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Diffusion model of the thermal conductivity plateau of weak solid solutions of neon in parahydrogen

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The diffusion kinetic of classic impurity particles has been investigated in the frame of one-dimensional two-level model and applied for the explanation of solid hydrogen thermal conductivity data with extremely low concentrations of neon impurity in samples growth at different crystallization rates in which the plateau effect was observed. The main idea is that heavy isotopic impurities could segregate into thin long chains near dislocation cores if the growth rate is slow. Neon impurity chains can persist for a long time. Such rigid linear objects ensure inelastic scattering of phonons. The diffusion coefficient of neon atoms in $(p\text{-}H_2)_{1-c}Ne_c$ mixtures was estimated for the experimental conditions with c = 0.0001 at. % and c = 0.0002 at. %.

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Introduction

The effect of heavy impurities on the thermal conductivity of solid parahydrogen for the first time has been investigated in [1–4]. The heat transfer experimental data for solid hydrogen have been analyzed but not to full completion up to now. It is possible to mention results for pure hydrogen (conclusions about the possibility of Poiseuille flow of phonons [5,6]), the huge anomaly for thermal conductivity of solid parahydrogen with extremely low concentrations of heavy impurities [2]. So, it is necessary to reconsider the plateau effect [7,8] as well as interesting impurity effects with argon in solid parahydrogen, as, for example, the chromatic polarization of light due to lattice deformations created by this heavy impurity [3].

The unusual plateau effect [7,8] is closely associated with the problem of the maximum of the thermal conductivity of pure solid hydrogen. This work proposes a simple two-level diffusive model which describes and explains why neon heavy impurities could segregate in chains when the sample is slowly grown from liquid in comparison with the average equal atomic distances when it grows from gas. It was assumed that the impurity redistribution into chains can explain the appearance of a symmetric plateau instead of a resonance pit. The latter is characteristic of the average equal distances between impurities. Since the neon impurity is heavy, its motion is governed by classical physics.

The stochastic dynamics was traditionally treated within the framework of Fokker–Planck equation [9]. This approach allows coming to several results [10,11]. However, more concrete results are obtained within simplified models. For example, the Van-Hove autocorrelation function $G(\mathbf{r},t)$ [12] was used in Chudley–Eliott model [13]. This function is the probability of the particle to move from origin to point $\mathbf{r}$ during time t.

The most general equation within this approach is the generalized Pauli equation (General master equation) [14]. It is possible to use simpler equation if there is the translation symmetry. Such equation is usually named Pauli equation (Master equation). For a simple case of equivalent positions only, Master equation looks like:

$$\frac{\partial G(l,t)}{\partial t} = \lambda \sum_{l'} [\, p(l-l')G(l',t) - p(l'-l)G(l,t)],$$

where $p(l-l')$ is the probability of particle displacement from cite l' in cite l. The function $p(l-l')$ depends on the potential barrier and is assumed to be known.

It is possible to use the continuous parameter x instead of discrete length argument $a(l-l')$ if the function $G(l,t)$ changes with the length a slowly. Then the average displacement and the average squared displacement as functions of time become:

$$\overline{x} = a(p_+ - p_-)t; \quad \overline{x^2} = a^2\lambda t = 2Dt,$$

where D is the diffusion coefficient. Here p_+ is the probability of jump to the nearest write site, p_- is the same to

the left nearest position ($p_- = p_+ = 1/2$ if the external force field is absent). So, in macroscopic limit the Pauli equation describes a classical diffusion.

Let us consider possible applications of this model in this paper. It was shown [5,6] that solid parahydrogen as well as solid helium due to their high purity has, as dielectric crystals, an unusual high thermal conductivity. It could indicate even a so rare phenomenon as the Poisseule flow of the phonon gas. Khodusov and Blinkina [15] formulated the conditions for second sound to exist in quantum crystals of ortho-D_2, para-H_2 and Ne. It was predicted exactly the same temperature range for solid parahydrogen as was found in [5,6]. The second sound and Poiseulle flow for thermal conductivity have the common physical nature.

The large values of solid parahydrogen thermal conductivity near phonon maximum make it extremely high sensitive to the presence of defects [2]. The solubility of neon in solid parahydrogen is a few 0.01 at. % [16]. Therefore, it is possible to state that experiments on samples grown from gas (with neon contents c = 0.0001 at. % and 0.0002 at. %) were such in which no segregation should occur. The observed resonance pit-like anomaly on the thermal conductivity curve was explained by the influence of vibrations of quasiisotopic heavy impurity. It was shown [4,17] that this impurity subsystem modifies the vibration spectrum. It is important to note that solid parahydrogen with argon impurity was also investigated in experimentally. But argon is far from being an isotopic impurity. It was discovered this impurity influence is substantially less [18].

In subsequent research of solid $(p\text{-}H_2)_{1-c}Ne_c$ with extremely small [7,8] a special attention was paid to the influence of sample preparation procedure on the thermal conductivity. It was shown that after a slow growth instead of a resonance pit an unusual symmetric plateau appeared. To explain of this effect it was suggested to use other mechanisms of phonon scattering. It implied that slow growth results in impurity chains due to ascending diffusion after neon atoms segregation near dislocation cores (Gorsky effect [19,20]). This work proposes a simple qualitative model which explains the origin of linear impurity structures in weak solid solutions $(p\text{-}H_2)_{1-c}Ne_c$.

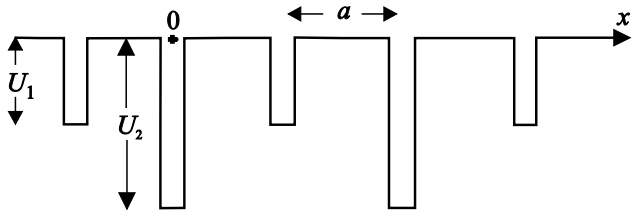

Fig. 1. Model of two-level alternating potential pits. The particle is at the origin (even site).

Theory

Let us investigate of the one-dimensional problem of particle diffusion in the field of alternating equally spaced potential (Fig. 1). We will make sure in that this model has an exact solution. Let for definiteness regularly alternating potential pits of the first type (less deep, Fig. 1) will be odd and the other one is even. The functions $G_1(2s+1,t)$ and $G_2(2s,t)$ are the probabilities to find of particle at moment t at the proper site (odd or even, here $s = 0, \pm1, \pm2, \pm3, ...$). Let us make the set of differential Pauli equations with the particle at moment t = 0 in even site (see the initial conditions):

$$\frac{\partial G_1(2s+1,t)}{\partial t} = \sum_{s'} \lambda_1 p[(2s+1)-(2s'+1)]G_1(2s'+1,t) - \lambda_1 p[(2s'+1)-(2s+1)]G_1(2s+1,t) +$$

$$+ \sum_{s'} \lambda_2 p[(2s+1)-2s')]G_2(2s',t) - \lambda_1 p[2s'-(2s+1)]G_1(2s+1,t);$$

$$\frac{\partial G_2(2s,t)}{\partial t} = \sum_{s'} \lambda_1 p[2s-(2s'+1)]G_1(2s'+1,t) - \lambda_2 p[(2s'+1)-2s]G_2(2s,t) +$$

$$+ \sum_{s'} \lambda_2 p[2s-2s']G_2(2s',t) - \lambda_2 p[2s'-2s]G_2(2s,t);$$

the initial conditions are: $G_2(2s,0) = \delta_{s,0}$; $G_1(2s+1,0) = 0$.

We suppose that the particle can accomplish jumps only to a nearby site by exchanging places with the molecule of the matrix. Then the set of equations simplifies and we go to its Laplace image to get an explicit solution:

$$\tilde{G}_1 = \int_0^\infty G_1 \exp(-ut)dt, \qquad \tilde{G}_2 = \int_0^\infty G_2 \exp(-ut)dt,$$

where u is a complex argument.

Then we Fourier transform the set of Laplace images:

$$\tilde{U}_1(k,u) = \sum_s G_1(2s+1,u)e^{ik(2s+1)},$$

$$\tilde{U}_2(k,u) = \sum_s G_2(2s,u)e^{ik(2s)}.$$

And obtain the set of algebraic equations for Fourier and Laplace images:

$$u\tilde{U}_1(k,u) = \lambda_2(p_+ e^{ik} + p_- e^{-ik})\tilde{U}_2(k,u) - \lambda_1\tilde{U}_1(k,u),$$

$$-1 + u\tilde{U}_2(k,u) = \lambda_1(p_+ e^{ik} + p_- e^{-ik})\tilde{U}_1(k,u) - \lambda_2\tilde{U}_2(k,u).$$

The zeros of denominators of functions $\tilde{U}_1$, $\tilde{U}_2$, which are the singular points, determine the roots of the equation:

$$u_{1,2} = \frac{1}{2}(-(\lambda_1+\lambda_2) \pm \sqrt{(\lambda_1+\lambda_2)^2 - 4\lambda_1\lambda_2(1-r^2)}).$$

Here $r = p_+ e^{ik} + p_- e^{-ik}$. The simple poles give the steady solutions because its real parts are negative. We obtain the originals $U_1(k,t)$, $U_2(k,t)$ after applying of the Riman–Mellin's formula. So, the solution to the initial set of Pauli equations are obtained as Fourier series:

$$G_1(2s+1,t) = \frac{1}{N}\sum_k U_1(k,t)\exp(-ik(2s+1)),$$

$$G_2(2s,t) = \frac{1}{N}\sum_k U_2(k,t)\exp(-ik(2s)).$$

Finding of the functions $G_1(2s+1,t)$, $G_2(2s,t)$ explicitly is connected with large difficulties. However it is enough to know the analytical dependences of the Fourier images $U_1(k,t)$, $U_2(k,t)$. Then we can deduce physically interesting results without inverting the Fourier transform. However, the model must assume that these probabilities are continuous functions of the site coordinates. As an example let us investigate the model of equivalent sites. We can calculate path $\bar{x}(t) = a\bar{l}$ for time t where $\bar{l} = \sum_l lG(l,t)$ is the average number of site. Then, using decomposition in Fourier series, in case of large N we will have:

$$\bar{l}(t) = \frac{1}{N}\sum_k U(k,t) i\frac{d}{dk}\sum_l e^{ikl} = i\sum_k U(k,t)\frac{d}{dk}\delta(k).$$

Using transition $\sum_k ... \to \int ... \, dk$ with integration of the first area of reverse space [19] after integrating the expression with a derivative of δ-function we get:

$$\bar{l}(t) = -iU_k'(0,t), \text{ where } U_k'(0,t) = \frac{d}{dk}U(k,t)\Big|_{k=0}.$$

We take into account that in our two-level model the average sum over all positions splits into two independent parts:

$$\bar{l}(t) = \bar{l}_1(t) + \bar{l}_2(t),$$

where

$$\bar{l}_1(t) = \sum_s (2s+1)G_1(2s+1,t), \quad \bar{l}_2(t) = \sum_s (2s)G_2(2s,t).$$

Then the average travel path of the particle becomes:

$$\bar{x}(t) = a(\bar{l}_1 + \bar{l}_2) = -ia(U_1'(0,t) + U_2'(0,t)).$$

We calculate the average quadratic displacement $\overline{x^2}$ of particle in absence of external field. It can be done as for $\bar{x}$:

$$\overline{x^2}(t) = a^2(\overline{l_1^2} + \overline{l_2^2}) = -a^2[U_1''(0,t) + U_2''(0,t)].$$

Results and discussion

Taking into consideration the expressions for $U_1(k,t)$ and $U_2(k,t)$, after their double differentiation we have $\overline{x^2}(t)$ for two cases of initial conditions (Fig. 2). This result is in good agreement with the one-level model because it has the classic diffusion character for the model of identical sites. However the deviations at small and large times differ substantially for the model of alternating sites. Thus for

$$t >> \tau = \frac{1}{\lambda_1 + \lambda_2}$$

the motion slows down if the particle at origin is in a shallow potential pit (Fig. 2(b)).

Formation of impurity chains near the dislocation cores in solid hydrogen under slow sample growth can be described by this phenomena, at least at a qualitative level. We will suppose that a is of order of the average distance between impurity chains. Their density was estimated to be [7,8]: $N = 10^{13}\,\text{m}^{-2}$. Then we have $a \approx \sqrt{N} = 3\cdot 10^{-7}$ m. The average atomic impurity displacement in classic diffusion requires $\bar{x} = a/2$ to reach a dislocation core during sample growth. The proper average quadratic displacement then is $x^2 = a^2/4$. We suppose that the average time to

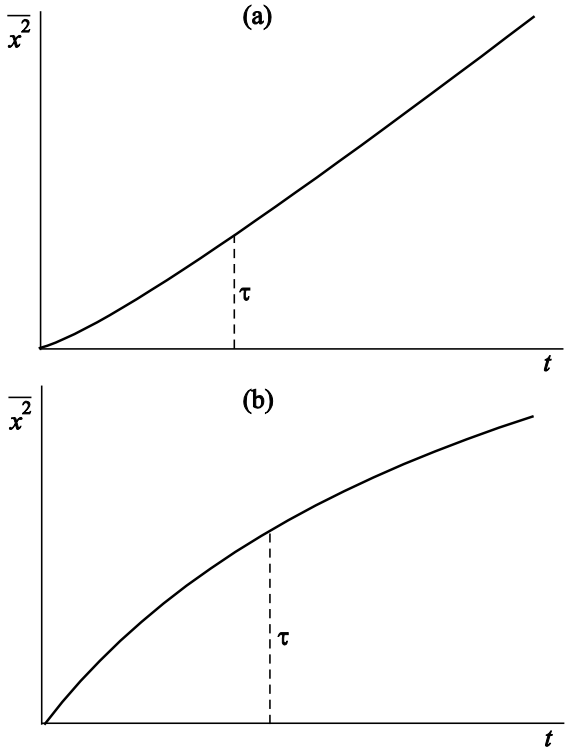

Fig. 2. The impurity particle starts from a deep potential pit (it is not actual for this paper) (a); the particle starts from a shallow pit (b).

reach of dislocation core is $t = a/(2v)$. Here v = 8 mm/h ≈ $\approx 2\cdot10^{-6}$ m/s is the sample growth rate for crystal in which the plateau appears. Making us of the expression $x^2 = 2Dt$, we get for the diffusion coefficient of neon in parahydrogen near the triple point (13.96 K [4]):

$$D = \overline{x^2}v/a = 1.6\cdot10^{-13}\ \mathrm{m}^2/\mathrm{s}.$$

Let us compare this result with the self-diffusion coefficient for parahydrogen at the same conditions [4] evaluated from NMR experiments. We get

$$D = D_0\exp(-E/kT) = 1.8\cdot10^{-13}\ \mathrm{m}^2/\mathrm{s},$$

where $D_0 = 3\cdot10^{-7}$ m^2/s, $E/k = 200$ K.

It is also possible to use theoretical calculations by Ebner and Sang [21]. Then we obtain the diffusion coefficient versus temperature near melting point: $D = 6\cdot10^{-8}\cdot\mathrm{e}^{-197/T}$ and finally $D \approx 4.5\cdot10^{-14}$ m^2/s.

Therefore the heavy isotopic neon impurity in the absence of other admixtures has the diffusivity near the melting temperature close to that of the self-diffusion of solid hydrogen. It was shown in [7,8] that a twice as least growth rate results in a disappearance of the plateau feature for the same Ne fraction. Presumably, impurities have no enough time to form linear structures under these conditions because larger diffusion coefficients are needed for this purpose. Therefore it is possible to assume that for simple estimate the neon diffusion coefficients in solid parahydrogen near the melting point does not exceed $2\cdot10^{-13}$ m^2/s.

After the particle reaches the dislocation core, its mobility can increase by several orders [22]. It is the reason why impurities segregation in linear chains which results in the plateau in the thermal conductivity as a result of the redistribution in the impurity subsystem.

Conclusions

Our theoretical model allows us to study at qualitative level the diffusive kinetics of heavy substitution impurities accomplishing stochastic jumps. The classical one-dimensional model of nearest jumps of a solitary heavy particle with the use of the Pauli equation (Master equation) gives an exact solution to the problem of the average displacements in the field of alternating potential pits of two types with equal distances.

The results help to understand the origin of the symmetric plateau in the temperature dependence of the thermal conductivity for bulk samples slowly grown. The main idea is that hard quasiisotopic impurity could segregate into thin long chains near dislocation cores. Neon impurity chains can be confined for a long time. Such a transition from the spatially homogeneous distribution of isolated atomic impurities to their segregation in chains provides a new collective mechanism of phonon scattering [8]. The result of such interactions leads to a temperature-independent thermal conductivity. The estimates of the neon diffusion coefficient for $(p\text{-H}_2)_{1-c}\text{Ne}_c$ solutions with c = 0.0001 at. %; 0.0002 at. % is close to the coefficients of self-diffusion of hydrogen. Thus our calculations indirectly confirm the model of phonons scattering on the heavy impurity chains suggested previously for the explanation of the plateau.

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