Lösungen zum Übungsblatt 3

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Problem 1: Simple model of 1-d ionic conductor

Introduction

In this task we regard mobile charged ions in a conductor that is a 1-d regular lattice of atoms. In one timestep, each ion performs a hop from one position x_i to the neigbored atom - either to the right or to the left. The probability of each direction is given by P_r and $P_l = 1 - P_r$ and depends on the applied electric field E and the temperature T:

$$P_R = \frac{1}{2}\left(1 + \frac{\varepsilon E}{kT}\right) \quad , \tag{1}$$

where k is the Bolzmann constant an ε a parameter. In this model we ignore any kind of interaction between two charged particles.

The following issues will be looked at:

a) The probability $P(i,n)$ of finding an ion at position i after the duration of n time steps.

b) The average position $\langle X(n) \rangle$ of one ion after n time steps and its variance $\langle X(n) - \langle X(n) \rangle \rangle$.

c) The way of decribing the process as a Markov chain.

Methods

a) We split the whole quantity of time steps n into the number of hops to the left n_l and such to the right n_r. Then, we derive the position i of the ion depending on n_l and n_r. Using the probabilities P_l and P_r we get the function $P(i,n)$ of interest.

b) Number a) leads to a binomial distribution, and we will derive its average and variance.

c) We set up the Master equation of this Markov process.

Results

a) The probability $P(i,n)$ of finding an ion at position i after the duration of n time steps is given by:

$$P(i,n) \;=\; \frac{n!}{\left(\frac{n+i}{2}\right)!\left(\frac{n-i}{2}\right)!} \cdot P_r^{(n+i)/2} \cdot P_l^{(n-i)/2} \quad . \tag{2}$$

b) Average and variance are given by:

$$\langle X(n)\rangle = n(P_r - P_l) \tag{3}$$

and

$$\Delta\langle X(n)\rangle^2 = 4nP_rP_l \quad . \tag{4}$$

c) The Master equation of this Markov process is:

$$\dot{P}(n) = [P_rP(i,n) - P_lP(i+1,n)] + [P_lP(i,n) - P_rP(i-1,n)] \quad . \tag{5}$$

Discussion

If the probability of hops to the left is greater than the probability of hops to the right, the majority of ions will get to the left side of the conductor, and vice-versa. Regarding (3), the average position after n time steps is obviously popotional to the difference $P_r - P_l$.

This model, that is very similar to the random walk problem, is a simple way to describe the process in an ionic conductor. Unfortunately, due to the neglect of any interaction between the charged particles, the model is very limited for treating real ionic conductors.

Appendix

a) Let Δa be the distance between two atoms. After the ion's performing n_r hops to the right and n_l to the left, it will be located at:

$$x_i = n_r \cdot \Delta a - n_l \cdot \Delta a \quad . \tag{6}$$

With $n_l = n - n_r$ we obtain:

$$x_i = (2n_r - n)\Delta a = i \cdot \Delta a \quad . \tag{7}$$

It's obvious that the last equation can only be true, if n and i both are either even or odd. Transfiguring the last relation, we obtain:

$$n_r = \frac{n+i}{2} \tag{8}$$

$$n_l = \frac{n-i}{2} \quad . \tag{9}$$

Two different ways from x_0 to position i within the same amount of time steps only differ in the arrangement of hops to the left and ones to the right, but not in the numbers n_l or n_r. That's why the probability of one way to position i is given by:

$$P_r^{n_r} \cdot P_l^{n_l} = P_r^{(n+i)/2} \cdot P_l^{(n-i)/2} \quad . \tag{10}$$

The number of possible ways to position i within n time steps is:

$$\binom{n}{n_r} = \binom{n}{n-n_r} = \binom{n}{n_l} \quad . \tag{11}$$

where n_r and n_l are given by (4) and (5). With the number of possible ways to position i within n steps and the probability of one single way, we obtain the probability of the ion getting there, no matter on witch way:

$$\begin{aligned} P(i,n) &= \binom{n}{n_r} \cdot P_r^{(n+i)/2} \cdot P_l^{(n-i)/2} & (12) \\ &= \frac{n!}{n_r!(n-n_r)!} \cdot P_r^{(n+i)/2} \cdot P_l^{(n-i)/2} & (13) \\ &= \frac{n!}{\left(\frac{n+i}{2}\right)!\left(\frac{n-i}{2}\right)!} \cdot P_r^{(n+i)/2} \cdot P_l^{(n-i)/2} \quad . & (14) \end{aligned}$$

b) The average $\langle n_r \rangle$ for a constant n is given by:

$$\langle n_r \rangle = \sum_{n_r=0}^{n} n \binom{n}{n_r} P_r^{n_r} \cdot P_l^{n_l} = \sum_{n_r=0}^{n} n \binom{n}{n_r} P_r^{n_r} \cdot P_l^{n-n_r} \quad . \tag{15}$$

This can obviously be written as:

$$\begin{aligned} \langle n_r \rangle &= P_r \frac{\partial}{\partial P_r} \left[\sum_{n_r=0}^{n} \binom{n}{n_r} P_r^{n_r} \cdot P_l^{n_l} \right] & (16) \\ &= P_r \frac{\partial}{\partial P_r} [(P_r + P_l)^n] & (17) \\ &= n\, P_r \underbrace{(P_r + P_l)}_{=1}{}^{n-1} & (18) \\ &= n\, P_r \quad . & (19) \end{aligned}$$

The same thoughts lead to:

$$\begin{aligned} \langle n_l \rangle &= P_l \frac{\partial}{\partial P_l} \left[\sum_{n_l=0}^{n} \binom{n}{n_l} P_r^{n_r} \cdot P_l^{n_l} \right] & (20) \\ &= P_l \frac{\partial}{\partial P_l} [(P_r + P_l)^n] & (21) \\ &= n\, P_l (P_r + P_l)^{n-1} & (22) \\ &= n\, P_l \quad . & (23) \end{aligned}$$

With $i = n_r - n_l$, we obtain:

$$\langle i \rangle = n(P_r - P_l) \quad . \tag{24}$$

Since the variance is given by $\left\langle i^2 \right\rangle - \langle i \rangle^2$, we derive $\langle i \rangle^2$ and $\left\langle i^2 \right\rangle$:

$$\begin{aligned}
\langle i \rangle^2 &= \big(n(P_r - P_l)\big)^2 &(25)\\
&= \big(n(P_r - (1-P_r))\big)^2 &(26)\\
&= \big(n(2P_r - 1)\big)^2 &(27)\\
&= n^2(2P_r-1)^2 &(28)\\
&= n^2(4P_r^2 - 4P_r^2 + 1) &(29)\\
&= 4\underbrace{n^2P_r^2}_{\langle n_r\rangle^2} - 4n^2P_r + n^2 &(30)\\
&= 4\langle n_r\rangle^2 - 4n^2P_r + n^2 \quad . &(31)
\end{aligned}$$

$$\begin{aligned}
\left\langle i^2 \right\rangle &= \sum_{n_r=0}^{n} i^2 \binom{n}{n_r} P_r^{n_r} P_l^{n-n_r} &(32)\\
&= \sum_{n_r=0}^{n} (2n_r - n)^2 \binom{n}{n_r} P_r^{n_r} P_l^{n-n_r} &(33)\\
&= \sum_{n_r=0}^{n} 4n_r^2 \binom{n}{n_r} P_r^{n_r} P_l^{n-n_r} - \sum_{n_r=0}^{n} 4n_r n \binom{n}{n_r} P_r^{n_r} P_l^{n-n_r} + \sum_{n_r=0}^{n} n^2 \binom{n}{n_r} P_r^{n_r} P_l^{n-n_r} &(34)\\
&= 4\cdot P_r \frac{\partial}{\partial P_r} P_r \frac{\partial}{\partial P_r}(P_r+P_l)^n - 4\cdot P_r \frac{\partial}{\partial P_r} n(P_r+P_l)^n + n^2(P_r+P_l)^n &(35)\\
&= 4\cdot P_r \frac{\partial}{\partial P_r} nP_r(P_r+P_l)^{n-1} - 4\cdot P_r \left(n^2(P_r+P_l)^{n-1}\right) + n^2 &(36)\\
&= 4P_r\left(n(P_r+P_l)^{n-1} + nP_r(n-1)(P_r+P_l)^{n-2}\right) - 4n^2P_r + n^2 &(37)\\
&= 4\left(nP_r + n(n-1)P_r^2\right) - 4n^2P_r + n^2 &(38)\\
&= 4\left(nP_r + (n^2-n)P_r(1-P_l)\right) - 4n^2P_r + n^2 &(39)\\
&= 4\left(nP_r + (n^2-n)P_r - (n^2-n)P_rP_l\right) - 4n^2P_r + n^2 &(40)\\
&= 4\left(nP_r + n^2P_r - nP_r - n^2P_rP_l + nP_rP_l\right) - 4n^2P_r + n^2 &(41)\\
&= 4\left(n^2P_r - n^2P_r(1-P_l) + nP_rP_l\right) - 4n^2P_r + n^2 &(42)\\
&= 4\left(n^2P_r - n^2P_r + n^2P_r^2 + nP_rP_l\right) - 4n^2P_r + n^2 &(43)\\
&= 4nP_rP_l + 4\underbrace{n^2P_r^2}_{\langle n_r\rangle^2} - 4n^2P_r + n^2 &(44)\\
&= 4nP_rP_l + 4\langle n_r\rangle^2 - 4n^2P_r + n^2 \quad . &(45)
\end{aligned}$$

Finally we obtain the variance:

$$\begin{aligned}
\Delta\langle i \rangle^2 &= \left\langle i^2 \right\rangle - \langle i \rangle^2 &(46)\\
&= 4nP_rP_l + 4\langle n_r\rangle^2 - 4n^2P_r + n^2 - 4\langle n_r\rangle^2 - 4n^2P_r + n^2 = 4nP_rP_l \quad . &(47)
\end{aligned}$$

Both results for average and variance contain the constant n, so they can be expressed with the random variable X, that contains the parameter n. We obtain $\langle X(n) \rangle = \langle i_n \rangle$ and $\Delta \langle X(n) \rangle^2 = \Delta \langle i_n \rangle^2$, where $\langle i_n \rangle$ and $\Delta \langle i_n \rangle^2$ are the above written results, as requested in the task.

c) The Master equation for the described process is given by:

$$\dot{P}(n) = [P_r P(i,n) - P_l P(i+1,n)] + [P_l P(i,n) - P_r P(i-1,n)] \tag{48}$$

where $i+1$, i and $i-1$ are neighbored cases.