

SAMPLE SOLUTION

1 Concepts and Understanding (S2024.1)

Note that the answers given below are more detailed (for didactical purposes!) than what was actually expected from the students during the examination.

- a. For a four-state quantum-mechanical system with equidistant non-degenerate energy levels $E_n = n\Delta E$ for $n = 0, 1, 2, 3$, the equation giving the populations in the canonical ensemble (Boltzmann distribution) reads

$$P_n = \frac{e^{-E_n/(k_B T)}}{e^{-E_0/(k_B T)} + e^{-E_1/(k_B T)} + e^{-E_2/(k_B T)} + e^{-E_3/(k_B T)}} .$$

Inserting $E_n = n\Delta E$ and $T = k_B^{-1}\tilde{T}\Delta E$, one gets

$$P_n = \frac{e^{-n/\tilde{T}}}{1 + e^{-1/\tilde{T}} + e^{-2/\tilde{T}} + e^{-3/\tilde{T}}} .$$

When $\tilde{T} \rightarrow 0$, *i.e.* at the absolute zero, the terms $e^{-n/\tilde{T}}$ become negligible unless $n = 0$ (in which case we get one), so that only the ground state is populated, corresponding to the populations $\{1, 0, 0, 0\}$ (*i.e.* the answer here is B→1). When $\tilde{T} \rightarrow \infty$, *i.e.* when the temperature gets extremely high, the terms $e^{-n/\tilde{T}}$ become equal to one (irrespective of n), so that all the states get equally populated (*i.e.* the answer here is A→4). For $\tilde{T} = 1$ and $\tilde{T} = 2$, the populations decreases exponentially with n , and the decrease is steeper in the former compared to the latter case (*i.e.* the answers here are D→2 and C→3).

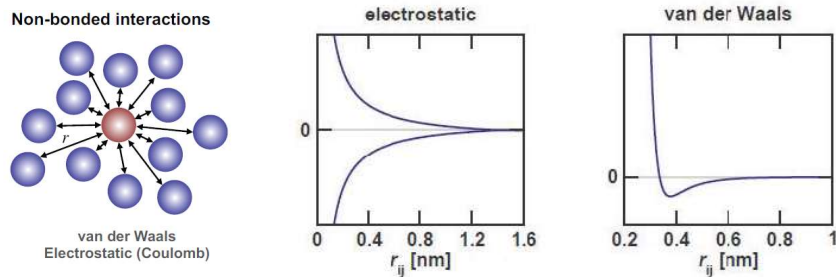
- b. Classical force fields typically include two types of pairwise non-bonded interaction terms that depend on the distance r_{ij} between two atoms i and j . The electrostatic term describes the charge-charge interaction between atomic partial charges (usually) located on the atoms. This interaction is typically described using Coulomb's law

$$V_{Cb}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_o r_{ij}} ,$$

where q_i and q_j are the partial charges and ϵ_o is the permittivity of vacuum. The van der Waals interaction describes the strong short-range repulsion upon atom overlap (due to Pauli exclusion) and the longer-range attraction caused by electron correlation (instantaneous-dipole-induced-dipole interactions, termed London dispersion). This interaction is commonly described using the Lennard-Jones function

$$V_{LJ}(r_{ij}) = -\frac{C_6}{r_{ij}^6} + \frac{C_{12}}{r_{ij}^{12}} ,$$

where C_6 and C_{12} are the dispersion and repulsion coefficient, respectively. A sketch of the corresponding two functions is shown below.



2 Fundamental Equations (S2024.2)

Note that the answers given below are more detailed (for didactical purposes!) than what was actually expected from the students during the examination. Watch out not to overlook the requirements “**explain the meaning** of all the involved symbols” and “**state the SI units** of these quantities”.

- a. The ideal-gas equation of state reads

$$PV = nRT ,$$

P is the pressure (units: $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{m}^{-3}$), V is the volume (units: m^3), n is the number of moles (units: mol), T is the absolute temperature (units: K) and R is the gas constant (units: $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). In terms of microscopic properties, the ideal-gas approximation is valid under the assumption that the interaction between the molecules (or atoms) in the gas is negligible. This amounts to the neglect of through-space interactions (*e.g.* medium-range dispersive attraction) as well as excluded-volume effects (*i.e.* short-range overlap repulsion). The only way the particles affect each other is through elastic collisions at contact between point-like objects. The latter effectively randomize the velocities (at constant total momentum and kinetic energy for each collision). In terms of macroscopic conditions, this is satisfied when the molar density n/V of the gas is low, which implies that the ratio P/T is low as well (*i.e.* ideality holds in the limit of low pressure and high temperature). The van der Waals real-gas equation of state reads

$$P = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2 .$$

The SI units are: a ($\text{kJ}\cdot\text{m}^3\cdot\text{mol}^{-3}$) and b ($\text{m}^3\cdot\text{mol}^{-1}$). The correction term involving a accounts for the effect of the intermolecular (or interatomic) interactions (typically slightly attractive). The correction term involving b accounts for the effect of the excluded volume of the molecules (or atoms).

- b. The typical potential-energy term for a bond-stretching term is the harmonic function

$$V_{\text{bnd}}(b) = \frac{1}{2} k_b (b - b_o)^2 .$$

Here, V_{bnd} is the potential energy (units: $\text{kJ}\cdot\text{mol}^{-1}$), b the bond length in a given configuration (units: nm), b_o the reference bond length (units: m), and k_b the harmonic force constant (units: $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{m}^{-2}$). Appropriate values of b_o for a given bond type can be inferred from quantum-mechanical calculations (theoretical) or from crystallographic structure determinations (experimental), as the bond distance in the relaxed geometry of simple model molecules. Appropriate values of k_b for a given bond type can be inferred from quantum-mechanical calculations (theoretical) or from infrared/Raman spectroscopy measurements (experimental), considering the frequency of the corresponding vibration in simple model molecules. The equation allowing to calculate the bond length i - j from the Cartesian position vectors \mathbf{r}_i and \mathbf{r}_j in a computer-simulation program reads

$$b = (\mathbf{r}_{ij} \cdot \mathbf{r}_{ij})^{1/2} ,$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. So, in practice, we must calculate the scalar product of the vector \mathbf{r}_{ij} with itself, and then take the square-root.

- c. The leap-frog equations read

$$\mathbf{v}(t + \Delta t/2) = \mathbf{v}(t - \Delta t/2) + \mathbf{a}(t)\Delta t$$

and

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t + \Delta t/2)\Delta t ,$$

where \mathbf{r} is the position, \mathbf{v} the velocity, and \mathbf{a} the acceleration (force divided by mass). Here, the SI units are: Δt (s), \mathbf{r} (m), \mathbf{v} ($\text{m}\cdot\text{s}^{-1}$) and \mathbf{a} ($\text{m}\cdot\text{s}^{-2}$). The order of magnitude of the error (largest neglected term) is $(\Delta t)^3$. This is the advantage of interleaving, *i.e.* of having asynchronous coordinates and velocities, namely that it cancels out the term in $(\Delta t)^2$ that would otherwise be the leading error. The trade-off involved in the choice of a reasonable Δt is the following. A too small Δt will lead to unnecessarily limited total sampling time for a given number of steps (*i.e.* for a given computational cost). A too large Δt will lead to an inaccurate integration of the equations of motion (*i.e.* numerical noise and, in the worst case, program failure). The order of magnitude of Δt typically selected in atomistic simulations is about a femtosecond (10^{-15} s). The application of bond-length constraints (rather than harmonic bonds) eliminates the fastest oscillations from the system, allowing to increase the timestep (typically from 0.5 to 2 fs).

3 Derivations (S2024.3)

a. The normalization condition reads

$$1 = \int_{-\infty}^{\infty} dx p(x) = c \int_{-\infty}^{\infty} dx e^{-(x-a)^2/b} = 2c \int_0^{\infty} dy e^{-y^2/b} = 2c \frac{1}{2} (\pi b)^{1/2} = c(\pi b)^{1/2} ,$$

where the third equality follows from the change of variable $y = x - a$ (with $dy = dx$) and from noting that the integrand is even around $y = 0$ after this change. This equation is satisfied with $c = (\pi b)^{-1/2}$, so that the normalized probability distribution reads

$$p(x) = (\pi b)^{-1/2} e^{-(x-a)^2/b} .$$

The mean μ of $p(x)$ is given by

$$\begin{aligned} \mu &= \int_{-\infty}^{\infty} dx x p(x) = (\pi b)^{-1/2} \int_{-\infty}^{\infty} dy (y + a) e^{-y^2/b} = (\pi b)^{-1/2} 2a \int_0^{\infty} dy e^{-y^2/b} \\ &= (\pi b)^{-1/2} 2a \frac{1}{2} (\pi b)^{1/2} = a , \end{aligned}$$

where the second equality follows from the change of variable $y = x - a$ (with $dy = dx$), while the third equality follows from noting that the part of the integrand involving y is odd around $y = 0$ (leading to a vanishing integral) and that the part of the integrand involving a is even. Thus, the mean μ is equal to the parameter a . The variance σ^2 of $p(x)$ is given by

$$\begin{aligned} \sigma^2 &= \int_{-\infty}^{\infty} dx (x - a)^2 p(x) = (\pi b)^{-1/2} \int_{-\infty}^{\infty} dy y^2 e^{-y^2/b} = (\pi b)^{-1/2} 2 \int_0^{\infty} dy y^2 e^{-y^2/b} \\ &= (\pi b)^{-1/2} 2 \frac{1}{4} (\pi b^3)^{1/2} = (1/2)b , \end{aligned}$$

where the second equality follows from the change of variable $y = x - a$ (with $dy = dx$). So, the variance σ^2 is equal to half the parameter b . If the unit of x is nm, the units of $p(x)$ and c are nm^{-1} , the units of a , μ and σ are nm, and the unit of b is nm^2 . It is a common mistake to think that a probability distribution is “unitless” or with “arbitrary units”. If the distribution is normalized, the normalization condition (see above) imposes that the product of the units of dx and $p(x)$ is unitless (like the resulting “one”). So, the units of $p(x)$ are inverse to the units of x .

b. The expression for the classical canonical ensemble average $\langle \mathcal{A} \rangle$ of an instantaneous observable \mathcal{A} in the unbiased ensemble (Hamiltonian \mathcal{H}) is

$$A = \langle \mathcal{A} \rangle = \xi Z^{-1} \int d\mathbf{r} d\mathbf{p} \mathcal{A} e^{-\beta \mathcal{H}} ,$$

where the classical partition function Z reads

$$Z = \xi \int d\mathbf{r} d\mathbf{p} e^{-\beta \mathcal{H}} ,$$

with $\xi = (h^{3N} N!)^{-1}$ for N indistinguishable particles, h being the Planck constant. The corresponding equations for the biased ensemble considering an observable \mathcal{X} are

$$X = \langle \mathcal{X} \rangle_B = \xi Z_B^{-1} \int d\mathbf{r} d\mathbf{p} \mathcal{X} e^{-\beta(\mathcal{H} + \mathcal{V}_B)} ,$$

with

$$Z_B = \xi \int d\mathbf{r} d\mathbf{p} e^{-\beta(\mathcal{H} + \mathcal{V}_B)} .$$

Replacing the observable \mathcal{X} by $\mathcal{A}e^{+\beta\mathcal{V}_B}$ in the two latter equations, one recovers the two former equations. Thus, one may write

$$A = \langle \mathcal{A} \rangle = \langle \mathcal{A}e^{+\beta\mathcal{V}_B} \rangle_B ,$$

which is the reweighting formula.

4 Explicit Calculations (S2024.4)

- a. Using the equation for the harmonic potential energy one has

$$V(\theta_o \pm \Delta\theta; \theta_o) = \frac{1}{2}k_\theta(\Delta\theta)^2.$$

Inserting the numerical values $k_\theta = 0.10 \text{ kJ}\cdot\text{mol}\cdot\text{deg}^{-2}$ and $\Delta\theta = 5 \text{ deg}$, one gets $V = 1.25 \text{ kJ}\cdot\text{mol}^{-1}$. In comparison, the thermal energy RT at $T = 300 \text{ K}$ is $2.49 \text{ kJ}\cdot\text{mol}^{-1}$. So, a bond-angle change of 5 deg corresponds to an energy increase by about $RT/2$, *i.e.* the typical H-O-H bond-angle fluctuations in molecular dynamics simulations using this water model are expected to be slightly larger than 5 deg. (for RT , one would get would be $5 \cdot 2^{1/2} \approx 7.1 \text{ deg}$).

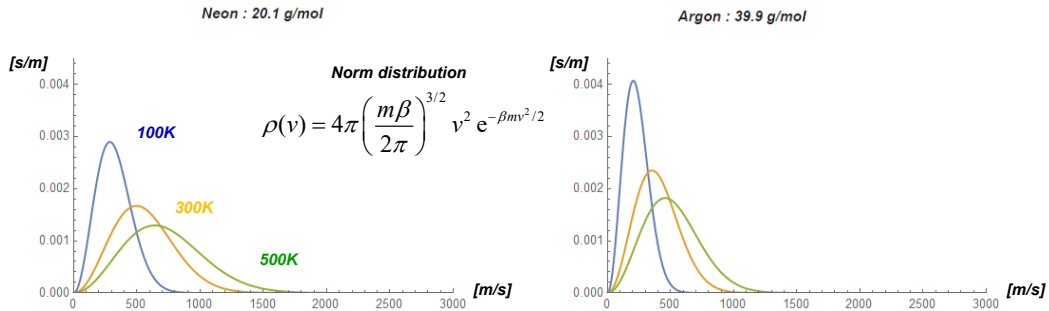
- b. Inserting the quantities with the appropriate units into the equation for $\overline{v^2}^{1/2}$, one gets

$$\overline{v^2}^{1/2} = \left(\frac{3 \times 8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times (25 + 275) \text{ K}}{0.02 \text{ kg} \cdot \text{mol}^{-1}} \right)^{1/2} = 600 \text{ m} \cdot \text{s}^{-1}. \quad (3)$$

When T is doubled, $\overline{v^2}^{1/2}$ is amplified by a factor $2^{1/2} \approx 1.41$, so, it is increased by 41%. When m is doubled, $\overline{v^2}^{1/2}$ is amplified by a factor $2^{-1/2} \approx 0.71$, so, it is decreased by 29%. These trends can be explained simply based on the equipartition principle. At a temperature T , each degree of freedom (*e.g.* each of the three Cartesian velocity components of an atom) stores on average a quantity $k_B T/2$ of kinetic energy. For an atom of mass m , the instantaneous kinetic energy is given by $mv^2/2$. It follows that on average, v grows in proportion to $T^{1/2}$ and to $m^{-1/2}$. The functional form of the Maxwell-Boltzmann distribution given by

$$p(v) = C v^2 e^{-\beta m v^2/2}. \quad (4)$$

This corresponds to the probability of realizing a vector norm v (given by the Boltzmann factor of the associated kinetic energy, *i.e.* proportional to $e^{-\beta m v^2/2}$) multiplied by the number of ways of realizing such a vector norm in terms of the three Cartesian components (given by the surface of a sphere of radius v , *i.e.* proportional to v^2). The constant C can be determined from the normalization constraint (but this was not asked here). The distribution is sketched below for different choices of m and T .



It is skewed towards the right. As a result, one expects the the most probable velocity v^* to be slightly lower than the the mean velocity \bar{v} , and the mean velocity to be slightly lower than the root-mean-square velocity $\overline{v^2}^{1/2}$. The corresponding equations are (but this was not asked here)

$$v^* = \left(\frac{2k_B T}{m} \right)^{1/2}, \quad \bar{v} = \left(\frac{8k_B T}{\pi m} \right)^{1/2}, \quad \text{and} \quad \overline{v^2}^{1/2} = \left(\frac{3k_B T}{m} \right)^{1/2}, \quad (5)$$

where $2^{1/2} = 1.41$, $(8/\pi)^{1/2} = 1.60$, and $3^{1/2} = 1.73$. The Maxwell-Boltzmann distribution (like the equipartition theorem) is generally valid, independently of the phase. So, the values of $\overline{v^2}^{1/2}$ in liquid neon and in gas-phase neon at the same temperature T are identical.

5 Algorithms and Implementation (S2024.5)

a. A possible code for the function MorseEnergy is given below

```
double MorseEnergy (int N, double x[], double y[], double z[],
                    double a, double b, double c) {
    int i,j; // particle indexes
    double r2; // for r^2
    double ene = 0;
    for ( i=0; i<N; i++ ) {
        for ( j=i+1; j<N; j++ ) {
            r2 = (x[j]-x[i])*(x[j]-x[i])
                + (y[j]-y[i])*(y[j]-y[i])
                + (z[j]-z[i])*(z[j]-z[i]);
            double r = sqrt(r2);
            double fac = 1.0 - exp( -a*(r-b) );
            ene += fac*fac;
        }
    }
    return c * ene;
}
```