Ab initio atomistic thermodynamics

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Thermodynamics

Why thermodynamics for materials?

A material is a collection of a large number of particles -- statistics starts to play a significant role at finite $T$

Thermodynamics determines defect concentrations and phase transformations, and influences magnetic properties, surface reactions, and crystal growth (the latter two are controlled by kinetics)

There is always a particle exchange between the material and its environment at finite $T$
Thermodynamics

Example

Consider a metal surface in an oxygen atmosphere

\[ \nu = \frac{p}{\sqrt{2\pi nmkT}} \]

For \( T = 300 \) K, \( p = 1 \) atm \( \Rightarrow \) \( \nu \sim 10^8 \) site\(^{-1}\) s\(^{-1}\)

Requires \( p \leq 10^{-12} \) atm to keep a “clean” surface clean; surface can also lose atoms

Adsorption will take place until the equilibrium is reached
Example

Consider a metal surface in an oxygen atmosphere.

The point of equilibrium depends on temperature, pressure, volume, …
Thermodynamics

- Thermodynamic potentials
  - Internal energy \( U(S, V, \{N\}) \)
  - Enthalpy \( H(S, p, \{N\}) = U + pV \)
  - Helmholtz free energy \( F(T, V, \{N\}) = U - TS \)
  - Gibbs free energy \( G(T, p, \{N\}) = U - TS + pV \)
  - Energy balance equation
    \[ dU = T dS - p dV + \sum_i \mu_i dN_i \]
  - With chemical potentials
    \[ \mu_i = \left( \frac{\partial U}{\partial N_i} \right)_{S,V} = \left( \frac{\partial H}{\partial N_i} \right)_{S,p} = \left( \frac{\partial F}{\partial N_i} \right)_{T,V} = \left( \frac{\partial G}{\partial N_i} \right)_{T,p} \]
Thermodynamics

- Reaching the equilibrium

At constant $T$ a system minimizes its free energy $(-TS)$, not the internal energy $U$

If also volume $V$ is constant, the energy minimized is the Helmholtz free energy $F = U - TS$

If $(T, p)$ are constant, the energy minimized is the Gibbs free energy $G = U + pV - TS$
Thermodynamics

Statistical thermodynamics

\[ S = k \log W \]

\( W \) - number of microstates for a given macrostate

This is “only” a postulate - but it works!

Why it should work: (i) in equilibrium \( W \to \text{max} \), so that \( S \to \text{max} \); (ii) \( S \) is additive, but \( W \) is multiplicative
Thermodynamics

Statistical thermodynamics

Let us consider a system that can be in one of states $i$ with energy $E_i$

At a given $T$, the probability of the system to be in state $i$ is

$$P_i = \frac{e^{-E_i/kT}}{Z}, \quad Z = \sum_i e^{-E_i/kT}, \quad \sum_i P_i = 1$$

Ergodic hypothesis: average over time is equal to the average over ensemble - holds if all states are equiprobable (for most realistic systems)

What are the values of entropy and thermodynamic potentials?
Thermodynamics

- **Statistical thermodynamics**
  Consider the ensemble of $N$ replicas of the system - let us count microstates of this ensemble

A microstate describes which replicas are in which state, while a macrostate describes how many replicas are in each state; thus: $W = \frac{N!}{N_1!(N-N_1)!} \frac{(N-N_1)!}{N_2!(N-N_1-N_2)!} \ldots = \frac{N!}{N_1!N_2!\ldots}$

where $N_1, N_2, \ldots$ are the numbers of the replicas in state 1, 2, 

$N_i = NP_i = N \frac{e^{-E_i/kT}}{Z}$, $\hat{S} = k\ln W = k\ln(N!) - k \sum_i \ln(N_i!)$

$Z$ - canonical *partition function*

Use Stirling’s formula: $\ln(N!) \approx N\ln N - N$
Thermodynamics

**Statistical thermodynamics**

\[
\tilde{S} = k \ln W = N k \ln Z + \frac{N}{TZ} \sum_i E_i e^{-E_i/kT}
\]

Internal energy, by definition:

\[
\tilde{U} = \frac{N}{Z} \sum_i E_i e^{-E_i/kT} = \frac{NkT^2}{Z} \frac{\partial Z}{\partial T}
\]

\[
U = \frac{\tilde{U}}{N} = \frac{kT^2}{Z} \frac{\partial Z}{\partial T} = kT^2 \frac{\partial \ln Z}{\partial T}
\]

\[
S = \frac{\tilde{S}}{N} = \frac{k \ln W}{N} = k \ln Z + \frac{U}{T} = k \ln Z + kT \frac{\partial \ln Z}{\partial T}
\]

\[
F = U - TS = -kT \ln Z
\]

\[
G = F + pV = -kT \ln Z + pV
\]

\[
\mu(T, p) = \left( \frac{\partial G}{\partial N_p} \right)_{T,p} = \frac{\partial}{\partial N} (-kT \ln Z + pV)_{T,p}
\]
Thermodynamics

- **Statistical thermodynamics**
  
  Practical example: surface free energy

\[ \mu_{O_2}(T, p_{O_2}) \]

Change in Gibbs free energy upon addition of O to the surface:

\[ \Delta G = G_{surf}(N_O + 1) - \left( G_{surf}(N_O) + \frac{1}{2} \mu_{O_2} \right) \]

since \( \mu_O = \frac{1}{2} \mu_{O_2} \)

Goal - find surface composition and structure that minimizes \( G \) at given \( T, p \)
Thermodynamics

- **Statistical thermodynamics**

  Practical example: surface free energy

  \[ \Delta \gamma (N_O, T, p) = \frac{1}{A} \left[ G_{\text{surf}} (N_O, T, p) - G_{\text{surf}} (N_{O}^{\text{ref}}, T, p) - \mu_O (N_O - N_{O}^{\text{ref}}) \right] \rightarrow \min_{N_O} \]

  where \( A \) is the surface area, \( N_{O}^{\text{ref}} \) is the number of O atoms in the reference system

  \[ G_{\text{surf}} (N_O) - G_{\text{surf}} (N_{O}^{\text{ref}}) = \Delta E_{\text{surf}} + \Delta U_{\text{vib}} - T \Delta S_{\text{vib}} - T \Delta S_{\text{conf}} + p \Delta V \]

  \[ \mu_O (T, p) - ? \]
Thermodynamics

- **Statistical thermodynamics**

  Let us consider a gas of \( N \) non-interacting diatomic (for simplicity) molecules.

  Each molecule has the following degrees of freedom: nuclear, electronic, *translational*, rotational, vibrational.

  \[
  Z = \frac{(z_{\text{transl}})^N}{N!} (z_{\text{rot}})^N (z_{\text{vib}})^N (z_{\text{el}})^N (z_{\text{nucl}})^N
  \]

  Translational states are invariant with respect to any permutations of molecules (indistinguishable molecules).

  \( z_x \) - partition function for the degree of freedom \( x \) for a single molecule.
Thermodynamics

- Statistical thermodynamics

\[ \mu(T, p) = \frac{\partial}{\partial N} (-NkT \ln(z_{transl}) + kT \ln N! - NkT \ln(z_{rot}) - \] 

Remember ideal gas law \( pV = NkT \) and Stirling’s formula

\[ \mu(T, p) = -kT \ln \left( \frac{z_{transl}}{N} \right) - kT \ln(z_{rot}) - kT \ln(z_{vib}) - kT \ln(z_{el}) - kT \ln(z_{nucl}) + kT \]

\[ \frac{z_{transl}}{N} = \frac{V}{N} \int e^{-\frac{\hbar k^2}{2mkt}} d^3k = \frac{V}{N} \left( \frac{2\pi mkT}{\hbar^2} \right)^{\frac{3}{2}} = \frac{kT}{p} \left( \frac{2\pi mkT}{\hbar^2} \right)^{\frac{3}{2}} \]

required input - molecule’s mass \( m \)

\[ z_{el} = \sum_i (2s_i + 1) e^{-\frac{E_i}{kT}} \approx (2s_0 + 1) e^{-\frac{E_0}{kT}} \rightarrow \mu_{el} \approx E_0 - kT \ln(2s_0 + 1) \]

required input - \( E_0, s_0 \)
Thermodynamics

- Statistical thermodynamics

\[ z_{\text{rot}} = \frac{1}{\sigma} \sum_J (2J + 1) e^{-\frac{B_0 J(J+1)}{kT}} \approx \frac{1}{\sigma} \int_0^\infty (2J + 1) e^{-\frac{B_0 J(J+1)}{kT}} dJ = \frac{T}{\sigma \theta_r} \]

where \( \sigma = 2 \) for homonuclear molecules (indistinguishable with respect to permutation of the two identical nuclei), \( \sigma = 1 \) for heteronuclear molecules,

\[ \theta_r = \frac{\hbar^2}{2kI}, \quad I = \frac{m_A m_B}{m_A + m_B} d^2, \quad d \text{ is the bond length} \]

\[ \mu_{\text{rot}} \approx -kT \ln \left( \frac{2kTI}{\sigma \hbar^2} \right), \text{required input - rotational constant } B_0 = \frac{\hbar^2}{2I} \]

(calculated or from microwave spectroscopy)
Thermodynamics

Statistical thermodynamics

$$z_{vib} = \prod_{i=1}^{M} \sum_{n=0}^{\infty} e^{-\left(n+\frac{1}{2}\right)\frac{\hbar\omega_i}{kT}} = \prod_{i=1}^{M} e^{-\frac{\hbar\omega_i}{2kT}} \sum_{n=1}^{\infty} e^{-\frac{n\hbar\omega_i}{kT}} =$$

$$= \prod_{i=1}^{M} \frac{e^{-\frac{\hbar\omega_i}{2kT}}}{1-e^{-\frac{\hbar\omega_i}{kT}}} \text{ (used the fact that sum over } n \text{ is a geometric series)}$$

For a diatomic molecule \(\mu_{vib} = \frac{\hbar\omega}{2} + kT \ln\left(1 - e^{-\frac{\hbar\omega}{kT}}\right)\)

required input - vibrational frequency \(\omega\)

In most practical cases, we can neglect the interaction between nuclear spins, so that \(z_{nucl} \approx 1\) (not correct at very low temperatures)
Ab initio atomistic thermodynamics

It is convenient to define a reference for \( \mu(T, p) \)

\[
\mu(T, p) = E_0 + \Delta \mu(T, p)
\]

Alternatively:

\[
\Delta \mu(T, p) = \Delta \mu(T, p^O) + k_B T \ln\left( \frac{p}{p^O} \right)
\]

and \( \Delta \mu(T, p^O = 1 \text{ atm}) \) from thermochemical tables (e.g., JANAF)
Thermodynamics

- *Ab initio* atomistic thermodynamics

\[
\mu_{O_2}(T, p_{O_2})
\]

\[
\Delta \gamma(N_O, T, p) = \frac{1}{A} \left[ \Delta E_{surf} + \Delta U_{vib} - T \Delta S_{vib} - T \Delta S_{conf} + p \Delta V - \mu_O \Delta N_O \right]
\]

electronic structure calculations

\[
\Delta F_{vib}(T, V) = V \int_0^\infty f(T, \omega) \left( \sigma(\omega) - \sigma_{ref}(\omega) \right) d\omega,
\]
 phonon density of states, \( f(T, \omega) = \frac{\hbar \omega}{2} + kT \ln(1 - e^{-\hbar \omega/kT}) \)
**Thermodynamics**

*Ab initio* atomistic thermodynamics

Example: Metal surface in contact with $O_2$ gas

Reservoir: $\mu_0(T, p_{O_2})$ from ideal gas, $N^\text{ref}_O = 0$ (bare metal surface is the reference system), $\frac{1}{2}E_{O_2}$ is the reference for the chemical potential of O: $\mu_0 = \Delta\mu_0 + \frac{1}{2}E_{O_2}$

Neglect for now $\Delta F_{\text{vib}}$ and $T\Delta S_{\text{conf}}$

$$\Delta\gamma(T, p_{O_2}) = \frac{1}{A} \left[ E_{\text{surf}}(N_O) - E_{\text{surf}}(0) - N_O \frac{1}{2}E_{O_2} \right] - \frac{1}{A} N_O \Delta\mu_0(T, p_{O_2})$$
Example: Pd(100)

\[ \Delta \gamma (T, p_{O_2}) = \frac{1}{A} \Delta E_{surf} (N_O) - \frac{1}{A} N_O \Delta \mu_O (T, p_{O_2}) \]

\( p(2\times2) \) O/Pd(100)

\( (\sqrt{5} \times \sqrt{5}) R27^\circ \) PdO(101)/Pd(100)

First-principles atomistic thermodynamics: constrained equilibria

\[ \mu_O(T, p_O) \quad \text{constrained equilibria} \quad \mu_CO(T, p_CO) \]

\[ \Delta \gamma(T, p_O) = \frac{1}{A} \left[ E_{surf}(N_O, N_CO) - E_{surf}^{ref} - N_O \frac{1}{2} E_{O2} - N_CO E_{CO} \right] \]

\[ -\frac{1}{A} N_O \Delta \mu_O(T, p_O) - \frac{1}{A} N_CO \Delta \mu_CO(T, p_CO) \]


Surface phase diagrams

CO oxidation on RuO₂(110)

When vibrations do matter

\[ \mu_0 \text{(eV)} \]

ZnO (0001) surface phase diagram in H$_2$O-O$_2$ atmosphere – no vibrations

No structure with (2x2) periodicity as seen at the ZnO(0001) surface annealed in a dry oxygen atmosphere (containing at maximum 2 ppm water)

When vibrations do matter

A (2x2)-O adlayer structure is stabilized by vibrational entropy effects

Observe at "humid" conditions

Thermodynamics of Defects

- Very small concentrations of defects can significantly alter materials properties

Small concentration of Fe impurities are visible by naked eye in intrinsically transparent MgO

Si semiconductors contain $10^{-9}$-$10^{-3}$ intentional impurities per atom
“My precious!”: Perfect defected gems

Cr:Al₂O₃  V:Al₂O₃  Fe:Al₂O₃  Fe:Al₂O₃

Impurities are responsible for the color of sapphire and many other precious stones

Typical concentrations: 100-10000 ppm

Fe,Ti:Al₂O₃
Entropy

\[ G = U + pV - TS \]

\[ S = k \ln W \]

\( W \) – number of microstates

1) Solid: vibrational entropy (phonons)
2) Solid: electronic entropy
3) Gas: vibrational, rotational, translational, etc. (part of \( \mu_i \))
4) Solid: defect disorder
Configurational entropy

\[ G = [U + pV - T(S - S_{\text{config}})] - TS_{\text{config}} = \tilde{G} - TS_{\text{config}} \]

\( N \) equivalent defect sites in the sold

\( n \) defects

If defects do not interact:

\[ S_{\text{config}} = k \ln \frac{N!}{n!(N-n)!} \]

Stirling’s formula:

\[ \ln(n!) = n(\ln n - 1 + \delta), \quad n \gg 1, \quad \delta \sim \frac{\ln(2\pi n)}{2n} \]

\[ S_{\text{config}} \approx k \left[ N \ln N - n \ln n - (N-n) \ln(N-n) \right] \]

Good approximation only on a macroscopic scale
Defect concentration

Minimize the free energy of the system with respect to the number of defects

\[ G(n) = \tilde{G}_0 + n\Delta G_f - TS_{\text{config}}(n) \]

If defects do not interact:

\[ \frac{n}{N} = \frac{1}{\exp(\Delta G_f / kT) + 1} \]

\[ \frac{n}{N} \ll 1 \iff \exp(\Delta G_f / kT) \gg 1 \]

\[ \frac{n}{N} \approx \exp\left(-\Delta G_f(T, p) / kT\right) \text{ – textbook formula} \]
Charged defects and charge compensation

\[ \frac{n}{N} = \frac{1}{\exp(\Delta G_f / kT) + 1} \]

for non-interacting defects

But can charged defects be considered as non-interacting?!

\[ V_{\text{interact}} = \frac{Q_1 Q_2}{|r_1 - r_2|} \]

Coulomb interaction – long-range!
For a system of charges:

\[ V_{\text{interact}} = \frac{Q_i Q_j}{|r_i - r_j|} \]

For a system of charges:

\[ V_{\text{interact}} = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{|r_i - r_j|} \]

In the thermodynamic limit \( (N \to \infty) \) the electrostatic energy of charges with any finite concentration diverges.

Charged defects must be compensated in realistic materials.
For a system of charges:

\[ V_{\text{interact}} = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{|r_i - r_j|} \]

In the thermodynamic limit \((N \to \infty)\) the electrostatic energy of charges with any finite concentration diverges.

Typical dependence of the defect formation energy as a function of unit cell size.
Charged defects and charge compensation

Typical dependence of the defect formation energy as a function of unit cell size

In standard periodic calculations the charge per unit cell is compensated by a uniform background charge (occurs naturally as a regularization of the Ewald summation)

The compensated defects interact much weaker with each other

But they do interact strongly with the compensating charge (~1/L)
Local and global effects of doping

In realistic semiconductors, charged defects can be compensated by the *depletion* of charge carriers (electrons or holes).

**Local effect of doping**
- Chemical bond formation,
- Local relaxation

**Global effect of doping**
- Interaction with the compensating charge

Formation energy and concentration of charged defects depend strongly on the distribution of the defects and the compensating charge.
Charged defects in a doped material

\[ \Delta G(n) = n \Delta G_f(n \to 0) + \frac{1}{2} \varepsilon_0 \int \varepsilon(\mathbf{r}) |\mathbf{E}|^2 d^3 r - TS_{\text{config}}(n) \]

- **formation energy in the dilute limit**
- **electrostatic energy at finite \( n \)**

\[ S_{\text{config}} = k \ln Z + \frac{U}{T} \]

The charged defects are screened by the compensating charge:

\[ S_{\text{config}} \approx k \ln \frac{N!}{n!(N-n)!} \]
Space charge formation and band bending

Space charge region $z_{SC} = \sigma/eN_D$ causes band bending and electric field

$N_D$ -- dopant concentration

$\sigma$ -- surface charge due to charged vacancies
Band bending

\[
\Delta G_f^{VCA} (\sigma, d) = E_{\text{vac}}^q (\sigma, d)(+q\varepsilon_{\text{VBM}}) - E_{\text{host}} (\sigma, d) + \frac{1}{2} E_{O_2}
\]
Band bending

$$\Delta G_f^{VCA} (\sigma, d) = E_{\text{vac}}^q (\sigma, d) (+q\varepsilon_{\text{VBM}}) - E_{\text{host}} (\sigma, d) + \frac{1}{2} E_{O_2}$$

\[ 1/L (\text{Å}^{-1}) \]

\[ \frac{1}{2} \varepsilon_0 \int |E|^2 d^3r = -C \sqrt{|\sigma|} + qE^{SC} (d), \quad E^{SC} (d) = \frac{e |\sigma|}{6\varepsilon_0} d \]
$^{2+}$ F concentration at $p$-MgO(001)

![Graphs showing the concentration of F as a function of dopant concentration at different temperatures.](image-url)
Sampling configurations

- Coarse-graining potential-energy surface (PES)
Sampling configurations: cluster expansion

- Coarse-graining potential-energy surface (PES)

Phase transformation in an alloy or adsorbate layer at a surface
Summary

- *Ab initio* atomistic thermodynamics approach allows to model materials in thermodynamic equilibrium at realistic temperatures and pressures from first principles.
- Surface phase diagrams and defect concentrations as a function of temperature and pressure are two prominent examples.
- Doping should be considered as a thermodynamic variable, along with temperature and pressure.