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NUMERICAL SOLUTION FOR DIFFUSION IN PERIODIC POTENTIALS: A COMPARISON WITH THE THEORY OF ACTIVATED PROCESSES

by

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Abstract: A numerical algorithm is implemented so as to explore brownian particle diffusion in a periodic potential throughout the full viscosity range. The predictions of the theory of activated processes are checked. In particular, a recent refinement of the vanishingly small viscosity limit of the Kramers approach by Büttiker et al. (Phys. Rev. B28 1268 (1983)) is found to fit better our numerical results.

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Some fresh interest has been generated recently/1,2/ in bridging the two limits of the Theory of Activated Rate Processes(TARP), first developed in a historic, pioneering paper by Kramers/3/. The authors of both ref.1 and ref.2 interpolate between the solutions for large and vanishingly small viscosity by having recourse to the Kramers' energy approach. Eventhough they almost share the same philosophy, their refined treatment of the underdamped case leads to appreciably different predictions/1,2,4/.

In the present note we show how to relate several statistical auto-correlation functions(a.c.f.) of the brownian motion in an M-fold cosine potential to the TARP predictions. We implemented Reid's algorithm/5/ so as to explore analytically the stochastic diffusion into a bounding potential throughout the full viscosity range. Our numerical results enable us to show that the predictions of ref.1 rely seemingly on a better determination of the extremely small viscosity rate of escape from a metastable state.

The starting point is the Fokker-Planck equation for the probability distribution $p(\underset{\sim}{x},\underset{\sim}{v};t)$

$$\frac{\partial}{\partial t} P = M\gamma\alpha \sin Mx \frac{\partial}{\partial v} P - v\frac{\partial}{\partial x} P + \beta\left(\frac{\partial}{\partial v} v + \alpha^2 \frac{\partial^2}{\partial v^2}\right) P, \qquad (1)$$

where the sinusoidal potential has been given the form $-V_0 \cos M\underset{\sim}{x}$. In our notation $\alpha^2 = k_B T/m$, $\gamma = V_0/m\alpha$, β is the friction constant (viscosity), k_B is the Boltzmann constant and T is the temperature. $\underset{\sim}{m}$, $\underset{\sim}{x}$ and $\underset{\sim}{v}$ are respectively the mass, position and velocity of the brownian particle. The relevance of such a model is well-known in many areas of science, most notably motions of defects or interstitials in crystalline materials/6/, diffusion of ions in superionic conductors /7,8/, relaxation and spectral properties of dipolar molecular liquids/5/.

Numerical The solution of eq.(1) is assumed to be of the form

$$p(x,v;t) = \exp\left(-v^2/4\alpha^2\right) \sum_{n=0}^{\infty} H_n(v/\alpha)\, q_n(x;t) , \qquad (2)$$

where $H_n(x)$ is the n-th orthogonal Hermite polynomial and the spatial dependence $q(x;t)$ may be expanded into a Fourier series:

$$q_n(x;t) = \sum_{p=-\infty}^{+\infty} A_p^n(t) \exp(ipx) . \tag{3}$$

On substituting eqs.(2) and (3) into (1) we obtain easily the set of linear differential-difference equations/7,8/

$$\dot{A}_p^n(t) + n\beta A_p^n(t) - i M\gamma/2 \left(A_{p-M}^{n-1}(t) - A_{p+M}^{n-1}(t) \right) + ip\alpha \left(A_p^{n-1}(t) + (n+1) A_p^{n+1}(t) \right) = 0 . \tag{4}$$

It is convenient to define normalized sums of coefficients by:

$$S_p^n(t) = \left(A_{-p}^n(t) + A_p^n(t) \right) / 2 A_0^0(0) . \tag{5}$$

Further, if the set of eqs.(4) are rewritten in terms of normalized sums and differences and then Laplace transformed ($\mathcal{L}\{S_p^n(t)\} = \hat{S}_p^n(s)$) into algebraic equations it is found that the differences can be eliminated to leave a recurrence relation which, in turn, may be written as an algebraic matrix equation/5/:

$$\underline{A}\ \underline{\hat{S}}_p^n(s) = \underline{S}_p^n(0) , \qquad p \in \mathbb{N} . \tag{6}$$

The elements of $\underline{A}$ are function of s and of the parameters α, β, γ and M, and $S_p^n(0)$ are related to the initial conditions(i.c.), $p(\underset{\sim}{x}(0), \underset{\sim}{v}(0);0)$. For delta function i.c., $\delta(\underset{\sim}{x}(0)-\underset{\sim}{x}_0)\ \delta(\underset{\sim}{v}(0)-\underset{\sim}{v}_0)$, $S_p^n(0)$ read:

$$S_p^n(0) = \exp\left(v^2(0)/4\alpha^2 \right) H_n\left(v(0)/\alpha \right) \cos(px(0)) / n! \tag{7}$$

To solve (6) requires that we restrict the number of equations(4) by assuming $\hat{S}_p^n(0)=0$ for $n > N$ (up to 50) or $p > P$ (up to 100). The consequent numerical

inversion of $\underline{A}$ yields a very accurate solution for $\hat{S}^n_p(s)$. Further details about the performances of this algorithm are available in refs.5 and 9. Good convergence has been achieved throughout the full viscosity range where previous attempt failed/7/.

Theoretical. $S^1_0(t)$ is readily related to the velocity a.c.f. by/5,9/

$$\langle v(t)\, v(0)\rangle_0 \,/\, \langle v^2(0)\rangle_0 \;=\; S^1_0(t) \,/\, S^1_0(0)\,. \tag{8}$$

Analogously one easily finds that

$$\langle \cos x(t)\, \cos x(0)\rangle_0 \,/\, \langle \cos^2 x(0)\rangle_0 \;=\; S^0_1(t) \,/\, S^0_1(0)\,. \tag{9}$$

If $\langle \ldots \rangle_0$ denotes delta function i.c., $\hat{S}^1_0(s)$ and $\hat{S}^0_1(s)$ are solutions to the algorithm of eqs.(6) and (7). The corresponding equilibrium a.c.f.'s, $\langle \ldots \rangle_{eq}$, are then obtained by using respectively $\langle \underset{\sim}{v}(0) S^n_p(0)\rangle_{eq}$ and $\langle \cos\underset{\sim}{x}(0) S^n_p(0)\rangle_{eq}$ rather than $S^n_p(0)$ in eq.(6)/10/. Reid's algorithm provides us with the Laplace transforms of the normalized a.c.f.'s of $\underset{\sim}{v}(t)$ (delta function i.c.) and $\cos\underset{\sim}{x}(t)$ (equilibrium i.c.), denoted from now on by $C_0(t)$ and $K_{eq}(t)$ respectively.

Ref.9 details the relation between the relaxation times of $C_0(t)$ and $K_{eq}(t)$, and the inverse of the rate of escape, η, of the brownian particle from a metastable potential well/11/. In particular we learn that for M=1 the s=0 value of $\hat{C}_0(s)$ coincides with the spatial diffusion coefficient. Indeed, in view of some Laplace transformation theorems, we have/12/

$$\mathcal{L}\left\{ \langle x(0)\;\; x(0)-x(t)\rangle_0 \right\} = \frac{1}{s}\langle x(0)\;\; x(0) - s\,\hat{x}(s)\rangle_0 = -\frac{1}{s}\langle x(0)\,\hat{v}(s)\rangle_0 = \tag{10}$$

$$= \frac{1}{s}\langle v(0)\,\hat{x}(s)\rangle_0 = \frac{1}{s^2}\mathcal{L}\left\{ \langle \hat{v}(s)\,\hat{v}(0)\rangle_0 \right\}.$$

The zero frequency value of $\langle \hat{\underset{\sim}{v}}(s)\hat{\underset{\sim}{v}}(0)\rangle_0$ is therefore the linear term in the time expansion of the translational a.c.f. $\langle \underset{\sim}{x}(0)\;\underset{\sim}{x}(0)-\underset{\sim}{x}(t)\rangle_0$ (the Einstein relation/13/). Such a diffusion coefficient can be estimated by means of the TARP/9/:

$$\hat{C}_0(0) \;=\; 8\,\eta \quad (M=1)\,, \tag{11}$$

where the factor 8 accounts for the both periodic and bistable nature of the potential under study/9/.

On the other hand, a detailed analysis/9,14/ of the orientational relaxation allows us to conclude that, for $M > 1$ and high activation energies ($\gamma >> \alpha$), $K_{eq}(t)$ exhibits an almost diffusional behaviour, no matter how small the friction constant β , i.e.

$$K_{eq}(t) \underset{\gamma >> \alpha}{\sim} \exp\left[- \varkappa_M \left(1 - \cos \frac{2\pi}{M} \right) t \right] , \qquad M > 1 , \tag{12}$$

where

$$\varkappa_M = 2 \eta (M) . \tag{13}$$

Both in eqs.(11) and (13) we have employed the TARP activation rate $\eta(M)$/11/. Two approximations for η are actually available. In our notation:

$$\eta^K (M) = \frac{1}{2\pi} \left[\left(\frac{\beta^2}{4} + M^2 \gamma \alpha \right)^{\frac{1}{2}} - \frac{\beta}{2} \right] \cdot \exp \left(- 2\gamma/\alpha \right) , \tag{14}$$

(large-intermediate values of β /11)

$$\eta^{BHL} (M) = \frac{\left[\left(1 + M \sqrt{\alpha/\gamma}\ \alpha/\beta \right)^{1/2} - 1 \right]}{\left[\left(1 + M \sqrt{\alpha/\gamma}\ \alpha/\beta \right)^{1/2} + 1 \right]} \cdot \frac{8\gamma}{\alpha \pi} \cdot \exp \left(- 2\gamma/\alpha \right) . \tag{15}$$

(small-intermediate values of β /1/)

We note immediately that

$$\lim_{\beta \to 0} \eta^K (M) = \lim_{\beta \to \infty} \eta^{BHL} (M) , \tag{16}$$

$$\lim_{\beta \to \infty} \eta^K (M) = M^2 \gamma \alpha / 2\pi\beta \cdot \exp \left(- 2\gamma/\alpha \right) , \tag{17}$$

$$\lim_{\beta \to 0} \eta^{BHL} (M) = \beta \left(4/\pi \right) 2\gamma/\alpha \cdot \exp \left(- 2\gamma/\alpha \right) . \tag{18}$$

The third limit enhances by a factor $4/\pi$ the corresponding expression introduced first by Kramers/3/ and then recovered by the authors of ref.2. This is the consequence of a more refined accounting of the energy trajectory flow about the top of the barrier/1/.

The results. Eqs.(11) and (13) suggest distinct measurements of $\eta(M)$ and a check on the internal consistency of our approach. In fig.1 we report our numerical results for $\eta(M=1)$ as obtained from eq.(11) for both an overdamped, fig.1a, and underdamped case, fig.1b. In fig.1b we compare the numerical calculations with the extremely small viscosity predictions of both Büttiker et al./1/ and Kramers/3/. Our results agree fairly closely with the more recent prediction, (eq.(18), which so far seems quite reliable.

Our results for $\eta(M=2)$, displayed in fig.2, have been determined by means of eq.(13). A very wide viscosity range is explored and, by way of comparison with the analytical predictions of ref.1, a curve interpolating $\eta^{K}(M)$, (14), and $\eta^{BHL}(M)$, (15), is reported. The bridging function $\eta_{th}(M=2)$ is defined as follows/15,16/

$$\eta_{th}(M=2) = \left[\eta^{K}(M=2)^{-1} + \eta^{BHL}(M=2)^{-1} \right]^{-1} . \qquad (19)$$

The agreement obtained is still very confortable. This allows us to conclude that the theoretical approach of ref.1 to the activation processes in the limit of very small viscosity is to be regarded as likely correct and, anyway, provides better results than preceding studies/2,3/.

In a final remark we emphasize that the escape rate theory developed by Kramers seems to explain very closely the relaxational dynamics into an M-fold periodic potential/9/ contrary to some claims about its breakdown/7/.

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FIGURE CAPTIONS

Fig.1 - a) the overdamped limit. $\eta(M=1)$, (11), versus $1/\beta$ for $M=1, \alpha=1$ and $\gamma=4$. Our numerical results (●) are compared with the corresponding Kramers limit, (17) (solid line);

b) the underdamped limit. $\eta(M=1)$, (11), versus β for $M=1, \alpha=1$ and $\gamma=10$. The dots (●) represent our numerical results. The solid lines represent the theoretical predictions of Kramers/3/ (K) and Büttiker et al./1/ (BHL) respectively (see eq.(18).

Fig.2 - η (M=2), (13), versus β for M=2, $\alpha=1$ and $\gamma=4$. Our numerical results (●) are compared with the interpolating function $\eta_{th}(M=2)$, (18) (dashed line).

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/10/ Indeed, for delta function i.c. one finds: $\langle \underset{\sim}{v}(t)\underset{\sim}{v}(0)\rangle_0=\underset{\sim}{v}(0)S_0^1(t)$ and $\langle \cos\underset{\sim}{x}(t)\cos\underset{\sim}{x}(0)\rangle_0=\cos\underset{\sim}{x}(0)S_1^0(t)$. The equilibrium a.c.f.'s are then obtained by assuming $\underset{\sim}{x}_0$ and $\underset{\sim}{v}_0$ distributed according the corresponding Maxwell--Boltzmann probability function (see also W.T. Coffey, M.W. Evans and P. Grigolini, 'Molecular Diffusion and Spectra', Wiley-Interscience, New-York (1984), chapter 5).

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/12/ Actually eq.(10) is rigorous when the equilibrium distribution for the initial values of $\underset{\sim}{x}(0)$ and $\underset{\sim}{v}(0)$ is taken or when delta function i.c. are assumed with $\underset{\sim}{v}_0=0$. We adopted the latter choice for computational convenience. However a comparison between the corresponding characterizations of η is straightforward (see e.g. F. Marchesoni and P. Grigolini, J. Chem. Phys. 78 6287 (1983)).

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Fig 1a
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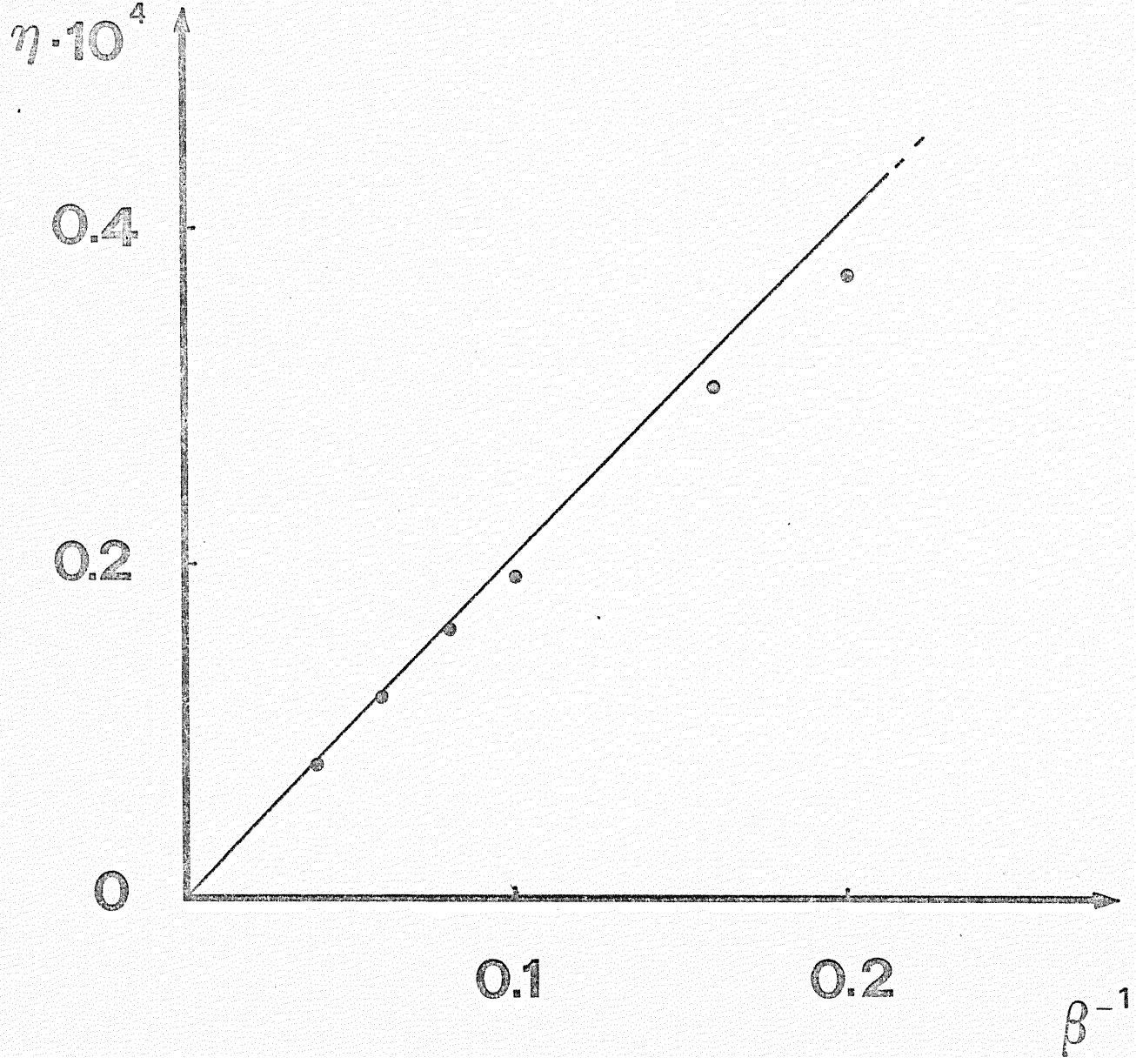

Fig 1b
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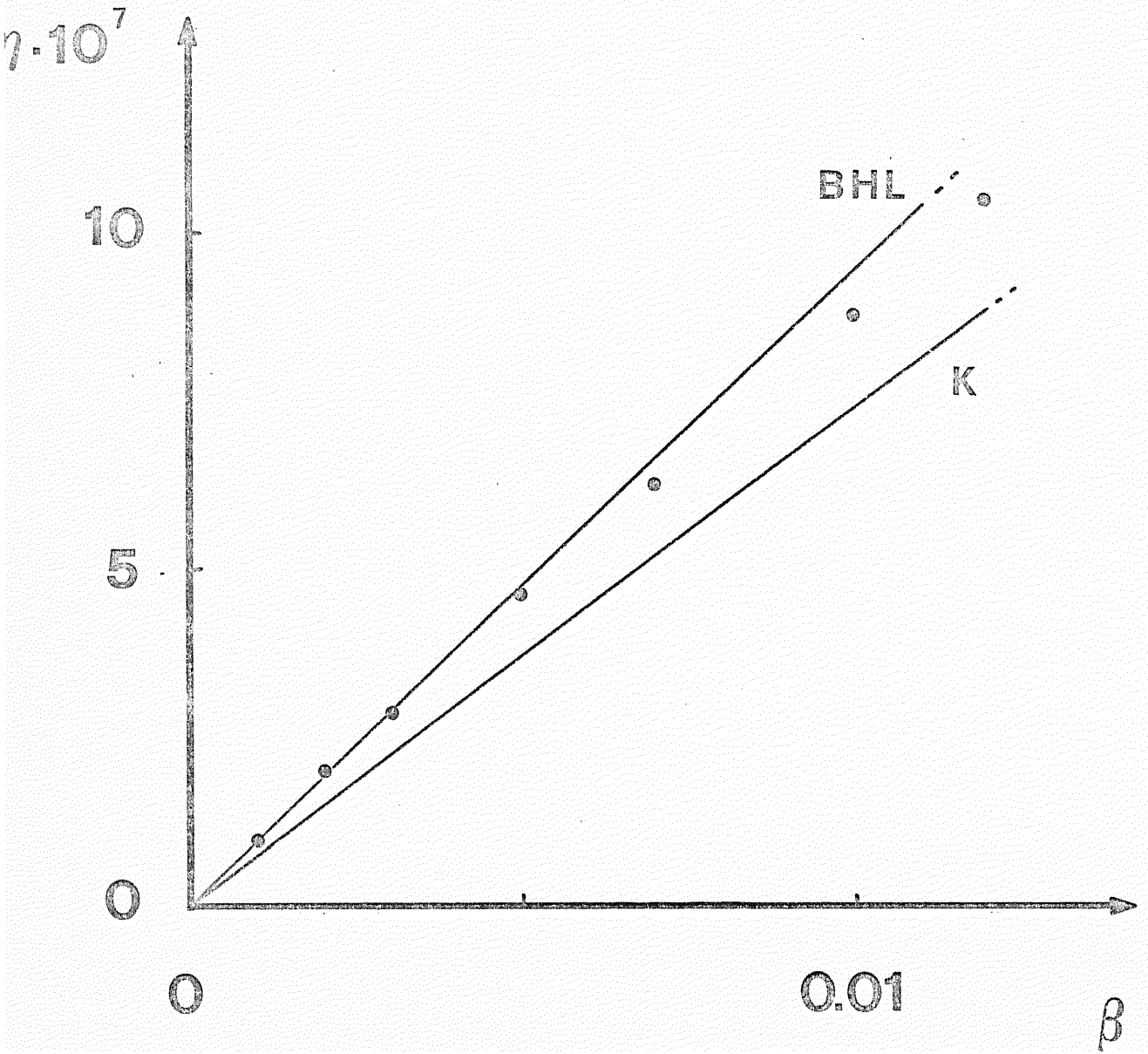

Fig 2
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