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 $T$. 
Example

Consider a metal surface in an oxygen atmosphere

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

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

Requires \( p \leq 10^{-12} \text{ atm} \) 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
    $$dU = TdS - pdV + \sum_i \mu_i dN_i$$

  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 $G = U + pV - TS = \sum_i \mu_i N_i$
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 \( W \to \max \), so that \( S \to \max \); (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:

  $W = \frac{N!}{N_1!(N-N_1)!} \frac{(N-N_1)!}{N_2!(N-N_1-N_2)!} \cdots = \frac{N!}{N_1!N_2!\cdots}$

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

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

  $Z$ - canonical partition function

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

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

Internal energy, by definition:

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

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

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

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

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

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

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

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

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

  \[ \mu_O(T, p) - ? \]
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
  \[ \mu(T, p) = \frac{\partial}{\partial N} \left( -NkT \ln(z_{\text{transl}}) + kT \ln N! - NkT \ln(z_{\text{rot}}) - NkT \ln(z_{\text{vib}}) - NkT \ln(z_{\text{el}}) - NkT \ln(z_{\text{nucl}}) + pV \right)_{T,p} \]

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

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

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

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

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

  required input - \( E_0, s_0 \)
**Thermodynamics**

- **Statistical thermodynamics**

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

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

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

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

(calculated or from microwave spectroscopy)
Thermodynamics

- Statistical thermodynamics

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

\[ = \prod_{i=1}^{M} e^{\frac{\hbar \omega_i}{2kT}} \frac{1}{1-e^{-\frac{\hbar \omega_i}{kT}}} \] (used the fact that sum over \(n\) 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)
Thermodynamics

- 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: $\Delta \mu(T, p) = \Delta \mu(T, p^\circ) + k_B T \ln(p / p^\circ)$

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

- **Ab initio** atomistic thermodynamics

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

\[
\Delta \gamma(N_0, T, p) = \frac{1}{A}\left[\Delta E_{surf} + \Delta U_{vib} - T\Delta S_{vib} - T\Delta S_{conf} + p\Delta V - \mu_0 \Delta N_0\right]
\]

Electronic structure calculations

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

Example: Metal surface in contact with $O_2$ gas

Reservoir: $\mu_0(T, p_{O_2})$ from ideal gas, $N_0^{ref} = 0$ (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 $\Delta F_{vib}$ and $T \Delta S_{conf}$

$$\Delta \gamma(T, p_{O_2}) = \frac{1}{A} \left[ E_{surf}(N_0) - E_{surf}(0) - N_0 \frac{1}{2} E_{O_2} \right] - \frac{1}{A} N_0 \Delta \mu_0(T, p_{O_2})$$
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

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

\[ \Delta \gamma(T, p_{O_2}) = \frac{1}{A} \left[ E_{surf}(N_O, N_{CO}) - E_{surf}^{ref} - N_O \frac{1}{2} E_{O_2} - N_{CO} E_{CO} \right] \]

\[ -\frac{1}{A} N_O \Delta \mu_O(T, p_{O_2}) - \frac{1}{A} N_{CO} \Delta \mu_{CO}(T, p_{CO}) \]


Surface phase diagrams

CO oxidation on RuO$_2$(110)

When vibrations do matter

$\mu_O (\text{eV})$

$\mu_H (\text{eV})$

ZnO (0001) surface phase diagram in $\text{H}_2\text{O-O}_2$ 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)

A (2x2)-O adlayer structure is stabilized by vibrational entropy effects. Observed at "humid" conditions.

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

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

Typical concentrations: 100-10000 ppm
Entropy

\[ G = U + pV - TS \]

\[ S = k \ln W \]

\[ W \text{ – number of microstates} \]

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 solid

\( n \) defects

If defects do not interact:

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

Stirling’s formula:

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

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

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:

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

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

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

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

for non-interacting defects

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

Q₁ ≠ 0  Q₂ ≠ 0

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

Coulomb interaction – long-range!
Charged defects and charge compensation

\[ Q_1 \neq 0 \quad \text{and} \quad Q_2 \neq 0 \]

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

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
Charged defects and charge compensation

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.
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 (\(\sim 1/L\)).
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)

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
Defect-defect interactions

\[ \frac{\partial G(T, \{p\}, \mu_e, \{n\})}{\partial n_i} = 0 \iff n_i \sim n_{\text{sites}} \exp(-\Delta G_f / kT) \]

Local interactions:
- Local relaxation
- Chemical bonding

Long-range (global) interactions:
- Charging
- Fermi level shifting

Charged defects at any finite concentration cannot be considered non-interacting
Charged defects in a doped material

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

formation energy in the dilute limit

electrostatic energy at finite \( n \)

\[ S_{\text{config}} = k \ln \left( \sum_m g_m(n) \exp(-E_m(n)/kT) \right) \]

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

For surface density of charged defects $\sigma$ with charge $qe$ per defect the surface charge density is $\sigma qe$

The thickness of the compensating charge layer: $z_{SC} = \frac{\sigma q}{n_d}$, where $n_d$ is a dopant concentration (assuming uniform distr.)

Using Gauss’ theorem:

$$E_z = \frac{1}{\varepsilon \varepsilon_0} (\sigma qe - n_d ez) - \text{electric field}$$

Electrostatic energy per area $S$:

$$\frac{E}{A} = \frac{1}{A} \int \frac{\varepsilon \varepsilon_0 E_z^2}{2} dV = \frac{\varepsilon \varepsilon_0}{2} \int_0^{z_{SC}} E_z^2 dz = \frac{1}{2 \varepsilon \varepsilon_0} \int_0^{n_d} (\sigma qe - n_d ez)^2 dz$$
Band bending

For surface density of charged defects $\sigma$ with charge $qe$ per defect the surface charge density is $\sigma q e$

The thickness of the compensating charge layer: $z_{SC} = \frac{\sigma q}{n_d}$, where $n_d$ is a dopant concentration (assuming uniform distr.)

Electrostatic energy per unit area: $\frac{E}{A} = \frac{\sigma^3 q^3 e^2}{6\varepsilon \varepsilon_0 n_d}$

The surface Gibbs free energy per unit area:

$$g = \sigma \left[ \Delta G_f (\sigma \rightarrow 0) - C q^2 \sqrt{\sigma} \right] + \frac{\sigma^3 q^3 e^2}{6\varepsilon \varepsilon_0 n_d} - T \frac{S_{\text{conf}}}{A}$$
$^2\text{F}^+$ concentration at $p$-MgO(001)

![Graphs showing concentration vs. dopant concentration at different temperatures](image)
Sampling configurations

- Coarse-graining potential-energy surface (PES)

![Diagram of potential-energy surface](image)
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 among the prominent examples.

- Doping should be considered as a thermodynamic variable, along with temperature and pressure.
The End ...