Mineral Physics I
Chapter 3. Lattice vibration
Section 1. Boltzmann distribution

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Fundamental concept of statistical mechanics

- Principle of equal a priori probabilities $\Rightarrow$ A state with the largest number of configurations, W, appears most probably.

- Entropy, S, is defined by:
  - $S \equiv k_B \ln W$ (3.2.1)
    - W: the number of configurations
    - $k_B = 1.380 \times 10^{-23}$ J/K: Boltzmann constant
    - The state with the largest S appears most probably.

- Temperature, T, is defined by:
  - $1/T = \left(\frac{\partial S}{\partial E}\right)_{other\ conditions}$ (3.2.2)
    - The rate of entropy increase with increasing energy

Boltzmann distribution

- Boltzmann distribution: the number of particles with energy ε_i in a system with the fixed large number of particles N and fixed energy E at a temperature T
  - $$n_i = \frac{N}{\sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)} \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \propto \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \quad (3.2.1)$$
    - $\exp\left(-\frac{\varepsilon_i}{k_B T}\right)$: Boltzmann factor
    - $\sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)$: partition function

- The average, mean, or expected value of a physical quantity x of the particle, $\langle x \rangle$
  - $$\langle x \rangle = \frac{\sum_i x_i n_i}{N} = \frac{\sum_i x_i \frac{N}{\sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)} \exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{N} = \frac{\sum_i x_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{\sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)} \quad (3.2.2)$$

Lagrange multiplier -1

- The method of Lagrange multipliers: a strategy for finding local maxima/ minima of a function subject to equality constraints
  - Find a point (a, b) where a function $f(x, y)$ has a maximum/minimum with a constraint $g(x, y) = 0$
    - Define Lagrangian function: $L(x, y) = f(x, y) + \lambda g(x, y)$ (3.2.3)
      - λ: Lagrange multiplier
    - The necessary conditions:
      - $\frac{\partial L(a,b)}{\partial x} = \frac{\partial L(a,b)}{\partial y} = \frac{\partial L(a,b)}{\partial \lambda} = 0$ (3.2.4)
      - The point (a, b) is different from points where $f(x, y)$ has maxima/minima without the constraint $g(x, y) = 0$
        - $g(x, y) = 0$ but $\frac{\partial f}{\partial x} \neq 0$ and $\frac{\partial f}{\partial y} \neq 0$ at (a, b)

Lagrange multiplier -2

q The reason for (3.2.4) $\frac{\partial L(a,b)}{\partial x} = \frac{\partial L(a,b)}{\partial y} = \frac{\partial L(a,b)}{\partial \lambda} = 0$

Ø $\frac{\partial L}{\partial \lambda} = \frac{\partial}{\partial \lambda}(f - \lambda g) = \frac{\partial \lambda}{\partial \lambda} g = g = 0$

ü Identical to the condition $g = 0$

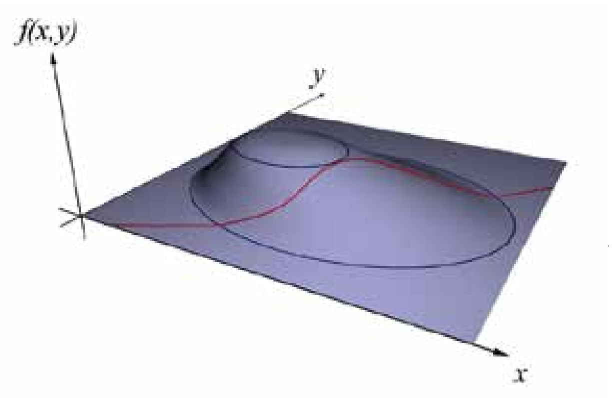
Ø $\frac{\partial L}{\partial x} = 0, \frac{\partial L}{\partial y} = 0$ à $\frac{\partial f}{\partial x} = \lambda \frac{\partial g}{\partial x}, \frac{\partial f}{\partial y} = \lambda \frac{\partial g}{\partial y}$

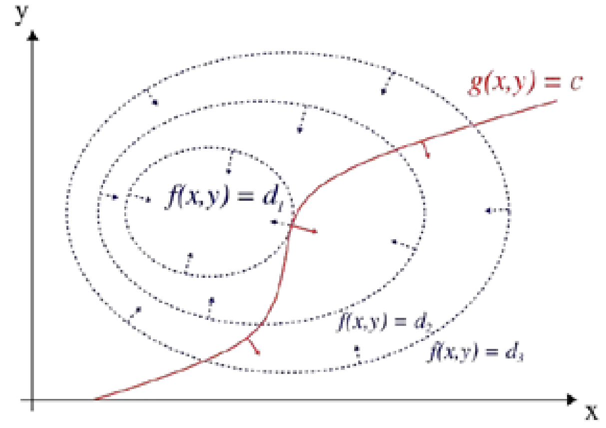
Ø $\left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}\right) = \lambda \left(\frac{\partial g}{\partial x}, \frac{\partial g}{\partial y}\right)$ (3.2.5)

ü $f = d_1$, $g = 0$ curves are parallel in the x-y plane

ü When (x, y) moves along $g = 0$, f does not change at a minimum/maximum (a, b)

§ à $f = d_1$, $g = 0$ are parallel at (a, b)





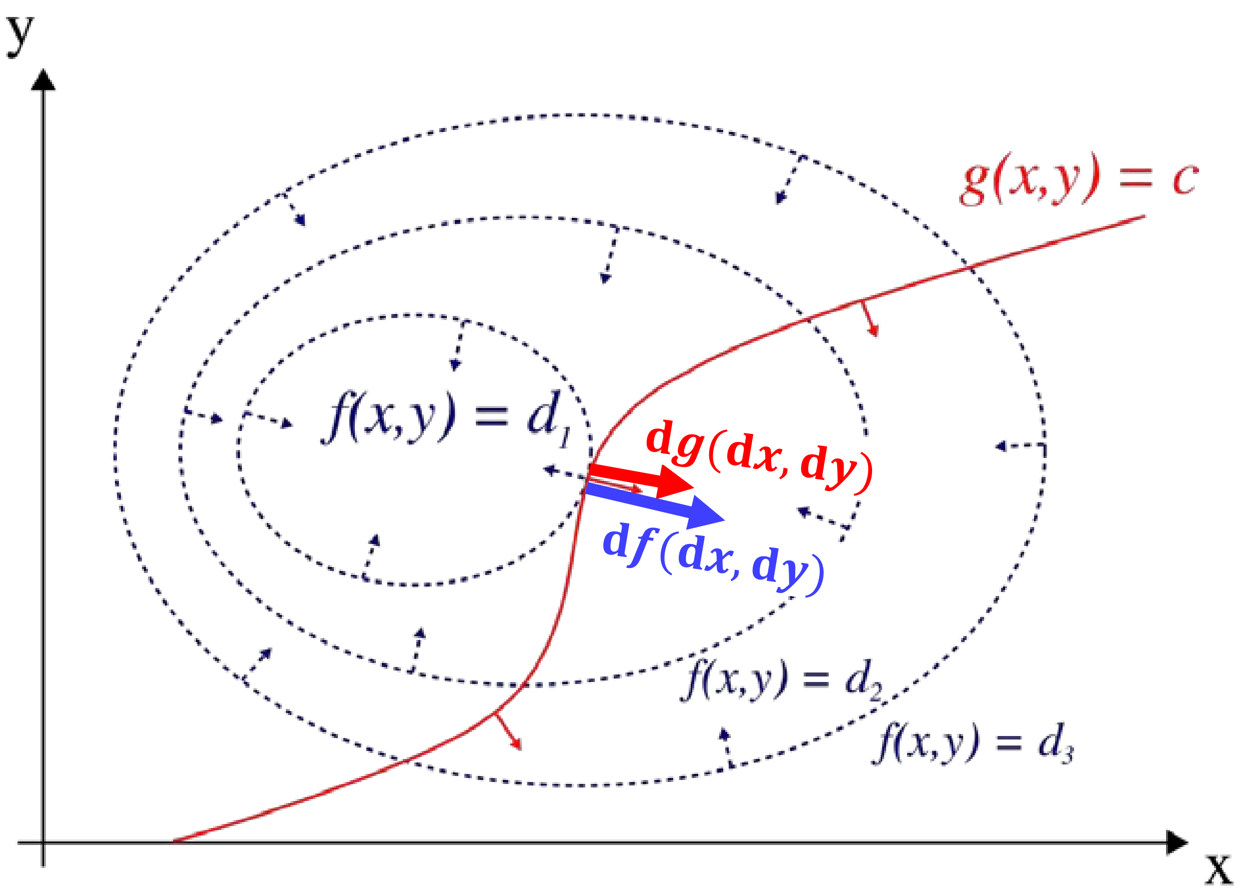
Red curve: the constraint $g(x, y) = c$. Blue curves: contours of $f(x, y)=d$.

Lagrange multiplier -3

q The meaning of λ

Ø $\left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}\right) = \lambda \left(\frac{\partial g}{\partial x}, \frac{\partial g}{\partial y}\right)$ (3.2.5)

ü The ratio of the change of $f(x, y)$ to the change of $g(x, y)$ by changing parameters (x, y), where $f(x, y)$ and $g(x, y)$ are not constant



Derivation of Boltzmann distribution -1

- Given conditions
  - A system composed of the fixed number of N particles with a fixed total energy E
    - N: very large
  - Energy of a particle: ε_i $\quad (i = 0, 1, 2, \ldots)$
  - The number of particles having an energy ε_i: n_i
- The total number of particles
  - $N = \sum_{i=0}^{\infty} n_i$ (3.2.6)
- The total energy of the system
  - $E = \sum_{i=0}^{\infty} n_i \varepsilon_i$ (3.2.7)
    - The total energy = sum of (energies of the particles)*(number of the particles)

Derivation of Boltzmann distribution -2

- The number of configuration of the system $(n_0, n_1, n_2, \ldots)$, W:
  - $W = \dfrac{N!}{n_0!n_1!\ n_2!\ldots}$ (3.2.8)
- The entropy of the system, S:
  - $S = k_B \ln W = k_B \ln \dfrac{N!}{n_0!n_1!\ n_2!\ldots} = k_B(\ln N! - \sum_i \ln n_i!)$ (3.2.9)
- The Stirling's approximation:
  - $\ln N! \cong N \ln N - N$ (3.2.10)
- Using the Stirling's approximation (3.2.10), $\ln W$ in (3.2.9) becomes
  - $\ln W \cong N \ln N - N - \sum_{i=0}^{\infty}(n_i \ln n_i - n_i)$ (3.2.11)

  $= N \ln N - \sum_{i=0}^{\infty} n_i \ln n_i - [N - \sum_{i=0}^{\infty} n_i] = N \ln N - \sum_{i=0}^{\infty} n_i \ln n_i$ (3.2.12)

  (3.2.6): $N = \sum_{i=0}^{\infty} n_i$

Derivation of Boltzmann distribution -3

q We will obtain the conditions for the largest $\ln W$ à $\mathrm{d}\ln W = 0$

q The total number of particles and the total energy of the system are fixed:

Ø (3.2.3) $N = \sum_{i=0}^{\infty} n_i$ à $\mathrm{d}N = \sum_{i=0}^{\infty} \mathrm{d}n_i = 0$ (3.2.13)

Ø (3.2.4) $E = \sum_{i=0}^{\infty} n_i \varepsilon_i$ à $\mathrm{d}E = \sum_{i=0}^{\infty} \varepsilon_i \mathrm{d}n_i = 0$ (3.2.14)

q Using (3.2.24), the change in the logarithmic number of microstates, $\ln W$, is

Ø
$$\begin{aligned}
\mathrm{d}\ln W &= \mathrm{d}\left(N \ln N - \sum_{i=0}^{\infty} n_i \ln n_i\right) \\
&= -\cancel{(\mathrm{d}N + N\mathrm{d}\ln N)} - \sum_{i=0}^{\infty}(\mathrm{d}n_i \ln n_i + n_i \mathrm{d}\ln n_i) \\
&= -\sum_{i=0}^{\infty}\left(\mathrm{d}n_i \ln n_i + \frac{\cancel{n_i}\mathrm{d}n_i}{\cancel{n_i}}\right) \\
&= -\sum_{i=0}^{\infty}(1 + \ln n_i)\,\mathrm{d}n_i \\
&\cong -\sum_{i=0}^{\infty} \ln n_i \,\mathrm{d}n_i \qquad (3.2.15)
\end{aligned}$$

ß $\mathrm{d}N = 0$, $\mathrm{d}\ln N = 0$, $\mathrm{d}\ln n_i = \frac{\mathrm{d}n_i}{n_i}$

Derivation of Boltzmann distribution -4

- Applying the method of Lagrange multiplier to obtain the maximum $\ln W$, which indicates the most probable state, under conditions of fixed N and E
  - $L = \ln W + \alpha N + \beta E$
    - α, β: Lagrange multiplier, constant
  - $\mathrm{d}L = \mathrm{d}\ln W + \alpha \mathrm{d}N + \beta \mathrm{d}E$

    $= -\sum_{i=0}^{\infty} \ln n_i \, \mathrm{d}n_i - \alpha \sum_{i=0}^{\infty} \mathrm{d}n_i - \beta \sum_{i=0}^{\infty} \varepsilon_i \mathrm{d}n_i$
    - (3.2.15): $\mathrm{d}\ln W = -\sum_{i=0}^{\infty} \ln n_i \, \mathrm{d}n_i$, (3.2.13): $\mathrm{d}N = \sum_{i=0}^{\infty} \mathrm{d}n_i$, (3.2.14): $\mathrm{d}E = \sum_{i=0}^{\infty} \varepsilon_i \mathrm{d}n_i$
  - $\mathrm{d}L = -\sum_{i=0}^{\infty} (\ln n_i + \alpha + \beta\varepsilon_i)\, \mathrm{d}n_i$ (3.2.16)
  - $\mathrm{d}L = \sum_{i=0}^{\infty} (\ln n_i + \alpha + \beta\varepsilon_i)\, \mathrm{d}n_i = 0$ (3.2.17)
  - $\ln n_i + \alpha + \beta\varepsilon_i = 0$ (3.2.18)

Derivation of Boltzmann distribution -5

- (3.2.18) $\ln n_i + \alpha + \beta\varepsilon_i = 0$ provides the form of the Boltzmann distribution
  - $n_i = \exp(-\alpha - \beta\varepsilon_i) = \exp(-\alpha)\exp(-\beta\varepsilon_i) = A\exp(-\beta\varepsilon_i)$ (3.2.19)
    - $\ln n_i$ and ε_i are balanced to maximize W at constant N and E

- Determining the constant β
    - $\ln n_i + \alpha + \beta\varepsilon_i = 0$
    - $n_i \ln n_i + \alpha n_i + \beta n_i \varepsilon_i = 0$
    - $\Sigma_i n_i \ln n_i + \alpha\Sigma_i n_i + \beta\Sigma_i n_i \varepsilon_i = 0$ (3.2.20)
  - Using (3.2.9) $\ln W \cong N\ln N - \Sigma_i n_i \ln n_i$
    - $N\ln N - \ln W + \alpha\Sigma_i n_i + \beta\Sigma_i n_i \varepsilon_i = 0$
  - By multiplying Eq. (3.2.21) by k_B
      - $k_B N\ln N - k_B\ln W + \alpha k_B\Sigma_i n_i + \beta k_B\Sigma_i n_i \varepsilon_i = 0$ (3.2.21)

Derivation of Boltzmann distribution -6

- From the definition of entropy (3.2.9) $S = k_B \ln W$, (3.2.21) $k_B N \ln N - k_B \ln W + \alpha k_B \Sigma_i n_i + \beta k_B \Sigma_i n_i \varepsilon_i = 0$ becomes
  - $k_B N \ln N - S + \alpha k_B N + \beta k_B E = 0$
  - $S = k_B N \ln N + \alpha k_B N + \beta k_B E$ (3.2.22)
- Differentiation of (3.2.22) by E
- $\frac{\mathrm{d}S}{\mathrm{d}E} = \frac{\mathrm{d}}{\mathrm{d}E}(k_B N \ln N + \alpha k_B N + \beta k_B E) = \beta k_B$ (3.2.23)
- From the definition of the temperature, T, $\frac{\mathrm{d}S}{\mathrm{d}E} = \frac{1}{T}$
  - $\beta k_B = \frac{1}{T} \Rightarrow \beta = \frac{1}{k_B T}$ (3.2.24)

Derivation of Boltzmann distribution -7

- Determination of the factor A
  - Substituting (3.2.35) $\beta = \frac{1}{k_B T}$ into (3.2.29) $\ln n_i + \alpha + \beta\varepsilon_i = 0$
    - $\ln n_i + \alpha + \varepsilon_i / k_B T = 0$ (3.2.36)
    - $n_i = \exp(-\alpha) \exp\left(-\frac{\varepsilon_i}{k_B T}\right) = A \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$ (3.2.37)
  - Substituting (3.2.37) into (3.2.17) $N = \sum_i n_i$
    - $N = \sum_i A \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$
    - $A = \frac{N}{\sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right)}$ (3.2.38)
- Boltzmann distribution
  - $n_i = \frac{N}{\sum_j \exp\left(-\frac{\varepsilon_j}{k_B T}\right)} \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \propto \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$ (3.2.39)

Why $n_i \propto \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$?

q The probability where a state $(n_0, n_1, n_2, \ldots)$ appears: proportional to the number of configuration, $W = \frac{N!}{n_0! n_1!\ n_2! \ldots}$

q The entropy is the natural logarithm of the number of configuration: $S = k_B \ln W$

Ø à The probability should proportional to $\exp(S/k_\mathrm{B})$

q When many particles have the same energy ε_i, the number of configuration decreases: $\mathrm{d} \ln W = -\sum_{i=0}^{\infty} \ln n_i \,\mathrm{d}n_i$

q The Lagrange multiplier $\beta = \frac{1}{k_B T}$: the ratio of the changes in $\frac{S}{k_\mathrm{B}} = \ln W$ to E à $\exp\left(-\frac{\varepsilon_i}{k_B T}\right)$: how W decreases by E change by ε_i increase à proportional to n_i

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