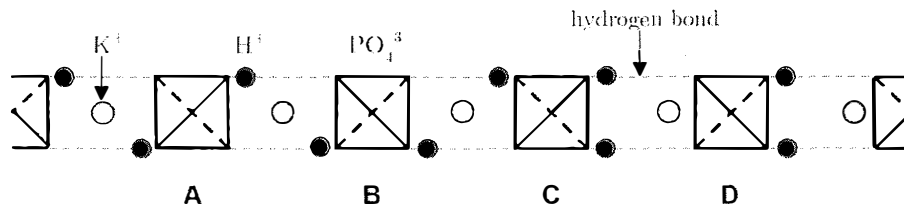


Physics B

【Two pages in total】

Potassium dihydrogen phosphate, KH_2PO_4 is a solid in which phosphate ions PO_4^{3-} are connected by hydrogen bonds. Let us consider a simplified model of KH_2PO_4 as shown in the figure.



In the figure, potassium ions K^+ are represented by open circles, and the phosphate ions PO_4^{3-} are represented by tetrahedra (\square). Each phosphate ion is connected to its nearest neighbors by two hydrogen bonds, depicted by dashed lines. The protons H^+ , represented by filled circles, lie off-center on the hydrogen bonds, and two protons and PO_4^{3-} form a phosphate group H_2PO_4^- .

The total energy of the system is assumed to consist of the sum of single phosphate group energies which are assigned as follows:

- A phosphate group which has two protons on the same side, such as D in the figure, has zero energy.
- A phosphate group which has two protons on different sides, such as A and B, has energy ε (> 0).
- A phosphate group which has three protons, such as C, has infinite energy, as do groups which have four, one, or zero protons.

We assume that the system consisting of N phosphate groups is in thermal equilibrium at temperature T . Let there be periodic boundary conditions to eliminate edge effects. Answer the following questions.

- (1) Show that the mean energy of the system in thermal equilibrium $\langle E \rangle$ is expressed in terms of the partition function Z as $\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z$, where β is given as $\beta = (k_B T)^{-1}$ with Boltzmann's constant k_B .
- (2) Choose the correct partition function Z for the system from the followings:

$$Z = 2 + 2^N e^{-\beta N \varepsilon}, \quad Z = 2 + 2N e^{-\beta \varepsilon}, \quad Z = 2^N + 2 e^{-\beta N \varepsilon}$$

- (3) Explain the physical reasons why you consider the partition function chosen in (2) to be correct.
- (4) Using the results of (1) and (2), find the mean energy of the system.
- (5) Given the limit of large N , show that the mean energy is discontinuous at a certain temperature, T_c . Express T_c in terms of ε and k_B .
- (6) Explain the physical meaning of the discontinuity observed in (5).

【The questions end.】