide it by h^{3N} (where h is usually taken to be Planck's constant).

Quantum mechanical discrete system

For a canonical ensemble that is quantum mechanical and discrete, the canonical partition function is defined as the [trace](#) of the Boltzmann factor:

$$Z = \text{tr}(e^{-\beta \hat{H}}),$$

where

β is the [thermodynamic beta](#), defined as $\frac{1}{k_B T}$,

\hat{H} is the [Hamiltonian operator](#).

The [dimension](#) of $e^{-\beta \hat{H}}$ is the number of [energy eigenstates](#) of the system.

Note: Trace

In [linear algebra](#), the [trace](#) (often abbreviated to [tr](#)) of a [square matrix](#) A is defined to be the sum of elements on the [main diagonal](#) (from the upper left to the lower right) of A .

The [trace of a matrix](#) is the sum of its (complex) [eigenvalues](#), and it is [invariant](#) with respect to a [change of basis](#). This characterization can be used to define the trace of a linear operator in general. The trace is only defined for a square matrix $(n \times n)$.

The trace is related to the derivative of the [determinant](#) (see [Jacobi's formula](#)).

Quantum mechanical continuous system

For a canonical ensemble that is quantum mechanical and continuous, the canonical partition function is defined as

$$Z = \frac{1}{h} \int \langle q, p | e^{-\beta \hat{H}} | q, p \rangle dq dp,$$

where

\hbar is the Planck constant,

β is the thermodynamic beta, defined as $\frac{1}{k_B T}$,

\hat{H} is the Hamiltonian operator,

q is the canonical position,

p is the canonical momentum.

In systems with multiple quantum states s sharing the same energy E_s , it is said that the energy levels of the system are degenerate. In the case of degenerate energy levels, we can write the partition function in terms of the contribution from energy levels (indexed by j) as follows:

$$Z = \sum_j g_j \cdot e^{-\beta E_j},$$

where g_j is the degeneracy factor, or number of quantum states s that have the same energy level defined by $E_j = E_s$.

The above treatment applies to quantum statistical mechanics, where a physical system inside a finite-sized box will typically have a discrete set of energy eigenstates, which we can use as the states s above. In quantum mechanics, the partition function can be more formally written as a trace over the state space (which is independent of the choice of basis):

$$Z = \text{tr}(e^{-\beta \hat{H}}),$$

where \hat{H} is the quantum Hamiltonian operator. The exponential of an operator can be defined using the exponential power series.

The classical form of Z is recovered when the trace is expressed in terms of coherent states^[1] and when quantum-mechanical uncertainties in the position and momentum of a particle are regarded as negligible. Formally, using bra–ket notation, one inserts under the trace for each degree of freedom the identity:

$$\mathbf{1} = \int |x, p\rangle \langle x, p| \frac{dx dp}{h},$$

where $|x, p\rangle$ is a normalised Gaussian wavepacket centered at position x and momentum p . Thus

$$Z = \int \text{tr}\left(e^{-\beta \hat{H}} |x, p\rangle \langle x, p|\right) \frac{dx dp}{h} = \int \langle x, p | e^{-\beta \hat{H}} |x, p\rangle \frac{dx dp}{h}.$$

A coherent state is an approximate eigenstate of both operators \hat{x} and \hat{p} , hence also of the Hamiltonian \hat{H} , with errors of the size of the uncertainties. If Δx and Δp can be regarded as zero, the action of \hat{H} reduces to multiplication by the classical Hamiltonian, and Z reduces to the classical configuration integral.

Connection to probability theory [edit]

For simplicity, we will use the discrete form of the partition function in this section. Our results will apply equally well to the continuous form.

Consider a system S embedded into a **heat bath** B . Let the total **energy** of both systems be E . Let p_i denote the **probability** that the **microstate** that system S is in has energy E_i . According to the **fundamental postulate of statistical mechanics** (which states that all attainable microstates of a system are equally probable), the probability p_i will be proportional to the number of microstates of the total **closed system** (S, B) in which S is in microstate i with energy E_i . Equivalently, p_i will be proportional to the number of microstates of the heat bath B with energy $E - E_i$:

$$p_i = \frac{\Omega_B(E - E_i)}{\Omega_B(E)}.$$

Assuming that the heat bath's internal energy is much larger than the energy of S ($E \gg E_i$), we can **Taylor-expand** Ω_B to first order in E_i and use the thermodynamic relation $\partial S_B / \partial E = 1/T$, where here S_B , T are the entropy and temperature of the bath respectively:

$$\begin{aligned} k \ln p_i &= k \ln \Omega_B(E - E_i) - k \ln \Omega_B(E) \\ &\approx -\frac{\partial(k \ln \Omega_B(E))}{\partial E} E_i \\ &\approx -\frac{\partial S_B}{\partial E} E_i \\ &\approx -\frac{E_i}{T} \end{aligned}$$

Thus

$$p_i \propto e^{-E_i/(kT)} = e^{-\beta E_i}.$$

Since the total probability to find the system in *some* microstate (the sum of all p_i) must be equal to 1, we can define the partition function as the **normalization constant**:

$$Z = \sum_i e^{-\beta E_i}.$$

Calculating the thermodynamic total energy [edit]

In order to demonstrate the usefulness of the partition function, let us calculate the thermodynamic value of the total energy. This is simply the expected value, or ensemble average for the energy, which is the sum of the microstate energies weighted by their probabilities:

$$\langle E \rangle = \sum_s E_s P_s = \frac{1}{Z} \sum_s E_s e^{-\beta E_s} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z(\beta, E_1, E_2, \dots) = -\frac{\partial \ln Z}{\partial \beta}$$

or, equivalently,

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Z}{\partial T}.$$

Incidentally, one should note that if the microstate energies depend on a parameter λ in the manner

$$E_s = E_s^{(0)} + \lambda A_s \quad \text{for all } s$$

then the expected value of A is

$$\langle A \rangle = \sum_s A_s P_s = -\frac{1}{\beta} \frac{\partial}{\partial \lambda} \ln Z(\beta, \lambda).$$

This provides us with a method for calculating the expected values of many microscopic quantities. We add the quantity artificially to the microstate energies (or, in the language of quantum mechanics, to the Hamiltonian), calculate the new partition function and expected value, and then set λ to zero in the final expression. This is analogous to the source field method used in the path integral formulation of quantum field theory.[citation needed]

Relation to thermodynamic variables [edit]

In this section, we will state the relationships between the partition function and the various thermodynamic parameters of the system. These results can be derived using the method of the previous section and the various thermodynamic relations.

As we have already seen, the thermodynamic energy is

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}.$$

The variance in the energy (or "energy fluctuation") is

$$\langle (\Delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2}.$$

The heat capacity is

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2} \langle (\Delta E)^2 \rangle.$$

In general, consider the [extensive variable X](#) and [intensive variable Y](#) where X and Y form a pair of [conjugate variables](#). In ensembles where Y is fixed (and X is allowed to fluctuate), then the average value of X will be:

$$\langle X \rangle = \pm \frac{\partial \ln Z}{\partial \beta Y}.$$

The sign will depend on the specific definitions of the variables X and Y. An example would be X = volume and Y = pressure. Additionally, the variance in X will be

$$\langle (\Delta X)^2 \rangle \equiv \langle (X - \langle X \rangle)^2 \rangle = \frac{\partial \langle X \rangle}{\partial \beta Y} = \frac{\partial^2 \ln Z}{\partial (\beta Y)^2}.$$

In the special case of [entropy](#), entropy is given by

$$S \equiv -k_B \sum_s P_s \ln P_s = k_B (\ln Z + \beta \langle E \rangle) = \frac{\partial}{\partial T} (k_B T \ln Z) = -\frac{\partial A}{\partial T}$$

where A is the [Helmholtz free energy](#) defined as $A = U - TS$, where $U = \langle E \rangle$ is the total energy and S is the [entropy](#), so that

$$A = \langle E \rangle - TS = -k_B T \ln Z.$$

Partition functions of subsystems [\[edit\]](#)

Suppose a system is subdivided into N sub-systems with negligible interaction energy, that is, we can assume the particles are essentially non-interacting. If the partition functions of the sub-systems are $\zeta_1, \zeta_2, \dots, \zeta_N$, then the partition function of the entire system is the *product* of the individual partition functions:

$$Z = \prod_{j=1}^N \zeta_j.$$

If the sub-systems have the same physical properties, then their partition functions are equal, $\zeta_1 = \zeta_2 = \dots = \zeta$, in which case

$$Z = \zeta^N.$$

However, there is a well-known exception to this rule. If the sub-systems are actually [identical particles](#), in the [quantum mechanical](#) sense that they are impossible to distinguish even in principle, the total partition function must be divided by a $N!$ (N factorial):

$$Z = \frac{\zeta^N}{N!}.$$

This is to ensure that we do not "over-count" the number of microstates. While this may seem like a strange requirement, it is actually necessary to preserve the existence of a thermodynamic limit for such systems. This is known as the [Gibbs paradox](#).

Meaning and significance [edit]

It may not be obvious why the partition function, as we have defined it above, is an important quantity. First, consider what goes into it. The partition function is a function of the temperature T and the microstate energies E_1, E_2, E_3 , etc. The microstate energies are determined by other thermodynamic variables, such as the number of particles and the volume, as well as microscopic quantities like the mass of the constituent particles. This dependence on microscopic variables is the central point of statistical mechanics. With a model of the microscopic constituents of a system, one can calculate the microstate energies, and thus the partition function, which will then allow us to calculate all the other thermodynamic properties of the system.

The partition function can be related to thermodynamic properties because it has a very important statistical meaning. The probability P_s that the system occupies microstate s is

$$P_s = \frac{1}{Z} e^{-\beta E_s}.$$

Thus, as shown above, the partition function plays the role of a normalizing constant (note that it does *not* depend on s), ensuring that the probabilities sum up to one:

$$\sum_s P_s = \frac{1}{Z} \sum_s e^{-\beta E_s} = \frac{1}{Z} Z = 1.$$

This is the reason for calling Z the "partition function": it encodes how the probabilities are partitioned among the different microstates, based on their individual energies. The letter Z stands for the German word *Zustandssumme*, "sum over states". The usefulness of the partition function stems from the fact that it can be used to relate macroscopic thermodynamic quantities to the microscopic details of a system through the derivatives of its partition function. Finding the partition function is also equivalent to performing a laplace transform of the density of states function from the energy domain to the β domain, and the inverse laplace transform of the partition function reclaims the state density function of energies.

The canonical ensemble assigns a probability P to each distinct microstate given by the following exponential:

$$P = e^{\frac{F-E}{kT}},$$

where E is the total energy of the microstate, and k is Boltzmann's constant.

The number F is the free energy (specifically, the Helmholtz free energy) and is a constant for the ensemble. However, the probabilities and F will vary if different N , V , T are selected. The free energy F serves two roles: first, it provides a normalization factor for the probability distribution (the probabilities, over the complete set of microstates, must add up to one); second, many important ensemble averages can be directly calculated from the function $F(N, V, T)$.

Properties [edit]

- *Uniqueness*: The canonical ensemble is uniquely determined for a given physical system at a given temperature, and does not depend on arbitrary choices such as choice of coordinate system (classical mechanics), or basis (quantum mechanics), or of the zero of energy.^[1]
- *Statistical equilibrium* (steady state): A canonical ensemble does not evolve over time, despite the fact that the underlying system is in constant motion. This is because the ensemble is only a function of a conserved quantity of the system (energy).^[1]
- *Thermal equilibrium with other systems*: Two systems, each described by a canonical ensemble of equal temperature, brought into thermal contact^[note 1] will each retain the same ensemble and the resulting combined system is described by a canonical ensemble of the same temperature.^[1]
- *Maximum entropy*: For a given mechanical system (fixed N, V), the canonical ensemble average $-\langle \log P \rangle$ (the [entropy](#)) is the maximum possible of any ensemble with the same $\langle E \rangle$.^[1]
- *Minimum free energy*: For a given mechanical system (fixed N, V) and given value of T , the canonical ensemble average $\langle E + kT \log P \rangle$ (the [Helmholtz free energy](#)) is the lowest possible of any ensemble.^[1] This is easily seen to be equivalent to maximizing the entropy.

Precise expressions for the ensemble [edit]

The precise mathematical expression for a statistical ensemble depends on the kind of mechanics under consideration—quantum or classical—since the notion of a "microstate" is considerably different in these two cases. In quantum mechanics, the canonical ensemble affords a simple description since [diagonalization](#) provides a discrete set of [microstates with specific energies](#). The classical mechanical case is more complex as it involves instead an integral over [canonical phase space](#), and the size of microstates in phase space can be chosen somewhat arbitrarily.

2) Hamiltonian mechanics & Hamiltonian Operator (quantum mechanics)

https://en.wikipedia.org/wiki/Hamiltonian_mechanics

[https://en.wikipedia.org/wiki/Hamiltonian_\(quantum_mechanics\)](https://en.wikipedia.org/wiki/Hamiltonian_(quantum_mechanics))

Hamiltonian (quantum mechanics)

From Wikipedia, the free encyclopedia

In quantum mechanics, a [Hamiltonian](#) is an [operator](#) corresponding to the sum of the [kinetic energies](#) plus the [potential energies](#) for all the particles in the system (this addition is the total [energy](#) of the system in most of the cases under analysis). It is usually denoted by H , but also \check{H} or \hat{H} to highlight its function as an operator. Its [spectrum](#) is the set of possible outcomes when one measures the total energy of a system. Because of its close relation to the time-evolution of a system, it is of fundamental importance in most formulations of quantum theory.

Introduction

"The [Hamiltonian](#) is the sum of the [kinetic energies](#) of all the particles, plus the [potential energy](#) of the particles associated with the system. The expression of the Hamiltonian can take different forms and simplifications taken into account the concrete characteristics of the system under analysis: single or several particles in the system; interaction between particles; kind of potential energy; time varying potential or time independent one; etc."

One Example

The Schrödinger Hamiltonian [\[edit\]](#)

One particle [\[edit\]](#)

By analogy with [classical mechanics](#), the Hamiltonian is commonly expressed as the sum of [operators](#) corresponding to the [kinetic and potential energies of a system in the form](#)

$$\hat{H} = \hat{T} + \hat{V},$$

where

$$\hat{V} = V = V(\mathbf{r}, t),$$

is the [potential energy](#) operator and

$$\hat{T} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2,$$

is the [kinetic energy](#) operator in which m is the [mass](#) of the particle, the dot denotes the [dot product](#) of vectors, and

$$\hat{p} = -i\hbar\nabla,$$

is the [momentum operator](#) where an ∇ is the [del operator](#). The [dot product](#) of ∇ with itself is the [Laplacian](#) ∇^2 . In three dimensions using [Cartesian coordinates](#) the Laplace operator is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Although this is not the technical definition of the [Hamiltonian in classical mechanics](#), it is the form it most commonly takes.

Combining these together yields the familiar form used in the [Schrödinger equation](#):

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} + V(\mathbf{r}, t) \\ &= -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t)\end{aligned}$$

which allows one to apply the Hamiltonian to systems described by a [wave function](#) $\Psi(\mathbf{r}, t)$. This is the approach commonly taken in introductory treatments of quantum mechanics, using the formalism of Schrödinger's wave mechanics.

One can also make substitutions to certain variables to fit specific cases, such as some involving electromagnetic fields.

Hamiltonian Mechanics

Overview [edit]

In Hamiltonian mechanics, a classical physical system is described by a set of canonical coordinates $\mathbf{r} = (\mathbf{q}, \mathbf{p})$, where each component of the coordinate q_i, p_i is indexed to the frame of reference of the system.

The time evolution of the system is uniquely defined by Hamilton's equations:^[1]

$$\frac{d\mathbf{p}}{dt} = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}} \quad , \quad \frac{d\mathbf{q}}{dt} = +\frac{\partial \mathcal{H}}{\partial \mathbf{p}}$$

where $\mathcal{H} = \mathcal{H}(\mathbf{q}, \mathbf{p}, t)$ is the Hamiltonian, which often corresponds to the total energy of the system.^[2] For a closed system, it is the sum of the kinetic and potential energy in the system.

In Newtonian mechanics, the time evolution is obtained by computing the total force being exerted on each particle of the system, and from Newton's second law, the time evolutions of both position and velocity are computed. In contrast, in Hamiltonian mechanics, the time evolution is obtained by computing the Hamiltonian of the system in the generalized coordinates and inserting it into Hamilton's equations. This approach is equivalent to the one used in Lagrangian mechanics.

The Hamiltonian is the Legendre transform of the Lagrangian when holding \mathbf{q} and t fixed and defining \mathbf{p} as the dual variable, and thus both approaches give the same equations for the same generalized momentum. The main motivation to use Hamiltonian mechanics instead of Lagrangian mechanics comes from the symplectic structure of Hamiltonian systems.

While Hamiltonian mechanics can be used to describe simple systems such as a bouncing ball, a pendulum or an oscillating spring in which energy changes from kinetic to potential and back again over time, its strength is shown in more complex dynamic systems, such as planetary orbits in celestial mechanics.^[3] The more degrees of freedom the system has, the more complicated its time evolution is and, in most cases, it becomes chaotic.

Basic physical interpretation [edit]

A simple interpretation of Hamiltonian mechanics comes from its application on a one-dimensional system consisting of one particle of mass m . The Hamiltonian can represent the total energy of the system, which is the sum of kinetic and potential energy, traditionally denoted T and V , respectively. Here q is the space coordinate and p is the momentum mv . Then

$$\mathcal{H} = T + V \quad , \quad T = \frac{p^2}{2m} \quad , \quad V = V(q)$$

T is a function of p alone, while V is a function of q alone (i.e., T and V are scleronomic).

In this example, the time derivative of the momentum p equals the Newtonian force, and so the first Hamilton equation means that the force equals the negative gradient of potential energy. The time derivative of q is the velocity, and so the second Hamilton equation means that the particle's velocity equals the derivative of its kinetic energy with respect to its momentum.

Note 1: What is the Spectrum (functional analysis) for an operator?

[https://en.wikipedia.org/wiki/Spectrum_\(functional_analysis\)](https://en.wikipedia.org/wiki/Spectrum_(functional_analysis))

Spectrum (functional analysis)

From Wikipedia, the free encyclopedia

(Redirected from [Spectrum of an operator](#))

In [mathematics](#), particularly in [functional analysis](#), the **spectrum** of a [bounded linear operator](#) (or, more generally, an [unbounded linear operator](#)) is a generalisation of the set of [eigenvalues](#) of a [matrix](#). Specifically, a [complex number](#) λ is said to be in the spectrum of a bounded linear operator T if $T - \lambda I$ is not [invertible](#), where I is the [identity operator](#). The study of spectra and related properties is known as [spectral theory](#), which has numerous applications, most notably the [mathematical formulation of quantum mechanics](#).

The [spectrum of an operator on a finite-dimensional vector space](#) is precisely the set of eigenvalues. However an operator on an infinite-dimensional space may have additional elements in its spectrum, and may have no eigenvalues. For example, consider the

The notion of spectrum extends to [unbounded operators](#). In this case a [complex number](#) λ is said to be in the spectrum of an operator $T : X \rightarrow X$ defined on domain $D(T) \subset X$ if there is no bounded inverse $(T - \lambda I)^{-1} : X \rightarrow D(T)$. If T is a [closed operator](#) (which includes the case that T is a bounded operator), boundedness of such inverses follows automatically if the inverse exists at all.

Note 2: [https://en.wikipedia.org/wiki/Partition_function_\(statistical_mechanics\)](https://en.wikipedia.org/wiki/Partition_function_(statistical_mechanics)) (Also see Above)

 This provides us with a method for calculating the expected values of many microscopic quantities. We add the quantity artificially to the [microstate energies](#) (or, in the language of quantum mechanics, to the [Hamiltonian](#)), calculate the new partition function and expected value, and then set λ to zero in the final expression. This is analogous to the [source field](#) method used in the [path integral formulation of quantum field theory](#).[citation needed]

Note 3: Operator (physics)

[https://en.wikipedia.org/wiki/Operator_\(physics\)#Operators_in_quantum_mechanics](https://en.wikipedia.org/wiki/Operator_(physics)#Operators_in_quantum_mechanics)

“In physics, an operator is [a function](#) over a space of physical states to another space of physical states.”

以前看 YouTube 上视频的回忆：Operator can be considered as a function that is applied to a matrix and then you can get the eigenvalues of the matrix.

3) Canonical coordinates (Canonical Position & Momentum)

https://en.wikipedia.org/wiki/Canonical_coordinates

“In classical mechanics, canonical coordinates are [sets of coordinates on phase space](#) which can be used to describe a physical system at any given point in time. Canonical coordinates are used in the Hamiltonian formulation of classical mechanics.”

Definition in classical mechanics [edit]

In [classical mechanics](#), **canonical coordinates** are coordinates q^i and p_i in [phase space](#) that are used in the [Hamiltonian formalism](#). The canonical coordinates satisfy the fundamental [Poisson bracket](#) relations:

$$\{q^i, q^j\} = 0 \quad \{p_i, p_j\} = 0 \quad \{q^i, p_j\} = \delta_{ij}$$

A typical example of canonical coordinates is for q^i to be the usual [Cartesian coordinates](#), and p_i to be the components of [momentum](#). Hence in general, the p_i coordinates are referred to as "conjugate momenta."

Canonical coordinates can be obtained from the [generalized coordinates](#) of the [Lagrangian formalism](#) by a [Legendre transformation](#), or from another set of canonical coordinates by a [canonical transformation](#).

4) Conjugate Variables (共轭变量)

4.1 中文

在热力学中，系统的内能可以由几组共轭变量的乘积来表示，例如温度/熵或压力/体积等。温度和熵二者互为共轭变量，压力和体积二者也互为共轭变量。除内能外，其他的热力学势也可以用共轭变量的乘积来表示。

在力学系统中，能量的微量变化可以表示为力和微量位移的乘积。在热力学中也有类似的情形，热力学中能量的变化可表示为几个（不平衡的）广义力和其产生的广义位移的乘积，广义力和广义位移称共轭变量，两者的乘积就是能量。热力学中的广义力恒为内含性质，而广义位移恒为外延性质。广义力是在其他外延性质不变的条件下，内能对广义位移的微分。

热力学势及共轭变量之间的关系可以用热力学方程来表示。

以下列出热力学中的共轭变量及其对应的国际单位制单位：

热参数：

- 温度: T (K)
- 熵: S ($J K^{-1}$)

力学参数：

- 压力: P ($Pa = J m^{-3}$)
- 体积: V ($m^3 = J Pa^{-1}$)

或是更广义的参数：

- 应力: σ_{ij} ($Pa = J m^{-3}$)
- 体积 \times 应变: $V \times \varepsilon_{ij}$ ($m^3 = J Pa^{-1}$)

材料参数：

- 化学势: μ (J)
- 粒子数: N (粒子数或摩尔数)

若一个系统有几种不同的粒子所组成，其内能的变化可以用下式来描述：

$$dU = TdS - PdV + \sum_i \mu_i dN_i ,$$

$-S$	U	V
H		F
$-p$	G	T

The thermodynamic square with potentials highlighted in red.

4.2 English Version

In thermodynamics, the internal energy of a system is expressed in terms of pairs of conjugate variables such as temperature and entropy or pressure and volume. In fact, all thermodynamic potentials are expressed in terms of conjugate pairs. The product of two quantities that are conjugate has units of energy or sometimes power.

For a mechanical system, a small increment of energy is the product of a force times a small displacement. A similar situation exists in thermodynamics. An increment in the energy of a thermodynamic system can be expressed as the sum of the products of certain generalized "forces" that, when unbalanced, cause certain generalized "displacements", and the product of the two is the energy transferred as a result. These forces and their associated displacements are called conjugate variables. The thermodynamic force is always an intensive variable and the displacement is always an extensive variable, yielding an extensive energy transfer. The intensive (force) variable is the derivative of the internal energy with respect to the extensive (displacement) variable, while all other extensive variables are held constant.

The number of particles is, like volume and entropy, the displacement variable in a conjugate pair. The generalized force component of this pair is the chemical potential. The chemical potential may be thought of as a force which, when imbalanced, pushes an exchange of particles, either with the surroundings, or between phases inside the system. In cases where there are a mixture of chemicals and phases, this is a useful concept. For example, if a container holds liquid water and water vapor, there will be a chemical potential (which is negative) for the liquid which pushes the water molecules into the vapor (evaporation) and a chemical potential for the vapor, pushing vapor molecules into the liquid (condensation). Only when these "forces" equilibrate, and the chemical potential of each phase is equal, is equilibrium obtained.

For a system with different types i of particles, a small change in the internal energy is given by:

$$dU = T dS - p dV + \sum_i \mu_i dN_i ,$$

where U is internal energy, T is temperature, S is entropy, p is pressure, V is volume, μ_i is the chemical potential of the i -th particle type, and N_i is the number of i -type particles in the system.

Here, the temperature, pressure, and chemical potential are the generalized forces, which drive the generalized changes in entropy, volume, and particle number respectively. These parameters all affect the internal energy of a thermodynamic system. A small change dU in the internal energy of the system is given by the sum of the flow of energy across the boundaries of the system due to the corresponding conjugate pair. These concepts will be expanded upon in the following sections.

While dealing with processes in which systems exchange matter or energy, classical thermodynamics is not concerned with the rate at which such processes take place, termed kinetics. For this reason, the term thermodynamics is usually used synonymously (同义) with equilibrium thermodynamics. A central notion for this connection is that of quasistatic processes, namely idealized, "infinitely slow" processes. Time-dependent thermodynamic processes far away from equilibrium are studied by non-equilibrium thermodynamics. This can be done through linear or non-linear analysis of irreversible processes, allowing systems near and far away from equilibrium to be studied, respectively.

Pressure/volume and stress/strain pairs

As an example, consider the PV conjugate pair. The pressure acts as a generalized force – pressure differences force a change in volume, and their product is the energy lost by the system due to mechanical work. Pressure is the driving force, volume is the associated displacement, and the two form a pair of conjugate variables.

The above holds true only for non-viscous fluids. In the case of viscous fluids, plastic and elastic solids, the pressure force is generalized to the stress tensor, and changes in volume are generalized to the volume multiplied by the strain tensor (Landau & Lifshitz 1986). These then form a conjugate pair. If σ_{ij} is the ij component of the stress tensor, and ε_{ij} is the ij component of the strain tensor, then the mechanical work done as the result of a stress-induced infinitesimal strain ε_{ij} is:

$$\delta w = V \sum_{ij} \sigma_{ij} d\varepsilon_{ij}$$

or, using Einstein notation for the tensors, in which repeated indices are assumed to be summed:

$$\delta w = V \sigma_{ij} d\varepsilon_{ij}$$

In the case of pure compression (i.e. no shearing forces), the stress tensor is simply the negative of the pressure times the unit tensor so that

$$\delta w = V (-p \delta_{ij}) d\varepsilon_{ij} = - \sum_k p V d\varepsilon_{kk}$$

The trace of the strain tensor (ε_{kk}) is the fractional change in volume so that the above reduces to $\delta w = -pdV$ as it should.

5) Grand Canonical Ensemble and Grand Canonical Partition Function

[https://en.wikipedia.org/wiki/Partition_function_\(statistical_mechanics\)](https://en.wikipedia.org/wiki/Partition_function_(statistical_mechanics))

Grand canonical partition function [\[edit\]](#)

Main article: Grand canonical ensemble

We can define a **grand canonical partition function** for a **grand canonical ensemble**, which describes the statistics of a constant-volume system that can exchange both heat and particles with a reservoir. The reservoir has a constant temperature T , and a **chemical potential** μ .

The grand canonical partition function, denoted by \mathcal{Z} , is the following sum over **microstates**

$$\mathcal{Z}(\mu, V, T) = \sum_i \exp\left(\frac{N_i \mu - E_i}{k_B T}\right).$$

Here, each microstate is labelled by i , and has total particle number N_i and total energy E_i . This partition function is closely related to the **Grand potential**, Φ_G , by the relation

$$-k_B T \ln \mathcal{Z} = \Phi_G = \langle E \rangle - TS - \mu \langle N \rangle.$$

This can be contrasted to the canonical partition function above, which is related instead to the **Helmholtz free energy**.

It is important to note that the number of microstates in the grand canonical ensemble may be much larger than in the canonical ensemble, since here we consider not only variations in energy but also in particle number. Again, the utility of the grand canonical partition function is that it is related to the probability that the system is in state i :

$$p_i = \frac{1}{\mathcal{Z}} \exp\left(\frac{N_i \mu - E_i}{k_B T}\right).$$

An important application of the grand canonical ensemble is in deriving exactly the statistics of a non-interacting many-body quantum gas (**Fermi–Dirac statistics** for fermions, **Bose–Einstein statistics** for bosons), however it is much more generally applicable than that. The grand canonical ensemble may also be used to describe classical systems, or even interacting quantum gases.

The grand partition function is sometimes written (equivalently) in terms of alternate variables as^[2]

$$\mathcal{Z}(z, V, T) = \sum_{N_i} z^{N_i} Z(N_i, V, T),$$

where $z \equiv \exp(\mu/kT)$ is known as the absolute **activity** (or **fugacity**) and $Z(N_i, V, T)$ is the canonical partition function.

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