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ORIGINAL PAPER

Qualitative analysis of the anisotropic two-body problem with generalized Lennard-Jones potential

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Abstract This paper continue the study of the generalized Lennard-Jones potential started in Bărbosu et al. (J Math Chem 49(9):1961–1975, 2011) for a more general situation. More precisely we study the two-body problem with generalized Lennard-Jones potential in an anisotropic space. We will show that the set of initial conditions leading to collisions and ejections have positive measure. We also study the capture and escape solutions in the zero-energy case using the infinity manifold. We also show that the flow on the zero energy manifold of a two-body problem given by the sum of the Newtonian potential and the two anisotropic perturbations corresponding to the generalized Lennard-Jones potential is chaotic.

Keywords Anisotropic two-body problem · Generalized Lennard-Jones potential · Melnikov method · Chaos

1 Introduction

In computational chemistry and molecular dynamics it is common to use mathematically simple models to describe the interaction between a pair of atoms or molecules (see, for instance [7, 10]).

Dedicated to Professor Jaume Llibre on the occasion of his 60th birthday with deep esteem and respect.

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The Lennard-Jones potential (see [9]) is a very famous empirical function in molecular dynamics. It models the interaction between two neutral atoms or molecules, which are subject to two distinct forces in the limit of large separation and small separation. These are: an attractive force at long ranges (van der Waals force, or dispersion force), and a repelling force at short ranges (result of overlapping electron orbitals, referred to as Pauli repulsion from Pauli's exclusion principle).

This potential (also called 6–12 potential or 12–6 potential) reads $U_{LJ} = 4\epsilon\left[(\sigma/r)^6 - (\sigma/r)^{12}\right]$, where: ϵ = depth of the potential energy well; σ = finite distance at which the interparticle potential is zero; r = distance between the two particles. These parameters can be fitted to reproduce experimental data, or can be deduced from results of accurate quantum chemistry calculations; an excellent exposure in this regard, together with a discussion on the validity of the use of classical approximations for interatomic and intermolecular interactions may be found in [2].

The Lennard-Jones potential is an empirical approximation. The form of the repulsion term, in $(1/r)^{12}$, has no theoretical substantiation. Actually, the repelling force should depend exponentially on the distance. But the repulsion term in the Lennard-Jones formula is more convenient due to the ease and efficiency of computing the square of $(1/r)^6$. It physically originates in Pauli's principle, but the exponent 12 was chosen exclusively because of ease of computation. As to the attractive long-range potential, it is derived from dispersion interactions.

Even if it is an empirical model, the Lennard-Jones potential proved itself to be a relatively good approximation. It is often used to describe the properties of gases, and to model dispersion and overlap interactions in molecular models.

The problem we approach in this paper is the anisotropic two-body problem with generalized Lennard-Jones potential. It is clear that this type of potential covers much more physical situations than the original Lennard-Jones one. We have to point out the fact that we are interested here only in the mathematical aspects of the dynamics and not in the concrete physical ones. The strategy and methods used in this paper follow closely [11].

The objective of this paper is to describe the flow of our system on the infinity manifold. In Sect. 2 using the McGehee transformations we study the so-called collision manifold which is important since the structure of the phase space of the system depends on the behavior of the solutions on this manifold. In Sect. 3 we describe the flow of our system on and near collision manifold. In particular we classify the collision-ejection orbits and prove that the set of initial conditions leading to them has positive measure. In Sect. 4 we investigate the existence of heteroclinic orbits on the collision manifold and we show that for $a = 6$, $b > a$ and an open and dense set of values of μ, saddle–saddle connections do not exist on the collision manifold. Finally, in Sect. 5 we consider a potential that is the sum of the classical Keplerian potential and an anisotropic perturbation coming from the generalized Lennard-Jones potential studied in the previous sections (again with the parameter μ measuring the strength of the anisotropy). With this model we obtain an extra dynamical property that we could not obtain for our initial potential given in the previous sections. Such mixed potential can be used, among others, to understand the dynamics of starts around black holes.

We apply the Melnikov method to show that the flow on the zero-energy manifold of the new potential is chaotic.

2 Equations of motion and symmetries

We consider the Hamiltonian

$$H'(\mathbf{q}, \mathbf{p}) = \frac{1}{2}\left(\mathbf{p}^T M^{-1}\mathbf{p}\right) + V(\mathbf{q})$$

where $H' : \left(\mathbb{R}^2 \setminus \{0\}\right) \times \mathbb{R}^2 \to \mathbb{R}$, the mass matrix

$$M^{-1} = \begin{pmatrix} \mu & 0 \\ 0 & 1 \end{pmatrix}.$$

with $\mu \geq 1$, and the potential energy

$$V(\mathbf{q}) = -\frac{A}{\|\mathbf{q}\|^a} + -\frac{B}{\|\mathbf{q}\|^b}$$

with $2 < a < b - 1$ and $A > 0$, $B > 0$.

The goal of study the anisotropic two-body problem with generalized Lennard-Jones potential is to described the solutions of the Hamiltonian system associated to H',

$$\begin{cases} \dot{\mathbf{q}} = M^{-1}\mathbf{p}, \\ \dot{\mathbf{p}} = -\operatorname{grad} V(\mathbf{q}). \end{cases} \tag{1}$$

They are a one parameter family of Hamiltonian systems depending analytically on the parameter $\mu \geq 1$. This system described the two-body problem with generalized Lennard-Jones potential when $\mu = 1$ (see [1]), and the case in which $\mu < 1$ the attraction-repulsive is weakest in the direction of the q_1–axis and strongest in that of the q_2–axis. The situation is reversed if $\mu > 1$. Since both remaining cases have a weakest-force and a strongest-force direction, we can assume without loss of generality that $\mu > 1$.

From now on, we shall consider the Hamiltonian system,

$$\begin{cases} \dot{q_1} = p_1, \\ \dot{q_2} = p_2, \\ \dot{p_1} = -\dfrac{\mu A a q_1}{(\mu q_1^2 + q_2^2)^{\frac{a}{2}+1}} + \dfrac{\mu B b q_1}{(\mu q_1^2 + q_2^2)^{\frac{b}{2}+1}}, \\ \dot{p_2} = -\dfrac{A a q_2}{(\mu q_1^2 + q_2^2)^{\frac{a}{2}+1}} + \dfrac{B b q_2}{(\mu q_1^2 + q_2^2)^{\frac{b}{2}+1}}, \end{cases}$$

associated to the Hamiltonian,

$$H(\mathbf{q},\mathbf{p}) = \frac{1}{2}\|\mathbf{p}\|^2 + V(\mathbf{q})$$

where

$$V(\mathbf{q}) = -\frac{A}{(\mu q_1^2 + q_2^2)^{\frac{a}{2}}} + \frac{B}{(\mu q_1^2 + q_2^2)^{\frac{b}{2}}} \tag{2}$$

and $H : \left(\mathbb{R}^2 \setminus \{0\}\right) \times \mathbb{R}^2 \to \mathbb{R}$. We remark that the Hamiltonian systems associated to H and H' are equivalent and the angular momentum, $C(\mathbf{q},\mathbf{p}) = \mathbf{q} \wedge \mathbf{p}$, is an integral if and only if $\mu = 1$.

We consider a $2n$-dimensional manifold $\mathcal{M}$ together with a diffeomorphism R of $\mathcal{M}$ satisfying,

(1) R^2 = identity and
(2) dim (Fix (R)) = n

then, R is called a *reversing involution*. A smooth vector field X on $\mathcal{M}$ is called *R-reversible* if $DR(X) = -XR$; for more details on reversible systems see [4].

It is easy to verify that the anisotropic two-body problem with generalized Lennard-Jones potential (1) is S_i–reversible for $i = 0, 1, 2$ where,

$$\begin{aligned} S_0(q_1, q_2, p_1, p_2) &= (q_1, q_2, -p_1, -p_2),\\ S_1(q_1, q_2, p_1, p_2) &= (q_1, -q_2, -p_1, p_2),\\ S_2(q_1, q_2, p_1, p_2) &= (-q_1, q_2, p_1, -p_2). \end{aligned}$$

This means that if $\gamma(t) = (q_1(t), q_2(t), p_1(t), p_2(t))$ is a solution of the anisotropic two-body problem with generalized Lennard-Jones potential such that $\gamma(0)$ belongs to Fix(S_0), Fix(S_1) or Fix(S_2), then $(q_1(-t), q_2(-t), -p_1(-t), -p_2(-t))$, $(q_1(-t), -q_2(-t), -p_1(-t), p_2(-t))$ or $(-q_1(-t), q_2(-t), p_1(-t), -p_2(-t))$ is, respectively, a solution.

The symmetry S_0 is the usual symmetry with the respect to the zero velocity curve, which is presented by all the Hamiltonian systems where the Hamiltonian can be written as kinetic energy $(\mathbf{p}^T M^{-1}\mathbf{p})/2$, plus potential energy, $V(\mathbf{q})$.

A plane in the phase space is called *invariant plane* if and only if every orbit which has a point in the plane is contained in it.

Let V_q be the gradient and V_{qq} be the Hessian of the potential V. Set $T = -JV_{qq}JV_q$, where

$$J = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}.$$

By Lemma 2.1 of [3], the irreductible factors of degree 1 of the equation $\langle T, JV_q\rangle = 0$ are the projections of the invariant planes on the configuration plane. Here, $\langle\cdot,\cdot\rangle$ denotes the Euclidian inner product.

If $V(\mathbf{q})$ is given by (2) then we have

$$\langle T, JV_q \rangle = \mu(1-\mu)q_1q_2\Big(\frac{Aa}{(\mu q_1^2+q_2^2)^{\frac{a}{2}+1}} - \frac{Bb}{(\mu q_1^2+q_2^2)^{\frac{b}{2}+1}}\Big)^3.$$

Therefore, the unique invariant planes of (1) are,

$$\pi_1 = \{(0, q_2, 0, p_2) \ : \ (q_2, p_2) \in \big(\mathbb{R}\setminus\{0\}\big)\times\mathbb{R}\},$$
$$\pi_2 = \{(q_1, 0, p_1, 0) \ : \ (q_1, p_1) \in \big(\mathbb{R}\setminus\{0\}\big)\times\mathbb{R}\},$$

where for $i = 1, 2$, π_i is invariant under the symmetry S_j for $j = 0, 1, 2$. In short we have proved the following proposition.

Proposition 1 *The anisotropic two-body problem with generalized Lennard-Jones potential has only two invariant planes,* π_1 *and* π_2.

3 The infinity manifold

McGehee's coordinates (r, θ, v, u) are defined by (for more details see [5]):

$$\begin{cases} r = \sqrt{q_1^2+q_2^2}, \qquad \theta = \arctan\Big(\dfrac{q_2}{q_1}\Big), \\ y = \dfrac{q_1p_1+q_2p_2}{\sqrt{q_1^2+q_2^2}}, \qquad x = \dfrac{q_1p_2-q_2p_1}{\sqrt{q_1^2+q_2^2}}, \\ v = r^{\frac{b}{2}}y, \qquad u = r^{\frac{b}{2}}x, \qquad d\tau = r^{-\frac{b+2}{2}}dt. \end{cases} \tag{3}$$

Then the Hamiltonian system associated to H becomes:

$$\begin{cases} \dot{r} = rv, \\ \dot{v} = \dfrac{b}{2}v^2 + u^2 - r^{b-a}\dfrac{Aa}{\Delta^{\frac{a}{2}}} + \dfrac{Bb}{\Delta^{\frac{b}{2}}}, \\ \dot{\theta} = u, \\ \dot{u} = \Big(\dfrac{b}{2}-1\Big)uv + \dfrac{\mu-1}{2}\sin 2\theta\Big[r^{b-a}\dfrac{Aa}{\Delta^{\frac{a}{2}+1}} - \dfrac{Bb}{\Delta^{\frac{b}{2}+1}}\Big], \end{cases} \tag{4}$$

where we keep the same "dot" notation for the derivative $d/d\tau$, and $\Delta = \mu\cos^2\theta + \sin^2\theta$.

Now, the relation energy is given by:

$$\frac{1}{2}(u^2+v^2) - r^{b-a}\frac{A}{\Delta^{\frac{a}{2}}} + \frac{B}{\Delta^{\frac{b}{2}}} = hr^b. \tag{5}$$

Remark 1 There is no collision manifold since if $r = 0$ then from the energy relation we get

$$\frac{1}{2}(u^2 + v^2) + \frac{B}{\Delta^{\frac{b}{2}}} = 0$$

which is impossible for $B > 0$.

Remark 2 There are no equilibria for positive energy levels.

Indeed, from the conservation of energy (5) if we equating the right side of the system (4) to zero, and taking into account the conservation of energy, the following relations must be satisfied:

$$u = v = 0$$
$$\frac{B}{\Delta^{\frac{b}{2}}}(a - b) = hr^b a,$$

and it follows that for $h > 0$, the equation cannot be satisfied.

Now we investigate the dynamics on the zero energy level set with focus on asymptotic configurations. Since unbounded motions are characterized by an infinity radius r of the system, we begin by using an inverting transformation that introduces

$$\rho = 1/r$$

as an inverse measure of the size. Thus motions with $\rho \to 0$ correspond to physical situations in the size r of the system becomes unbounded. When $h = 0$, the energy relation take the form

$$\frac{1}{2}(u^2 + v^2) - r^{b-a}\frac{A}{\Delta^{\frac{a}{2}}} + \frac{B}{\Delta^{\frac{b}{2}}} = 0.$$

With the transformations

$$\bar{u} := u\rho^{\frac{b-a}{2}}, \quad \bar{v} := v\rho^{\frac{b-a}{2}}$$

the energy relation becomes

$$\bar{u}^2 + \bar{v}^2 = \frac{2A}{\Delta^{\frac{a}{2}}} - \frac{2B}{\Delta^{\frac{b}{2}}}\rho^{b-a}. \tag{6}$$

We define the infinity manifold I_0 as

$$I_0 := \left\{(\rho, \bar{v}, \theta, \bar{u}) \,\middle|\, \rho = 0,\ \bar{u}^2 + \bar{v}^2 = \frac{2A}{\Delta^{\frac{a}{2}}}\right\}. \tag{7}$$

Note that I_0 is a torus, i.e. $\theta \in \mathbb{S}^1$. After rescaling the time τ with the transformation $d\tau = \rho^{\frac{b-a}{2}}ds$, system (4) (with $h = 0$) becomes

$$\begin{cases} \dot{\rho} = -\rho\bar{v} \\ \dot{\bar{v}} = \frac{a}{2}\bar{v}^2 + \bar{u}^2 - \frac{Aa}{\Delta^{\frac{a}{2}}} + \rho^{b-a}\frac{Bb}{\Delta^{\frac{b}{2}}} \\ \dot{\theta} = \bar{u} \\ \dot{\bar{u}} = \left(\frac{a}{2} - 1\right)\bar{u}\bar{v} + \frac{\mu - 1}{2}\sin 2\theta\left(\frac{Aa}{\Delta^{\frac{a}{2}+1}} - \rho^{b-a}\frac{Bb}{\Delta^{\frac{b}{2}+1}}\right) \end{cases} \tag{8}$$

where we keep the same "dot" notation for the derivative d/ds. The flow on the infinity manifold is given by

$$\begin{cases} \dot{\bar{v}} = \left(1 - \frac{a}{2}\right)\bar{u}^2 \\ \dot{\theta} = \bar{u} \\ \dot{\bar{u}} = \left(\frac{a}{2} - 1\right)\bar{u}\bar{v} + \frac{\mu - 1}{2}\sin 2\theta\frac{Aa}{\Delta^{\frac{a}{2}+1}}. \end{cases} \tag{9}$$

Lemma 2 *All the equilibrium solutions of the flow given by* (8) *lie on the infinity manifold* I_0 *and they satisfy:*

$$\rho = 0, \quad \bar{v} = \pm\sqrt{2A\Delta^{-\frac{a}{2}}},$$
$$\theta = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}, \quad \bar{u} = 0$$

Proof Imposing that $(\rho, \bar{v}, \theta, \bar{u})$ is an equilibrium point of system (8), it must satisfy $\dot{\rho} = \dot{\bar{v}} = \dot{\theta} = \dot{\bar{u}} = 0$. It follows from $\dot{\rho} = \dot{\theta} = 0$, that in particular, $\rho\bar{v} = 0$ and $\bar{u} = 0$. If $\rho \neq 0$, we must have $\bar{v} = 0$, but then we reach a contradiction with the energy relation (6) taking into account that $a, b, A, B > 0$ and $a \neq b$. Indeed, from the second equation in (8) we get

$$\rho^{b-a} = \frac{Aa}{Bb}\Delta^{\frac{b-a}{2}}$$

and from the energy relation (6) we get

$$\rho^{b-a} = \frac{A}{B}\Delta^{\frac{b-a}{2}}$$

which implies $a = b$, contradiction. Thus, from the first equation in (8) we get $\rho = 0$ and then the second one yields $\bar{v} = \pm\sqrt{2A\Delta^{-\frac{a}{2}}}$ Finally, the last equation in (8) yields

$$\frac{\mu - 1}{2}\sin 2\theta\left(\frac{Aa}{\Delta^{\frac{a}{2}+1}} - \rho^{b-a}\frac{Bb}{\Delta^{\frac{b}{2}+1}}\right) = 0,$$

that is, $\sin 2\theta = 0$, which concludes the proof of the lemma. □

The equilibrium points of the flow on the infinity manifold I_0 are:

$$\bar{v} = \pm\sqrt{2A\Delta^{-\frac{a}{2}}}, \qquad \theta = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}, \qquad \bar{u} = 0. \tag{10}$$

We denote by $E_0^{\pm}$, $E_{\pi/2}^{\pm}$, $E_{\pi}^{\pm}$ and $E_{3\pi/2}^{\pm}$, respectively, the equilibrium points. Clearly the superindex matches the sign of v and the subindex matches the value of θ. We observe that $\Delta(0) = \Delta(\pi) = \mu$ and $\Delta(\pi/2) = \Delta(3\pi/2) = 1$. Let

$$a^* = 1 + \frac{1}{2a}\left(\frac{a}{2} - 1\right)^2.$$

Theorem 3 *On the infinity manifold I_0, the equilibria $E_0^{\pm}$ and $E_{\pi}^{\pm}$ are saddles. When $\mu \in (1, a^*]$ the equilibria $E_{\pi/2}^{\pm}$ and $E_{3\pi/2}^{\pm}$ are saddles and when $\mu \in (a^*, +\infty)$ are saddle-foci. Outside I_0, the equilibria E_0^{+}, E_{π}^{+}, $E_{\pi/2}^{-}$ and $E_{3\pi/2}^{-}$ have a local one-dimensional unstable analytic manifold, whereas E_0^{-}, E_{π}^{-}, $E_{\pi/2}^{+}$ and $E_{3\pi/2}^{+}$ have a local one-dimensional stable analytic manifold.*

Proof Consider the function

$$G(\rho, \bar{v}, \theta, \bar{u}) = \bar{u}^2 + \bar{v}^2 - \frac{2A}{\Delta^{\frac{a}{2}}} + \frac{2B}{\Delta^{\frac{b}{2}}}\rho^{b-a}.$$

The surface defined by the equation $G(\rho, \bar{v}, \theta, \bar{u}) = 0$ is a three-dimensional manifold. At every point y of this manifold, the tangent space is given by

$$T_y G = \{(\rho, \bar{v}, \theta, \bar{u}) \mid \nabla G(y) \cdot (\rho, \bar{v}, \theta, \bar{u}) = 0\}.$$

At any equilibrium point x, the tangent space is defined by

$$T_x G = \{(\rho, \bar{v}, \theta, \bar{u}) \mid \bar{v} = 0\}.$$

One can easy check that at the equilibria $E_0^{\pm}$ and $E_{\pi}^{\pm}$ the linearized system corresponding to (8) has the matrix

$$\begin{pmatrix} \mp\sqrt{2A\mu^{-a/2}} & 0 & 0 & 0 \\ 0 & \pm a\sqrt{2A\mu^{-a/2}} & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & (\mu-1)Aa\mu^{-a/2} & \pm\left(\frac{a}{2} - 1\right)\sqrt{2A\mu^{-a/2}} \end{pmatrix}.$$

Therefore, the linear part of the vector field (8) restricted to the tangent space of $E_0^{\pm}$ and $E_\pi^{\pm}$ is given by

$$l = \begin{pmatrix} \mp\sqrt{2A\mu^{-a/2}}\rho \\ 0 \\ \bar{u} \\ (\mu-1)Aa\mu^{-a/2}\theta \pm \left(\frac{a}{2}-1\right)\sqrt{2A\mu^{-a/2}}\bar{u} \end{pmatrix}.$$

As a basis for the tangent space of $E_0^{\pm}$ and $E_\pi^{\pm}$ we can take the vectors

$$\eta_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \qquad \eta_2 = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \qquad \eta_3 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \tag{11}$$

The representation of the linear part l relative to this basis is given by the matrix

$$L = \begin{pmatrix} \mp\sqrt{2A\mu^{-a/2}} & 0 & 0 \\ 0 & 0 & 1 \\ 0 & (\mu-1)Aa\mu^{-a/2} & \pm\left(\frac{a}{2}-1\right)\sqrt{2A\mu^{-a/2}} \end{pmatrix}.$$

The eigenvalues of this matrix are

$$\begin{aligned} \lambda_1 &= \mp\sqrt{2A\mu^{-a/2}}, \\ \lambda_2 &= \frac{1}{2}\left\{\pm\left(\frac{a}{2}-1\right)\sqrt{2A\mu^{-a/2}} + \sqrt{2A\mu^{-a/2}\left(\frac{a}{2}-1\right)^2 + 4(\mu-1)Aa\mu^{-a/2}}\right\}, \\ \lambda_3 &= \frac{1}{2}\left\{\pm\left(\frac{a}{2}-1\right)\sqrt{2A\mu^{-a/2}} - \sqrt{2A\mu^{-a/2}\left(\frac{a}{2}-1\right)^2 + 4(\mu-1)Aa\mu^{-a/2}}\right\}. \end{aligned}$$

Note that since $a > 2$, $A > 0$ and $\mu > 1$, we have that $\lambda_i \in \mathbb{R}$ for $i = 1, 2, 3$. So the equilibria are hyperbolic. The equilibria E_0^- and E_π^- have a one-dimensional stable manifold and a two-dimensional unstable one, whereas E_0^+ and E_π^+ have a two-dimensional stable manifold and a one-dimensional unstable one.

At the equilibria $E^{\pm}_{\pi/2}$ and $E^{\pm}_{3\pi/2}$ the same linearized system has the matrix

$$\begin{pmatrix} \mp\sqrt{2A} & 0 & 0 & 0 \\ 0 & \pm a\sqrt{2A} & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -(\mu-1)Aa & \pm\left(\frac{a}{2}-1\right)\sqrt{2A}. \end{pmatrix}.$$

Using again the vectors in (11) as a basis for the tangent space of $E^{\pm}_{\pi/2}$ and $E^{\pm}_{3\pi/2}$, the linear part is given by the matrix

$$L_1 = \begin{pmatrix} \mp\sqrt{2A} & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -(\mu-1)Aa & \pm\left(\frac{a}{2}-1\right)\sqrt{2A}. \end{pmatrix}.$$

The eigenvalues of this matrix are

$$\lambda_1 = \mp\sqrt{2A},$$
$$\lambda_2 = \frac{1}{2}\left\{\pm\left(\frac{a}{2}-1\right)\sqrt{2A} + \sqrt{2A\left(\frac{a}{2}-1\right)^2 - 4(\mu-1)Aa}\right\},$$
$$\lambda_3 = \frac{1}{2}\left\{\pm\left(\frac{a}{2}-1\right)\sqrt{2A} - \sqrt{2A\left(\frac{a}{2}-1\right)^2 - 4(\mu-1)Aa}\right\}.$$

Let denote

$$\delta = 2A\left(\frac{a}{2}-1\right)^2 - 4(\mu-1)Aa.$$

Its easy to check that

1. If $\mu \in (1, a^*)$ then $\delta > 0$ and consequently $\lambda_{2,3} \in \mathbb{R}$.
2. If $\mu = a^*$ then $\delta = 0$ and consequently $\lambda_2 = \lambda_3 \in \mathbb{R}$.
3. If $\mu \in (a^*, +\infty)$ then $\delta < 0$ and consequently $\lambda_{2,3} \in \mathbb{C}$.

Now we summerize the signs of the eigenvalues at each equilibrium point:

– at $E^+_0 = (0, \sqrt{2A/\mu^{a/2}}, 0, 0)$ we have $\lambda_1 < 0, \lambda_2 > 0, \lambda_3 < 0$.
– at $E^-_0 = (0, -\sqrt{2A/\mu^{a/2}}, 0, 0)$ we have $\lambda_1 > 0, \lambda_2 > 0, \lambda_3 < 0$.
– at $E^+_\pi = (0, \sqrt{2A/\mu^{a/2}}, \pi, 0)$ we have $\lambda_1 < 0, \lambda_2 > 0, \lambda_3 < 0$.
– at $E^-_\pi = (0, -\sqrt{2A/\mu^{a/2}}, \pi, 0)$ we have $\lambda_1 > 0, \lambda_2 > 0, \lambda_3 < 0$.

For the other four equilibrium points we have different situations depends on the values of the parameter μ as follows:

1. If $\mu \in (1, a^*]$ we get:

- at $E^{+}_{\pi/2} = (0, \sqrt{2A}, \pi/2, 0)$ we have $\lambda_1 < 0, \lambda_2 > 0, \lambda_3 > 0$.
- at $E^{-}_{\pi/2} = (0, -\sqrt{2A}, \pi/2, 0)$ we have $\lambda_1 > 0, \lambda_2 < 0, \lambda_3 < 0$.
- at $E^{+}_{3\pi/2} = (0, \sqrt{2A}, 3\pi/2, 0)$ we have $\lambda_1 < 0, \lambda_2 > 0, \lambda_3 > 0$.
- at $E^{-}_{3\pi/2} = (0, -\sqrt{2A}, 3\pi/2, 0)$ we have $\lambda_1 > 0, \lambda_2 < 0, \lambda_3 < 0$.

2. If $\mu \in (a^*, +\infty)$ we get:
   - at $E^{+}_{\pi/2} = (0, \sqrt{2A}, \pi/2, 0)$ we have $\lambda_1 < 0, \operatorname{Re} \lambda_2 > 0, \operatorname{Re} \lambda_3 > 0$.
   - at $E^{-}_{\pi/2} = (0, -\sqrt{2A}, \pi/2, 0)$ we have $\lambda_1 > 0, \operatorname{Re} \lambda_2 < 0, \operatorname{Re} \lambda_3 < 0$.
   - at $E^{+}_{3\pi/2} = (0, \sqrt{2A}, 3\pi/2, 0)$ we have $\lambda_1 < 0, \operatorname{Re} \lambda_2 > 0, \operatorname{Re} \lambda_3 > 0$.
   - at $E^{-}_{3\pi/2} = (0, -\sqrt{2A}, 3\pi/2, 0)$ we have $\lambda_1 > 0, \operatorname{Re} \lambda_2 < 0, \operatorname{Re} \lambda_3 < 0$.

4 Connections on the infinity manifold

To understand the global flow on the infinity manifold I_0, we analyze the invariant submanifolds associated to the equilibrium points on the infinity manifold as well as their connection orbits.

We introduce the change of variables

$$\bar{u} = \frac{\sqrt{2A}}{\Delta^{\frac{a}{4}}} \sin\psi, \qquad \bar{v} = \frac{\sqrt{2A}}{\Delta^{\frac{a}{4}}} \cos\psi.$$

Then Eq. (9) become on I_0

$$\begin{cases} \dot{\theta} = \dfrac{\sqrt{2A}}{\Delta^{\frac{a}{4}}} \sin\psi \\ \dot{\psi} = \left(\dfrac{a}{2} - 1\right) \dfrac{\sqrt{2A}}{\Delta^{\frac{a}{4}}} \sin\psi + \dfrac{\mu - 1}{2} \sin 2\theta \dfrac{\sqrt{A}a}{\sqrt{2}\Delta^{\frac{a}{4}+1}} \cos\psi. \end{cases} \tag{12}$$

The equilibrium points in the variables (θ, ψ) are

$$\begin{array}{ll} E_0^+ = (0, 0), & E_0^- = (0, \pi), \\ E_\pi^+ = (\pi, 0), & E_\pi^- = (\pi, \pi), \\ E^{+}_{\pi/2} = \left(\frac{\pi}{2}, 0\right), & E^{-}_{\pi/2} = \left(\frac{\pi}{2}, \pi\right), \\ E^{+}_{3\pi/2} = \left(\frac{3\pi}{2}, 0\right), & E^{-}_{3\pi/2} = \left(\frac{3\pi}{2}, \pi\right). \end{array}$$

For the following result we will restrict to the case $a = 6$. We note that the Lennard-Jones potential corresponds to $a = 6$ and $b = 12$.

Theorem 4 *For $a = 6$ and an open dense set of real numbers $\mu > 1$, the unstable manifold at $E_\pi^- = E^{-}_{3\pi/2}$ does not intersect the stable manifold at E_π^+ and the unstable manifold at E_π^- does not intersect the stable manifold at $E^{+}_{-\pi} = E^{+}_{3\pi/2}$.*

Proof Dividing the second equation in (12) by the first one, we get

$$\frac{d\psi}{d\theta} = \left(\frac{a}{2} - 1\right) + \frac{a}{4}\frac{(\mu - 1)}{\Delta}\sin 2\theta \frac{\cos\psi}{\sin\psi} = F(\theta, \psi, \epsilon) \tag{13}$$

where $\epsilon = \mu - 1$ and $\Delta = \mu\cos^2\theta + \sin^2\theta = 1 + \epsilon\cos^2\theta$.

We note that Eq. (13) has the symmetries

$$(\theta, \psi) \to (-\theta, \pi - \psi) \quad \text{and} \quad (\theta, \psi) \to (-\theta, -\psi). \tag{14}$$

We first consider the unstable manifolds $W^u(\pi, 0) = W^u(-\pi, 0)$, where we have taken the notation $W^u(\theta, \psi)$ to denote the unstable manifold of the point E in the (θ, ψ)-variables. In this case, $W^u(\pi, 0)$ is the unstable manifold of E_π^+. When $\epsilon = 0$, Eq. (13) yields

$$\frac{d\psi}{d\theta} = \frac{a}{2} - 1 \text{ that is } (a - 2)\theta = 2\psi - \pi \tag{15}$$

and clearly $W^s(\pi, \pi)$ coincides with $W^s(-\pi, 0)$. Consider the branch of $W^u(-\pi, 0) = W^u(\pi, 0)$ that contains $(0, \pi/2)$. This curve lies on the line (13). When $\epsilon \neq 0$, this branch on the unstable manifold varies smoothly on I_0. Then $\psi = \psi(\theta, \epsilon)$ denotes the ψ-coordinate of this curve satisfying $\psi(-\pi, \epsilon) = 0$ for all ϵ. We observe that it follows from (13) that ψ satisfies the equation

$$\psi(\theta, \epsilon) = \int_{-\pi}^{\theta} F(\zeta, \psi(\zeta), \epsilon)d\zeta. \tag{16}$$

For ϵ sufficiently small we write

$$\psi(\theta, \epsilon) = \psi(\theta, 0) + \epsilon\frac{\partial\psi}{\partial\epsilon}(\theta, 0) + \epsilon^2\frac{\partial^2\psi}{\partial\epsilon^2}(\theta, 0) + O(\epsilon^3). \tag{17}$$

Note that $\psi(\theta, 0) = (a/2 - 1)\theta + \pi/2$ and that from (16) we have

$$\frac{\partial\psi}{\partial\epsilon}(\theta, 0) = \int_{-\pi}^{\theta}\left[\frac{\partial}{\partial\epsilon}F(\zeta, \psi(\zeta, 0), 0) + \frac{\partial}{\partial\psi}F(\zeta, \psi(\zeta, 0), 0)\frac{\partial\psi}{\partial\epsilon}(\zeta, 0)\right]d\zeta. \tag{18}$$

From (13) we have

$$F(\theta, \psi, \epsilon) = \left(\frac{a}{2} - 1\right) + \frac{a}{4}\epsilon\sin 2\theta\frac{\cos\psi}{\sin\psi}\frac{1}{1 + \epsilon\cos^2\theta} \tag{19}$$

and thus

$$\frac{\partial F}{\partial\epsilon} = \frac{a}{4}\sin 2\theta\frac{\cos\psi}{\sin\psi}\frac{1}{1 + \epsilon\cos^2\theta} - \frac{a}{4}\epsilon\sin 2\theta\frac{\cos\psi\cos^2\theta}{\sin\psi(1 + \epsilon\cos^2\theta)^2}$$

which yields that

$$\frac{\partial F}{\partial \epsilon}_{|\epsilon=0,\theta=\zeta,\psi=\psi(\zeta,0)} = \frac{a}{4}\sin 2\zeta \frac{\cos\psi(\zeta,0)}{\sin\psi(\zeta,0)} \tag{20}$$

and

$$\frac{\partial F}{\partial \psi}_{|\epsilon=0,\theta=\zeta,\psi=\psi(\zeta,0)} = 0. \tag{21}$$

Then from (20) and (21) we get

$$\frac{\partial \psi}{\partial \epsilon}(\theta,0) = \frac{a}{4}\int_{-\pi}^{\theta} \sin 2\zeta \frac{\cos\psi(\zeta,0)}{\sin\psi(\zeta,0)} d\zeta.$$

Furthermore from (15), $\psi(\zeta,0) = \pi/2 + (a/2-1)\zeta$ and hence

$$\begin{aligned}\frac{\partial \psi}{\partial \epsilon}(\theta,0) &= \frac{a}{4}\int_{-\pi}^{\theta} \sin 2\zeta \frac{\cos\left[\frac{\pi}{2}+\left(\frac{a}{2}-1\right)\zeta\right]}{\sin\left[\frac{\pi}{2}+\left(\frac{a}{2}-1\right)\zeta\right]} d\zeta \\ &= -\frac{a}{4}\int_{-\pi}^{\theta} \sin 2\zeta \frac{\sin\left[\left(\frac{a}{2}-1\right)\zeta\right]}{\cos\left[\left(\frac{a}{2}-1\right)\zeta\right]} d\zeta\end{aligned} \tag{22}$$

Since $a = 6$ Eq. (22) becomes

$$\frac{\partial \psi}{\partial \epsilon}(\theta,0) = -\frac{3}{2}\int_{-\pi}^{\theta} \sin 2\zeta \frac{\sin 2\zeta}{\cos 2\zeta}\, d\zeta = \frac{3}{4}\left(\log\frac{\cos\theta-\sin\theta}{\cos\theta+\sin\theta} + \sin 2\theta\right). \tag{23}$$

On $\theta = 0$, $\partial\psi/\partial\epsilon(0,0) = 0$. Hence, we compute $\partial^2\psi/\partial\epsilon^2(0,0)$. It follows from (18) that

$$\begin{aligned}\frac{\partial^2 \psi}{\partial \epsilon^2}(\theta,0) = \int_{-\pi}^{\theta} &\left[\frac{\partial^2}{\partial \epsilon^2}F(\zeta,\psi(\zeta,0),0) + 2\frac{\partial^2}{\partial\epsilon\partial\psi}F(\zeta,\psi(\zeta,0),0)\frac{\partial\psi}{\partial\epsilon}(\zeta,0)\right. \\ &+ \frac{\partial^2}{\partial\psi^2}F(\zeta,\psi(\zeta,0),0)\left(\frac{\partial\psi}{\partial\epsilon}(\zeta,0)\right)^2 \\ &\left.+\frac{\partial}{\partial\psi}F(\zeta,\psi(\zeta,0),0)\frac{\partial^2\psi}{\partial\epsilon^2}(\zeta,0)\right] d\zeta.\end{aligned}$$

From (19) we have

$$\frac{\partial^2 F}{\partial \epsilon^2}_{|\epsilon=0,\theta=\zeta,\psi=\psi(\zeta,0)} = -3\sin 2\zeta \cos^2\zeta \frac{\cos\psi(\zeta,0)}{\sin\psi(\zeta,0)},$$

$$\frac{\partial^2 F}{\partial \epsilon \partial \psi}_{|\epsilon=0,\theta=\zeta,\psi=\psi(\zeta,0)} = -\frac{3}{2}\sin 2\zeta \frac{1}{\sin^2\psi(\zeta,0)},$$

$$\frac{\partial F}{\partial \psi}_{|\epsilon=0,\theta=\zeta,\psi=\psi(\zeta,0)} = 0, \quad \frac{\partial^2 F}{\partial \psi^2}_{|\epsilon=0,\theta=\zeta,\psi=\psi(\zeta,0)} = 0.$$

Using also (23) we get

$$\frac{\partial^2 \psi}{\partial \epsilon^2}(\theta,0) = -3\int_{-\pi}^{\theta} \sin 2\zeta \cos^2\zeta \frac{\sin 2\zeta}{\cos 2\zeta}\, d\zeta$$
$$- 3\int_{-\pi}^{\theta} \frac{\sin 2\zeta}{\cos^2 2\zeta}\left[\frac{3}{4}\log\frac{\cos\zeta - \sin\zeta}{\cos\zeta + \sin\zeta} + \frac{3}{4}\sin 2\zeta\right] d\zeta,$$

and thus on $\theta = 0$

$$\frac{\partial^2 \psi}{\partial \epsilon^2}(0,0) = -\frac{3\pi}{4} + \frac{9\pi}{4} = \frac{3\pi}{2} > 0.$$

Then for $\epsilon > 0$ we have that $\psi(0,\epsilon) > 0$ and then $v = \sqrt{2A}/\Delta^{3/2}\cos\psi(0,\epsilon) < 0$. By the first relation in (14) the stable manifold through $(-\pi, 0)$ is mapped into the unstable manifold through (π, π). Hence the stable manifold intersects the line $\theta = 0$ at some point $(0, \psi_0)$ such that $v(0, \psi_0) > 0$, a contradiction. Consequently, for $\epsilon > 0$ sufficiently small, the stable manifold does not intersect the unstable one.

Remark 3 We conjecture that the result stated on the theorem above is still valid for values a greater than 6 but for proof one need to compute derivatives of higher and higher orders which becomes more and more difficult to be evaluated.

5 Melnikov method

In this section, we study the appearance of chaos on the zero-energy manifold for the Hamiltonian

$$H = \frac{1}{2}(p_1^2 + p_2^2) - \frac{\alpha}{(q_1^2 + q_2^2)^{1/2}} - \frac{A}{(\mu q_1^2 + q_2^2)^{a/2}} + \frac{B}{(q_1^2 + q_2^2)^{b/2}} \tag{24}$$

truncated to the second order in ϵ, A, B and α, that is, the Hamiltonian

$$\begin{aligned} H &= \frac{1}{2}(p_1^2 + p_2^2) - \frac{\alpha}{r} - \frac{A}{r^a} + \frac{B}{r^b} + \epsilon A \frac{a\cos^2\theta}{2r^a} - \epsilon B \frac{b\cos^2\theta}{2r^b} \\ &= H_0(p_1, p_2, r) + AH_1(r) + BH_2(r) + \epsilon AH_3(r,\theta) + \epsilon BH_4(r,\theta), \end{aligned} \tag{25}$$

with $\epsilon, \alpha, A, B \ll 1$, i.e. with small values of ϵ, α, A, B, being A and B of the same order smaller than α.

For the hamiltonian system with Hamiltonian given in (25) we have the following result.

Theorem 5 *For ϵ, α, A, B sufficiently small, with $\epsilon, A, B \ll \alpha$ of the same order, the Hamiltonian system with Hamiltonian H given in (25) exhibits chaotic dynamics on the zero energy manifold provide that*

$$\frac{Aa}{Bb} \neq \frac{I_{2,b}}{I_{2,a}},$$

where $I_{2,a}$ and $I_{2,b}$ are define below.

Proof Consider the Hamiltonian H in (25). We will apply the Melnikov perturbative method described in detail in [8], following the ideas in [6]. To apply the Melnikov method we need to obtain the homoclinic manifold, that is, the set of solutions of the unperturbed equation which are asymptotic to $r = \infty$, $\dot{r} = 0$. For this, we consider the unperturbed problem ($\epsilon = A = B = 0$) in (25), that is, H_0, and we consider its parabolic solutions on the zero-energy manifold. These solutions satisfy the equations

$$\dot{r} = \pm\frac{\sqrt{2\alpha r - k^2}}{r}, \quad \dot{\theta} = \frac{k}{r^2}, \tag{26}$$

where $k \neq 0$ is the angular momentum, the $-$ sign holds for $t < 0$ and the $+$ sign holds for $t > 0$. From (26) we get

$$\begin{aligned} \pm t &= \frac{k^2 + \alpha r}{3\alpha^2}\sqrt{2r\alpha - k^2} + \text{ const.}, \\ \theta &= \pm 2\arctan\frac{\sqrt{2r\alpha - k^2}}{k} + \text{ const.} \end{aligned} \tag{27}$$

We denote by $R = R(t)$ and $\Theta = \Theta(t)$ the expressions giving the dependence of r and of θ on the time t which can be obtained by inverting the expressions in (27) with the condition $R(0) = k^2/2$ and $\Theta(0) = 0$. As pointed out in [8], it is important to note that $R(t)$ is an even function of the time t and $\Theta(t)$ is an odd function of the time t. The choice of $\Theta(0) = 0$ corresponds to select the solution describing the parabola with axis coinciding with the x-axis going to $+\infty$ when $x \to -\infty$.

For $p = k^2 \neq 0$, the parabolic orbits can also be described in parametric form as

$$\begin{aligned} \eta &= \tan\frac{\theta}{2}, \quad r = \frac{p}{2\alpha}(1+\eta^2) \\ t &= \frac{p^{3/2}\eta(3+\eta^2)}{6\alpha^2}, \quad \cos 2\theta = 2\frac{(1-\eta^2)^2}{(1+\eta^2)^2} - 1. \end{aligned} \tag{28}$$

The homoclinic manifold is thus given by the family of solutions

$$R(t-t_0), \quad \Theta(t-t_0)+\theta_0,$$

where $R(t)$ and $\Theta(t)$ where defined above and t_0, θ_0 are arbitrary. Since the Hamiltonian $H_0 + AH_1(r) + BH_2(r)$ is integrable it follows from (25) that the first nonvanishing terms of the Melnikov integrals are of the order ϵA and ϵB.

Taking into account that $H_3(r,\theta) \sim 1/r^a$, $H_4(r,\theta) \sim 1/r^b$ and $2 < a < b$ we have that the Melnikov integrals converge and we can apply the Melnikov method (see again [8] for details). Proceeding in the same way as in [8] and in [6] and taking into account that the perturbations $\epsilon AH_3(r,\theta)$ and $\epsilon BH_4(r,\theta)$ are not time dependent, the Melnikov method for H in (25) summarizes in obtaining the solutions of $M(\theta_0) = 0$ with

$$M(\theta_0) = \epsilon A\frac{a}{2}\int_{-\infty}^{\infty}\frac{\sin[2(\Theta(t)+\theta_0)]}{R(t)^a}dt - \epsilon B\frac{b}{2}\int_{-\infty}^{\infty}\frac{\sin[2(\Theta(t)+\theta_0)]}{R(t)^b}dt. \tag{29}$$

Such solutions correspond to intersections at the orders ϵA, ϵB of the positively and negatively asymptotic sets of the critical point at infinity. If one such solution exists then there are infinitely many and if the solutions correspond to simple zeroes of $M(\theta_0)$ then the intersection is transversal and for ϵ, A and B sufficiently small, higher order terms are not going to destroy the intersections.

Using that $\sin[2(\Theta(t)+\theta_0)] = \sin[2\Theta(t)]\cos(2\theta_0) + \cos[2\Theta(t)]\sin(2\theta_0)$ we can rewrite the integral in (29) as

$$M(\theta_0) = I_1\cos(2\theta_0) + I_2\sin(2\theta_0), \tag{30}$$

with

$$\begin{aligned} I_1 &= \epsilon A\frac{a}{2}\int_{-\infty}^{\infty}\frac{\sin[2(\Theta(t)]}{R(t)^a}dt - \epsilon B\frac{b}{2}\int_{-\infty}^{\infty}\frac{\sin[2(\Theta(t)]}{R(t)^b}dt, \\ I_2 &= \epsilon A\frac{a}{2}\int_{-\infty}^{\infty}\frac{\cos[2(\Theta(t)]}{R(t)^a}dt - \epsilon B\frac{b}{2}\int_{-\infty}^{\infty}\frac{\cos[2(\Theta(t)]}{R(t)^b}dt. \end{aligned} \tag{31}$$

Using that $R(t)$ is even in t and $\Theta(t)$ is odd in t we have that $I_1 = 0$ and

$$M(\theta_0) = I_2\sin(2\theta_0).$$

Then $M(\theta_0)$ has infinitely many zeroes, provided that $I_2 \neq 0$. Therefore, the proof of the theorem will be completed if we verify that $I_2 \neq 0$. We rewrite I_2 as

$$I_2 = \epsilon A \frac{a}{2} I_{2,a} - \epsilon B \frac{b}{2} I_{2,b} \tag{32}$$

with

$$I_{2,\beta} = \int_{-\infty}^{\infty} \frac{\cos[2(\Theta(t)]}{R(t)^{\beta}} dt, \quad \beta = a, b.$$

We compute $I_{2,\beta}$ using the parametric form of the parabolic orbits defined in (28). Since

$$dt = \frac{p^{3/2}}{2\alpha^2}(1+\eta^2) d\eta,$$

we can write

$$\begin{aligned} I_{2,\beta} &= 2^{\beta-1}\alpha^{\beta-2}p^{3/2-\beta} \int_{-\infty}^{\infty} \frac{1}{(1+\eta^2)^{\beta-1}} \left(\frac{2(1-\eta^2)^2}{(1+\eta^2)^2} - 1 \right) d\eta \\ &= \frac{\alpha^{\beta-2} 2^{\beta-2} p^{3/2-\beta} \sqrt{\pi}\,\Gamma\left(\beta+\frac{1}{2}\right)}{(\beta-1)\left(\beta-\frac{1}{2}\right)\left(\beta-\frac{3}{2}\right)\Gamma(\beta-1)} (\beta^2 - 5\beta + 6). \end{aligned} \tag{33}$$

Consequently, $I_2 \neq 0$ is equivalent with

$$\frac{Aa}{Bb} \neq \frac{I_{2,b}}{I_{2,a}}. \tag{34}$$

Remark 4 For the classical Lennard-Jones potential, when $a = 6$ and $b = 12$, relation (34) is equivalent with

$$\frac{A}{B} \neq 281.18 \left(\frac{\alpha}{p} \right)^6.$$

Remark 5 We note that if $\alpha = 0$, which means that we don't perturb the Lennard-Jones potential by a small order Newtonian potential, the Melnikov method would not be conclusive. This was the reason to consider in this section the Hamiltonian (24).

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