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Forcing and Anti–Forcing Polynomials of Perfect Matchings of a Pyrene System*

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Abstract

The forcing number of a perfect matching M of a graph G is the smallest number of edges in a subset $S \subset M$ such that S is in no other perfect matching. The anti-forcing number of M is the smallest number of edges in a subset $S' \subset E(G) \setminus M$ such that M is the unique perfect matching of $G - S'$. Recently the forcing and anti-forcing polynomials of perfect matchings of a graph were proposed as counting polynomials for perfect matchings with the same forcing number and anti-forcing number respectively. In this paper, we obtain the explicit expressions of forcing and anti-forcing polynomials of a pyrene system. As consequences, the distributions of forcing and anti-forcing numbers of perfect matchings of the pyrene system are revealed respectively.

1 Introduction

Let G be a simple graph with vertex set $V(G)$ and edge set $E(G)$. A *perfect matching* of G is a set of independent edges which covers all vertices of G. A perfect matching coincides with a Kekulé structure of a conjugated molecule graph (the graph representing the carbon-atoms). Klein and Randić [17, 24] observed that a Kekulé structure can be determined by a few number of fixed double bonds, and they defined the *innate degree*

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of freedom of a Kekulé structure as the smallest number of fixed double bonds required to determine it. The sum over innate degree of freedom of all Kekulé structures of a graph was called the *degree of freedom* of the graph, which was proposed as a novel invariant to estimate the resonance energy. In 1991, Harary, Klein and Živković [12] extended the concept of "innate degree of freedom" to a perfect matching M of a graph G, and renamed it as the *forcing number* of M, denoted by $f(G, M)$. Over the past 30 years, many researchers were attracted in this field [3], in addition, the anti-forcing number [20, 32, 33] was proposed from the point of opposite view of forcing number. In general, to compute the forcing number of a perfect matching of a bipartite graph with the maximum degree 3 is an NP-complete problem [1], and to compute the anti-forcing number of a perfect matching of a bipartite graph with the maximum degree 4 is also an NP-complete problem [8]. But the particular structure of a graph enables us to do much better. In this paper, we will calculate the forcing and anti-forcing polynomials of a pyrene system. As consequences, the distributions of forcing and anti-forcing numbers of perfect matchings of the pyrene system are revealed respectively.

A *forcing set* S of a perfect matching M of a graph G is a subset of M such that S is contained in no other perfect matchings of G. Therefore, $f(G, M)$ equals the smallest cardinality over all forcing sets of M. The *minimum* (resp. *maximum*) *forcing number* of G is the minimum (resp. maximum) value over forcing numbers of all perfect matchings of G, denoted by $f(G)$ (resp. $F(G)$). Afshani et al. [2] proved that the smallest forcing number problem is NP-complete for bipartite graphs with maximum degree four. In order to investigate the distribution of forcing numbers of all perfect matchings of a graph G, the *forcing spectrum* [1] was proposed, denoted by $\mathrm{Spec}_f(G)$, which is the collection of forcing numbers of all perfect matchings of G. Further, Zhang et al. [42] introduced the *forcing polynomial* of a graph, which can enumerate the number of perfect matchings with the same forcing number.

A *hexagonal system* (or *benzenoid*) is a finite 2-connected planar bipartite graph in which each interior face is surrounded by a regular hexagon of side length one. Hexagonal systems are extensively used in the study of benzenoid hydrocarbons [5], as they properly represent the skeleton of such molecules. Zhang and Li [38] and Hansen and Zheng [11] characterized independently the hexagonal systems with minimum forcing number 1, and the forcing spectrum of such a hexagonal system was determined by Zhang and Deng [39].

Zhang and Zhang [41] characterized plane elementary bipartite graphs with minimum forcing number 1. Xu et al. [35] proved that the maximum forcing number of a hexagonal system equals its *Clar number*, which is an invariant used to measure the stability of benzenoid hydrocarbons. Similar results also hold for polyomino graphs [43] and (4,6)-fullerenes [28]. Zhang et al. [40] proved that the minimum forcing number of a fullerene graph is not less than 3, and the lower bound can be achieved by infinitely many fullerene graphs. Randić, Vukičević and Gutman [25, 30, 31] determined the forcing spectra of fullerene graphs C_{60}, C_{70} and C_{72}, in particular there is a single Kekulé structure of C_{60} that has the highest innate degree of freedom 10 such that all hexagons of C_{60} have three double CC bonds, which represents the Fries structure of C_{60} and is the most important valence structure. For forcing polynomial, only a few types of hexagonal systems have been studied, such as catacondensed hexagonal systems [42] and benzenoid parallelogram [45]. For more results on forcing number, we refer the reader to see [4, 15, 16, 18, 19, 23, 26, 27, 34, 47–49].

Given a perfect matching M of a graph G. A subset $S \subset E(G) \setminus M$ is called an *anti-forcing set* of M if M is the unique perfect matching of $G-S$. The smallest cardinality over all anti-forcing sets of M is called the *anti-forcing number* of M, denoted by $af(G, M)$. The *minimum* (resp. *maximum*) *anti-forcing number* $af(G)$ (resp. $Af(G)$) of graph G is the minimum (resp. maximum) value of anti-forcing numbers over all perfect matchings of G. The minimum anti-forcing number of a graph was first introduced by Vukičević and Trinajstić [32, 33] in 2007-2008. Actually, the hexagonal systems with minimum anti-forcing number 1 had been characterized by Li [21] in 1997, where he called such a hexagonal system has a forcing single edge. Deng [6,7] obtained the minimum anti-forcing numbers of benzenoid chains and double benzenoid chains. Zhang et al. [44] computed the minimum anti-forcing number of catacondensed phenylene. Yang et al. [36] showed that a fullerene graph has the minimum anti-forcing number at least 4, and characterized the fullerene graphs with minimum anti-forcing number 4.

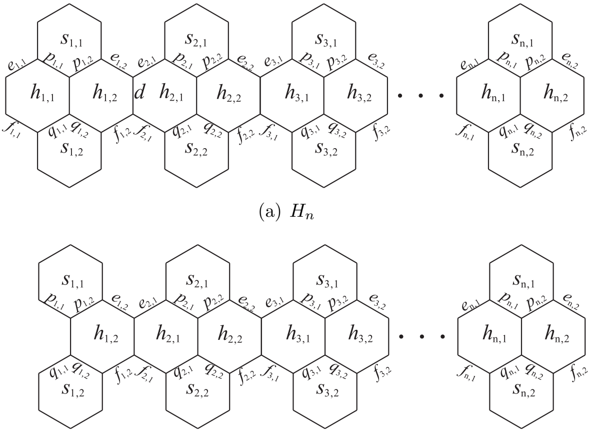
By an analogous manner as the forcing number, the *anti-forcing spectrum* of a graph G was proposed, denoted by $\mathrm{Spec}_{af}(G)$, which is the collection of anti-forcing numbers of all perfect matchings of G. Further, Hwang et al. [14] introduced the *anti-forcing polynomial* of a graph, which can enumerate the number of perfect matchings with the same anti-forcing number. Lei et al. [20] proved that the maximum anti-forcing number of a hexagonal system equals its Fries number, which can measure the stability of benzenoid hydrocarbons. Analogous result was also obtained on (4,6)-fullerenes [28]. Further more, two tight upper bounds on the maximum anti-forcing numbers of graphs were obtained [10, 29]. The anti-forcing spectra of some types of hexagonal systems were proved to be continuous, such as monotonic constructable hexagonal systems [8], catacondensed hexagonal systems [9]. Zhao and Zhang computed the anti-forcing polynomials of benzenoid systems with minimum forcing number 1 [46], and $2 \times n$ and $3 \times 2n$ rectangle grids [47].

In this paper, we will calculate the forcing and anti-forcing polynomials of a pyrene system H_n. In section 2, as a preparation, some basic results on forcing and anti-forcing numbers are introduced, and we characterize the maximum set of disjoint M-alternating cycles and the maximum set of compatible M-alternating cycles with respect to a perfect matching M of H_n. In section 3, we give a recurrence formula for the forcing polynomial of H_n, and derive the explicit expressions of forcing polynomial of H_n. As corollaries, the distribution of forcing numbers of all perfect matchings of H_n are determined, and an asymptotic behavior of degree of freedom of H_n is revealed. In section 4, we obtain a recurrence formula for the anti-forcing polynomial of H_n, and derive the explicit expressions of anti-forcing polynomial of H_n. As consequences, the distribution of anti-forcing numbers of all perfect matchings of H_n are determined, and an asymptotic behavior of the sum over anti-forcing numbers of all perfect matchings of H_n is obtained.

2 Preliminaries

Let M be a perfect matching of a graph G. A cycle C of G is called an *M-alternating cycle* if the edges of C appear alternately in M and $E(G) \setminus M$. If C is an M-alternating cycle, then the symmetric difference $M \triangle C$ is the another perfect matching of G, here C may be viewed as its edge set. Let $c(M)$ be the maximum number of disjoint M-alternating cycles of G. Since any forcing set of M has to contain at least one edge of each M-alternating cycle, $f(G, M) \geq c(M)$. Pachter and Kim [23] proved the following theorem by using the minimax theorem on feedback set [22].

Theorem 2.1 [23]**.** Let M be a perfect matching in a planar bipartite graph G. Then $f(G, M) = c(M)$.



(a) H_n

(b) G_n

Figure 1. (a) Pyrene system H_n with n pyrene fragments (b) The auxiliary graph G_n

A pyrene system with n pyrene fragments is denoted by H_n, see Fig. 1(a). H_n is a special hexagonal system, and also is a plane bipartite graph, by Theorem 2.1, $f(H_n, M) = c(M)$ for any perfect matching M of H_n.

Lemma 2.2 [37, 41]**.** Let M be a perfect matching of a hexagonal system H, C an M-alternating cycle. Then there is an M-alternating hexagon in the interior of C.

Let H be a hexagonal system with a perfect matching M. A set of disjoint M-alternating hexagons of H is called an *M-resonant set*, the size of a *maximum M-resonant set* is denote by $h(M)$.

Lemma 2.3. Let M be a perfect matching of the pyrene system H_n. Then $f(H_n, M) = h(M)$.

Proof. Let $\mathcal{A}$ be a maximum set of disjoint M-alternating cycles, and $\mathcal{A}$ contain hexagons as more as possible. By Theorem 2.1, $f(H_n, M) = |\mathcal{A}|$. We claim that $\mathcal{A}$ is an M-resonance set, otherwise $\mathcal{A}$ contains a non-hexagonal cycle C. By Lemma 2.2 there is an M-alternating hexagon h in the interior of C. Note that $\mathcal{A}' = (\mathcal{A} \setminus \{C\}) \cup \{h\}$ also is a maximum set of disjoint M-alternating cycles, but $\mathcal{A}'$ contains more hexagons than $\mathcal{A}$, a contradiction. We have $|\mathcal{A}| \leq h(M) \leq f(H_n, M) = |\mathcal{A}|$, i.e. $f(H_n, M) = h(M)$. ∎

Let M be a perfect matching of a graph G. A set $\mathcal{A}'$ of M-alternating cycles of G is called a compatible M-alternating set if any two cycles of $\mathcal{A}'$ either are disjoint or intersect only at edges in M. Let $c'(M)$ denote the maximum cardinality over all compatible M-alternating sets of G. Since any anti-forcing set of M must contain at least one edge of each M-alternating cycle, $af(G, M) \geq c'(M)$. Lei et al. [20] gave the following minimax theorem.

Theorem 2.4 [20]**.** Let G be a plane bipartite graph with a perfect matching M. Then $af(G, M) = c'(M)$.

Let $\mathcal{A}'$ be a compatible M-alternating set of a plane bipartite graph with a perfect matching M. Two cycles C_1 and C_2 of $\mathcal{A}'$ are *crossing* if they share an edge f in M and the four edges adjacent to f alternate in C_1 and C_2 (i.e., C_1 enters into C_2 from one side and leaves for the other side via f). $\mathcal{A}'$ is called *non-crossing* if any two cycles of $\mathcal{A}'$ are non-crossing.

Lemma 2.5 [10, 20]**.** Let G be a plane bipartite graph with a perfect matching M. Then there is a non-crossing compatible M-alternating set $\mathcal{A}'$ such that $|\mathcal{A}'| = c'(M)$.

A triphenylene is a benzenoid consisting of four hexagons, one hexagon at the center, for the other three disjoint hexagons, each of them has a common edge with the center one. For example, the four hexagons $s_{1,1}, s_{1,2}, h_{1,2}, h_{2,1}$ form a triphenylene, see Fig. 1(a).

Lemma 2.6. Let M be a perfect matching of the pyrene system H_n. Then there is a maximum non-crossing compatible M-alternating set $\mathcal{A}'$ such that each member of $\mathcal{A}'$ either is a hexagon or the periphery of a triphenylene.

Proof. By Lemma 2.5, there is a maximum non-crossing compatible M-alternating set $\mathcal{A}'$ such that $I(\mathcal{A}') = \sum_{C \in \mathcal{A}'} I(C)$ as small as possible, where $I(C)$ denotes the number of hexagons in the interior of C. Let C' be a member of $\mathcal{A}'$. Suppose C' is not a hexagon, by Lemma 2.2, there is an M-alternating hexagon h' in the interior of C'. Note that C' and h' must be compatible, otherwise $\mathcal{A}'' = (\mathcal{A}' \backslash \{C'\}) \cup \{h'\}$ can be a maximum non-crossing compatible M-alternating set such that $I(\mathcal{A}'') < I(\mathcal{A}')$, a contradiction. In fact, C' has to be compatible with any M-alternating hexagon, which implies that h' is a hexagon of type $h_{i,j}$ (see Fig. 1(a)). Without loss of generality, let $h' = h_{i,1} (i \neq 1)$. Then $e_{i,1}, f_{i,1}$ and the right vertical edge of $h_{i,1}$ all belong to M. Let $M' = M \triangle h_{i,1}$. Then $s_{i,1}$ and $s_{i,2}$ both are M'-alternating hexagons.

Claim 1. $h_{i-1,2}$ is M'-alternating.

Proof. Suppose $h_{i-1,2}$ is not M'-alternating. Then at least one of $p_{i-1,2}$ and $q_{i-1,2}$ does not belong to M. If only one of $p_{i-1,2}$ and $q_{i-1,2}$ belongs to M, say $p_{i-1,2} \in M$, then $s_{i-1,2}$ is an M-alternating hexagon which is not compatible with C', a contradiction. Therefore both of $p_{i-1,2}$ and $q_{i-1,2}$ are not in M, then $h_{i-1,1}$ is M-alternating. If $p_{i-2,2}$ and $q_{i-2,2}$ both belong to M, then the four hexagons $h_{i-2,2}$, $h_{i-1,1}$, $s_{i-1,1}$, and $s_{i-1,2}$ form a triphenylene whose periphery T is an M-alternating cycle. Note that T is compatible with each cycle of $\mathcal{A}' \setminus \{C'\}$, thus $(\mathcal{A}' \setminus \{C'\}) \cup \{T\}$ can be a maximum non-crossing compatible M-alternating set with $I((\mathcal{A}' \setminus \{C'\}) \cup \{T\}) < I(\mathcal{A}')$, a contradiction. Hence at least one of $p_{i-2,2}$ and $q_{i-2,2}$ does not belong to M, similar as above, we can show that $h_{i-2,1}$ is M-alternating. Keeping on this process, we will finally prove that $h_{1,1}$ is M-alternating, but $h_{1,1}$ is not compatible with C', a contradiction. ■

According to Claim 1 and the minimality of $I(\mathcal{A}')$, C' has to be the periphery of the triphenylene consisting of the four hexagons $h_{i-1,2}$, $h_{i,1}$, $s_{i,1}$ and $s_{i,2}$ (see Fig. 1(a)). ■

3 Forcing polynomial of pyrene system

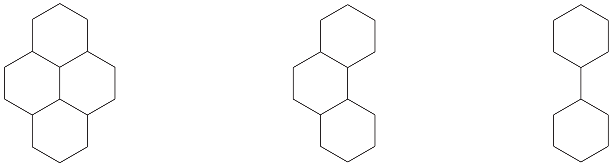
The forcing polynomial of a graph G is defined as follow [42]:

$$F(G,x) = \sum_{M \in \mathcal{M}(G)} x^{f(G,M)} = \sum_{i=f(G)}^{F(G)} w_i x^i, \tag{1}$$

where $\mathcal{M}(G)$ is the collection of all perfect matchings of G, w_i is the number of perfect matchings of G with the forcing number i.

As a consequence, let $\Phi(G)$ be the number of perfect matchings of a graph G, then $\Phi(G) = F(G,1)$. Recall that the degree of freedom of a graph G is the sum over the forcing numbers of all perfect matchings of G, denoted by $IDF(G)$, then $IDF(G) = \frac{d}{dx}F(G,x)|_{x=1}$. $\Phi(G)$ and $IDF(G)$ both are chemically meaningful indices within a resonance theoretic context [17,24]. Note that if G is a null graph or a graph has a unique perfect matching, then $F(G,x) = 1$.

In the following we will derive a recurrence formula for forcing polynomial of the pyrene system H_n, as preparations the forcing polynomials of pyrene, phenanthrene and diphenyl are computed: $F(H_1,x) = 4x^2 + 2x$, $F(L,x) = 4x^2 + x$, $F(N,x) = 4x^2$ (see Fig. 2).



(a) H_1 (b) L (c) N

Figure 2. (a) Pyrene, (b) Phenanthrene and (c) Diphenyl

Theorem 3.1. Let H_n be a pyrene system with n pyrene fragments. Then

$$F(H_n, x) = (4x^2 + 2x)F(H_{n-1}, x) - x^2F(H_{n-2}, x), \tag{2}$$

where $n \geq 2$, $F(H_0, x) = 1$ and $F(H_1, x) = 4x^2 + 2x$.

Proof. First we introduce an auxiliary graph G_n obtained by deleting the leftmost hexagon $h_{1,1}$ from H_n, see Fig. 1(b). We divide $\mathcal{M}(H_n)$ in two subsets: $\mathcal{M}^{e_{1,2}}_{f_{1,2}}(H_n) = \{M \in \mathcal{M}(H_n) \mid e_{1,2}, f_{1,2} \in M\}$, $\mathcal{M}^{\bar{e}_{1,2}}_{\bar{f}_{1,2}}(H_n) = \{M \in \mathcal{M}(H_n) \mid e_{1,2}, f_{1,2} \notin M\}$. If $M \in \mathcal{M}^{e_{1,2}}_{f_{1,2}}(H_n)$, then $h_{1,2}$ is a unique M-alternating hexagon in the leftmost pyrene fragment, and $M' = M \cap E(G_{n-1})$ is a perfect matching of the graph G_{n-1} obtained by deleting vertices of the leftmost pyrene fragment and their incident edges from H_n. By Lemma 2.3, $f(H_n, M) = f(G_{n-1}, M') + 1$. If $M \in \mathcal{M}^{\bar{e}_{1,2}}_{\bar{f}_{1,2}}(H_n)$, then the restriction M_1 of M on the phenanthrene L consisting of three hexagons $s_{1,1}, h_{1,1}, s_{1,2}$ is a perfect matching of L, and $M_2 = M \cap E(H_{n-1})$ is a perfect matching of the subsystem H_{n-1} obtained by deleting vertices of L and their incident edges from H_n, see Fig. 1(a). According to Lemma 2.3, $f(H_n, M) = f(L, M_1) + f(H_{n-1}, M_2)$. By Eq. (1), we have

$$\begin{aligned}
F(H_n, x) &= \sum_{M \in \mathcal{M}(H_n)} x^{f(H_n,M)} = \sum_{M \in \mathcal{M}^{e_{1,2}}_{f_{1,2}}(H_n)} x^{f(H_n,M)} + \sum_{M \in \mathcal{M}^{\bar{e}_{1,2}}_{\bar{f}_{1,2}}(H_n)} x^{f(H_n,M)} \\
&= \sum_{M' \in \mathcal{M}(G_{n-1})} x^{f(G_{n-1},M')+1} + \sum_{M_1 \in \mathcal{M}(L), M_2 \in \mathcal{M}(H_{n-1})} x^{f(L,M_1)+f(H_{n-1},M_2)} \\
&= x \sum_{M' \in \mathcal{M}(G_{n-1})} x^{f(G_{n-1},M')} + \sum_{M_1 \in \mathcal{M}(L), M_2 \in \mathcal{M}(H_{n-1})} x^{f(L,M_1)} x^{f(H_{n-1},M_2)} \\
&= xF(G_{n-1}, x) + \Big(\sum_{M_1 \in \mathcal{M}(L)} x^{f(L,M_1)}\Big)\Big(\sum_{M_2 \in \mathcal{M}(H_{n-1})} x^{f(H_{n-1},M_2)}\Big) \\
&= xF(G_{n-1}, x) + F(L, x)F(H_{n-1}, x) \\
&= xF(G_{n-1}, x) + (4x^2 + x)F(H_{n-1}, x)\ .
\end{aligned} \tag{3}$$

Now we deduce a recurrence relation for forcing polynomial of the auxiliary graph G_n. We can divide $\mathcal{M}(G_n)$ in two types, one is perfect matchings which containing edges

$e_{1,2}$ and $f_{1,2}$, and another is on the converse. For a perfect matching $M \in \mathcal{M}(G_n)$, if $e_{1,2}, f_{1,2} \in M$, then $h_{1,2}$ is a unique M-alternating hexagon in the leftmost phenanthrene consisting of three hexagons $s_{1,1}, s_{1,2}, h_{1,2}$, and the restriction M' of M on the graph G_{n-1} obtained by deleting vertices of the leftmost phenanthrene and their incident edges from G_n is a perfect matching of G_{n-1}. By Lemma 2.3, $f(G_n, M) = f(G_{n-1}, M') + 1$. On the other hand, if $e_{1,2}, f_{1,2} \notin M$, then the restriction M_1 of M on the leftmost diphenyl N is a perfect matching of N, and the restriction M_2 of M on the successive subsystem H_{n-1} is a perfect matching of H_{n-1}. Therefore $f(G_n, M) = f(N, M_1) + f(H_{n-1}, M_2)$, see Fig. 1(b). By a similar deducing as Eq. (3), we can obtain the following formula

$$F(G_n, x) = xF(G_{n-1}, x) + 4x^2 F(H_{n-1}). \tag{4}$$

Eq. (3) minus Eq. (4), we have

$$F(G_n, x) = F(H_n, x) - xF(H_{n-1}, x),$$

which implies

$$F(G_{n-1}, x) = F(H_{n-1}, x) - xF(H_{n-2}, x).$$

Substituting this expression into Eq. (3), we can obtain Eq. (2), the proof is completed. ■

Theorem 3.2. Let H_n be a pyrene system with n pyrene fragments. Then

$$F(H_n, x) = x^n \sum_{j=0}^{n} \sum_{i=\lceil \frac{j+n}{2} \rceil}^{n} (-1)^{n-i} 2^{2i+j-n} \binom{i}{n-i} \binom{2i-n}{j} x^j.$$

Proof. For convenience, let $F_n := F(H_n, x)$, then the generating function of sequence $\{F_n\}_{n=0}^{\infty}$ is obtained as follow

$$\begin{aligned} G(z) = \sum_{n=0}^{\infty} F_n z^n &= 1 + (4x^2 + 2x)z + \sum_{n=2}^{\infty} F_n z^n \\ &= 1 + (4x^2 + 2x)z + \sum_{n=2}^{\infty} ((4x^2 + 2x)F_{n-1} - x^2 F_{n-2}) z^n \\ &= 1 + (4x^2 + 2x)z + (4x^2 + 2x)z(G(z) - 1) - x^2 z^2 G(z) \\ &= 1 + (4x^2 + 2x)zG(z) - x^2 z^2 G(z). \end{aligned}$$

Therefore

$$\begin{aligned} G(z) &= \frac{1}{1-((4x^2+2x)z-x^2z^2)} = \sum_{i=0}^{\infty}((4x^2+2x)z-x^2z^2)^i \\ &= \sum_{i=0}^{\infty} x^i z^i \sum_{j=0}^{i} \binom{i}{j} (4x+2)^{i-j}(-xz)^j \\ &= \sum_{n=0}^{\infty} \sum_{i=\lceil \frac{n}{2} \rceil}^{n} (-1)^{n-i} \binom{i}{n-i} (4x+2)^{2i-n} x^n z^n, \end{aligned}$$

which implies

$$\begin{aligned} F_n &= x^n \sum_{i=\lceil \frac{n}{2} \rceil}^{n} (-1)^{n-i} \binom{i}{n-i} (4x+2)^{2i-n} \\ &= x^n \sum_{i=\lceil \frac{n}{2} \rceil}^{n} (-1)^{n-i} \binom{i}{n-i} \sum_{j=0}^{2i-n} 2^{2i+j-n} \binom{2i-n}{j} x^j \\ &= x^n \sum_{j=0}^{n} \sum_{i=\lceil \frac{j+n}{2} \rceil}^{n} (-1)^{n-i} 2^{2i+j-n} \binom{i}{n-i} \binom{2i-n}{j} x^j. \end{aligned}$$

The proof is completed. ∎

As a consequence, the following corollary is immediate.

Corollary 3.3. Let H_n be a pyrene system with n pyrene fragments. Then

1. $f(H_n) = n$;
2. $F(H_n) = 2n$;
3. $\mathrm{Spec}_f(H_n) = [n, 2n]$.

In the following we compute the degree of freedom of H_n, and discuss its asymptotic behavior. He and He [13] gave the following formula:

$$\Phi(H_n) = 6\Phi(H_{n-1}) - \Phi(H_{n-2}), \tag{5}$$

further we can obtain an general formula as follow:

$$\Phi(H_n) = \frac{17-12\sqrt{2}}{16-12\sqrt{2}}(3-2\sqrt{2})^n + \frac{17+12\sqrt{2}}{16+12\sqrt{2}}(3+2\sqrt{2})^n. \tag{6}$$

Theorem 3.4.

$$\begin{aligned} IDF(H_n) &= \frac{\sqrt{2}}{32}(3-2\sqrt{2})^n + \frac{7-5\sqrt{2}}{8}n(3-2\sqrt{2})^n - \frac{\sqrt{2}}{32}(3+2\sqrt{2})^n \\ &\quad + \frac{7+5\sqrt{2}}{8}n(3+2\sqrt{2})^n. \end{aligned} \tag{7}$$

Proof. According to Eq. (2),

$$\begin{aligned}\frac{d}{dx}F(H_n,x) &= (8x+2)F(H_{n-1},x)+(4x^2+2x)\frac{d}{dx}F(H_{n-1},x)\\ &\quad -2xF(H_{n-2},x)-x^2\frac{d}{dx}F(H_{n-2},x).\end{aligned}$$

For convenience, let $\Phi_n := \Phi(H_n)$ and $IDF_n := IDF(H_n)$, then we have

$$\begin{aligned}IDF_n &= \frac{d}{dx}F(H_n,x)\Big|_{x=1}\\ &= 6IDF_{n-1}-IDF_{n-2}+10\Phi_{n-1}-2\Phi_{n-2}.\end{aligned}$$

So

$$\begin{aligned}IDF_{n+1} &= 6IDF_n-IDF_{n-1}+10\Phi_n-2\Phi_{n-1},\\ IDF_{n+2} &= 6IDF_{n+1}-IDF_n+10\Phi_{n+1}-2\Phi_n,\end{aligned}$$

by Eq. (5), $\Phi_{n+1} = 6\Phi_n - \Phi_{n-1}$ and $\Phi_n = 6\Phi_{n-1} - \Phi_{n-2}$, which implies

$$\begin{aligned}IDF_{n+2} &= 6IDF_{n+1}-IDF_n+10(6\Phi_n-\Phi_{n-1})-2(6\Phi_{n-1}-\Phi_{n-2})\\ &= 6IDF_{n+1}-IDF_n+60\Phi_n-22\Phi_{n-1}+2\Phi_{n-2}\\ &= 6IDF_{n+1}-IDF_n+6(6IDF_n-IDF_{n-1}+10\Phi_n-2\Phi_{n-1})-(6IDF_{n-1}\\ &\quad -IDF_{n-2}+10\Phi_{n-1}-2\Phi_{n-2})-36IDF_n+12IDF_{n-1}-IDF_{n-2}\\ &= 12IDF_{n+1}-38IDF_n+12IDF_{n-1}-IDF_{n-2}. \qquad (8)\end{aligned}$$

Therefore the homogeneous characteristics equation of recurrence formula (8) is $x^4 - 12x^3 + 38x^2 - 12x + 1 = 0$, and its roots are $x_1 = x_2 = 3 - 2\sqrt{2}$, $x_3 = x_4 = 3 + 2\sqrt{2}$. Suppose the general solution of Eq. (8) is $IDF_n = \lambda_1(3-2\sqrt{2})^n + \lambda_2 n(3-2\sqrt{2})^n + \lambda_3(3+2\sqrt{2})^n + \lambda_4 n(3+2\sqrt{2})^n$. According to the initial values $IDF_3 = 1036$, $IDF_4 = 8068$, $IDF_5 = 58854$ and $IDF_6 = 411978$, we can obtain $\lambda_1 = \frac{\sqrt{2}}{32}$, $\lambda_2 = \frac{7-5\sqrt{2}}{8}$, $\lambda_3 = -\frac{\sqrt{2}}{32}$ and $\lambda_4 = \frac{7+5\sqrt{2}}{8}$, so Eq. (7) holds for $n \geq 3$. In fact, we can check that Eq. (7) also holds for $n = 0, 1, 2$, so the proof is completed. ∎

By Eqs. (6) and (7), the following result is obtained.

Corollary 3.5. Let H_n be a pyrene system with n pyrene fragments. Then

$$\lim_{n\to\infty}\frac{IDF(H_n)}{n\Phi(H_n)} = 1+\frac{\sqrt{2}}{2}.$$

4 Anti–forcing polynomial of pyrene system

The anti-forcing polynomial of a graph G is defined as follow [14]:

$$Af(G,x)=\sum_{M\in\mathcal{M}(G)}x^{af(G,M)}=\sum_{i=af(G)}^{Af(G)}u_ix^i, \tag{9}$$

where u_i is the number of perfect matchings of G with the anti-forcing number i.

As a consequence, $\Phi(G)=Af(G,1)$, and the sum over the anti-forcing numbers of all perfect matchings of G equals $\frac{d}{dx}Af(G,x)\big|_{x=1}$. If G is a null graph or a graph with unique perfect matching, then $Af(G,x)=1$. We obtain the following recursive formula.

Theorem 4.1. Let H_n be the pyrene system with n pyrene fragments. Then

$$Af(H_n,x)=(2x^3+2x^2+2x)Af(H_{n-1},x)-x^2Af(H_{n-2},x), \tag{10}$$

where $n\geq 2$, $Af(H_0,x)=1$ and $Af(H_1,x)=2x^3+2x^2+2x$.

Proof. First we divide $\mathcal{M}(H_n)$ in two subsets: $\mathcal{M}^{e_{1,2}}_{f_{1,2}}(H_n)=\{M\in\mathcal{M}(H_n)\mid e_{1,2},f_{1,2}\in M\}$, $\mathcal{M}^{\bar{e}_{1,2}}_{\bar{f}_{1,2}}(H_n)=\{M\in\mathcal{M}(H_n)\mid e_{1,2},f_{1,2}\notin M\}$. There are two cases to be considered.

Case 1. Suppose $e_{1,2}$ and $f_{1,2}$ both belong to M. Then the restriction M_1 of M on the leftmost pyrene fragment is a perfect matching of it, and $h_{1,2}$ is an M-alternating hexagon ,see Fig. 1(a).

Subcase 1.1. If $p_{2,1}$ and $q_{2,1}$ both belong to M, then the hexagons $s_{2,1}$ and $s_{2,2}$ both are M-alternating, and the four hexagons $s_{1,1},s_{1,2},h_{1,2},h_{2,1}$ form a triphenylene whose perimeter T is an M-alternating cycle, and $\{h_{1,2},s_{2,1},s_{2,2},T\}$ is a non-crossing compatible M-alternating set. Note that the restriction M' of M on the subsystem H_{n-2} obtained by the removal of the leftmost two pyrene fragments from H_n is a perfect matching of H_{n-2}. Let $\mathcal{A}'$ be a maximum non-crossing compatible M'-alternating set of H_{n-2}, by Lemma 2.6, then $\{h_{1,2},s_{2,1},s_{2,2},T\}\cup\mathcal{A}'$ is a maximum non-crossing compatible M-alternating set of H_n. By Theorem 2.4, $af(H_n,M)=4+af(H_{n-2},M')$. Let $Y_1=\{M\in\mathcal{M}^{e_{1,2}}_{f_{1,2}}(H_n)|\ p_{2,1},q_{2,1}\in M\}$, by Eq. (9),

$$\sum_{M\in Y_1}x^{af(H_n,M)}=\sum_{M'\in\mathcal{M}(H_{n-2})}x^{4+af(H_{n-2},M')}=x^4Af(H_{n-2},x). \tag{11}$$

Subcase 1.2. If one of $p_{2,1},q_{2,1}$ does not belong to M, then the perimeter of the triphenylene consisting of the four hexagons $s_{1,1},s_{1,2},h_{1,2},h_{2,1}$ is not an M-alternating cycle. Recall that $M_1 \subseteq M$ is a perfect matching of the first pyrene fragment, thus $M_2 = M \setminus M_1$ is a perfect matching of the subgraph G_{n-1} (see Fig. 1(b)). By Lemma 2.6, $af(H_n, M) = 1 + af(G_{n-1}, M_2)$. Let X be a perfect matching of G_{n-1}. Suppose X contains edges $p_{2,1}, q_{2,1}$, then $s_{2,1}$ and $s_{2,2}$ both are X-alternating hexagons, and $X_1 = X \cap E(H_{n-2})$ is a perfect matching of the subsystem H_{n-2} obtained by deleting the vertices of the leftmost diphenyl of G_{n-1} and their incident edges. Note that Lemma 2.6 also holds for the auxiliary graph G_n, and $h_{2,2}$ is not X-alternating, so $af(G_{n-1}, X) = 2 + af(H_{n-2}, X_1)$. Let $\mathcal{M}^{p_{2,1}}_{q_{2,1}}(G_{n-1}) = \{X \in \mathcal{M}(G_{n-1}) | p_{2,1}, q_{2,1} \in X\}$, $Y_2 = \mathcal{M}^{e_{1,2}}_{f_{1,2}}(H_n) \setminus Y_1$, then

$$\begin{aligned}
\sum_{M \in Y_2} x^{af(H_n,M)} &= \sum_{M_2 \in \mathcal{M}(G_{n-1}) \setminus \mathcal{M}^{p_{2,1}}_{q_{2,1}}(G_{n-1})} x^{1+af(G_{n-1},M_2)} \\
&= x\Big(\sum_{X \in \mathcal{M}(G_{n-1})} x^{af(G_{n-1},X)} - \sum_{X \in \mathcal{M}^{p_{2,1}}_{q_{2,1}}(G_{n-1})} x^{af(G_{n-1},X)}\Big) \\
&= x\Big(Af(G_{n-1},x) - \sum_{X_1 \in \mathcal{M}(H_{n-2})} x^{2+af(H_{n-2},X_1)}\Big) \\
&= xAf(G_{n-1},x) - x^3 Af(H_{n-2},x). \qquad (12)
\end{aligned}$$

Case 2. Suppose $e_{1,2}$ and $f_{1,2}$ both are not in M, then we can divide $\mathcal{M}^{\bar{e}_{1,2}}_{\bar{f}_{1,2}}(H_n)$ in two subsets $Y_3 = \{M \in \mathcal{M}^{\bar{e}_{1,2}}_{\bar{f}_{1,2}}(H_n) | e_{2,1}, f_{2,1} \in M\}$ and $Y_4 = \{M \in \mathcal{M}^{\bar{e}_{1,2}}_{\bar{f}_{1,2}}(H_n) | e_{2,1}, f_{2,1} \notin M\}$.

Subcase 2.1. Suppose $M \in Y_3$, then $h_{2,1}$ must be an M-alternating hexagon, and the restrictions M_1 and M_2 of M on the leftmost phenanthrene L and the rightmost subsystem H_{n-2} are perfect matchings of L and H_{n-2} respectively (see Fig. 1(a)). Let $\mathcal{A}'$ be a maximum non-crossing compatible M_2-alternating set of H_{n-2}. Note that M_1 contains only five distinct members, we can divide Y_3 in five subsets: $Y_{3,1} = \{M \in Y_3 | p_{1,2}, q_{1,2} \in M\}$, $Y_{3,2} = \{M \in Y_3 | p_{1,1}, q_{1,1} \in M\}$, $Y_{3,3} = \{M \in Y_3 | e_{1,1}, f_{1,1} \in M\}$, $Y_{3,4} = \{M \in Y_3 | p_{1,2} \in M, q_{1,2} \notin M\}$, $Y_{3,5} = \{M \in Y_3 | p_{1,2} \notin M, q_{1,2} \in M\}$. If $M \in Y_{3,1}$, then the four hexagons $h_{1,2}, h_{2,1}, s_{2,1}, s_{2,2}$ form a triphenylene whose perimeter T is an M-alternating cycle, and $\{s_{1,1}, s_{1,2}, h_{2,1}, T\}$ is a non-crossing compatible M-alternating set. By Lemma 2.6, $\{s_{1,1}, s_{1,2}, h_{2,1}, T\} \cup \mathcal{A}'$ is a maximum non-crossing compatible M-alternating set of H_n. By Theorem 2.4, $af(H_n, M) = 4 + af(H_{n-2}, M_2)$, which implies that $\sum_{M \in Y_{31}} x^{af(H_n,M)} = x^4 Af(H_{n-2}, x)$. If $M \in Y_{3,2}$, then $\{s_{1,1}, s_{1,2}, h_{1,1}, h_{2,1}\}$ is an non-crossing compatible M-alternating set, and $\{s_{1,1}, s_{1,2}, h_{1,1}, h_{2,1}\} \cup \mathcal{A}'$ is a maximum non-crossing compatible M-alternating set of H_n. By Theorem 2.4, $af(H_n, M) = 4 + af(H_{n-2}, M_2)$, so $\sum_{M \in Y_{3,2}} x^{af(H_n,M)} = x^4 Af(H_{n-2}, x)$. If $M \in Y_{3,3}$, then $\{h_{1,1}, h_{2,1}\} \cup \mathcal{A}'$ is a maximum non-crossing compatible M-alternating set of H_n. By Theorem 2.4, $af(H_n, M) = 2 + af(H_{n-2}, M_2)$, we have $\sum_{M\in Y_{3,3}} x^{af(H_n,M)} = x^2 Af(H_{n-2}, x)$. If $M \in Y_{3,4}$ or $M \in Y_{3,5}$, then $\{s_{1,1}, s_{1,2}, h_{2,1}\} \cup \mathcal{A}'$ is a maximum non-crossing compatible M-alternating set of H_n. By Theorem 2.4, $af(H_n, M) = 3 + af(H_{n-2}, M_2)$, thus $\sum_{M\in Y_{3,4}} x^{af(H_n,M)} + \sum_{M\in Y_{3,5}} x^{af(H_n,M)} = 2x^3 Af(H_{n-2}, x)$. Finally, we have

$$\sum_{M\in Y_3} x^{af(H_n,M)} = \sum_{j=1}^{5} \sum_{M\in Y_{3,j}} x^{af(H_n,M)} = (2x^4 + 2x^3 + x^2) Af(H_{n-2}, x). \tag{13}$$

Subcase 2.2. If $M \in Y_4$, then the common vertical edge d of $h_{1,2}$ and $h_{2,1}$ belongs to M, and the restrictions M_1 and M_2 of M on the leftmost pyrene fragment H_1 and the rightmost subsystem H_{n-1} are perfect matchings of H_1 and H_{n-1} respectively (see Fig. 1(a)). We divide $\mathcal{M}(H_1)$ in two subsets: $\mathcal{M}_d(H_1) = \{M_1 \in \mathcal{M}(H_1) | d \in M_1\}$, $\mathcal{M}_{\bar d}(H_1) = \{M_1 \in \mathcal{M}(H_1) | d \notin M_1\}$. Note that $\mathcal{M}_{\bar d}(H_1)$ contains only one perfect matching M_1' of H_1, and $h_{1,2}$ is the unique M_1'-alternating hexagon in H_1, so $af(H_1, M_1') = 1$, we have

$$\begin{aligned}\sum_{M_1\in\mathcal{M}_d(H_1)} x^{af(H_1,M_1)} &= \sum_{M_1\in\mathcal{M}(H_1)} x^{af(H_1,M_1)} - \sum_{M_1'\in\mathcal{M}_{\bar d}(H_1)} x^{af(H_1,M_1')} \\ &= Af(H_1, x) - x = 2x^3 + 2x^2 + x\ . \end{aligned} \tag{14}$$

We also divide $\mathcal{M}(H_{n-1})$ in two subsets: $\mathcal{M}_d(H_{n-1}) = \{M_2 \in \mathcal{M}(H_{n-1}) | d \in M_2\}$ and $\mathcal{M}_{\bar d}(H_{n-1}) = \{M_2 \in \mathcal{M}(H_{n-1}) | d \notin M_2\}$. Suppose $M_2 \in \mathcal{M}_{\bar d}(H_{n-1})$, then $e_{2,1}, f_{2,1} \in M_2$ and $h_{2,1}$ is an M_2-alternating hexagon, and the restriction M_2' of M_2 on the rightmost subsystem H_{n-2} is a perfect matching of H_{n-2}. Let $\mathcal{A}'$ be a maximum non-crossing compatible M_2'-alternating set of H_{n-2}. Then $\mathcal{A}' \cup \{h_{2,1}\}$ is a maximum non-crossing compatible M_2-alternating set of H_{n-1}. Thus $af(H_{n-1,M_2}) = 1 + af(H_{n-2}, M_2')$, we have

$$\begin{aligned}\sum_{M_2\in\mathcal{M}_d(H_{n-1})} x^{af(H_{n-1},M_2)} &= \sum_{M_2\in\mathcal{M}(H_{n-1})} x^{af(H_{n-1},M_2)} - \sum_{M_2\in\mathcal{M}_{\bar d}(H_{n-1})} x^{af(H_{n-1},M_2)} \\ &= Af(H_{n-1}, x) - \sum_{M_2'\in\mathcal{M}(H_{n-2})} x^{1+af(H_{n-2},M_2')} \\ &= Af(H_{n-1}, x) - xAf(H_{n-2}, x). \end{aligned} \tag{15}$$

Recall that d is the common edge of $h_{1,2}$ and $h_{2,1}$, for any $M \in Y_4$, then $M = M_1 \cup M_2$, where M_1 is a perfect matching of the first pyrene fragment H_1 and M_2 is a perfect matching of the rightmost subsystem H_{n-1}, and $\{d\} = M_1 \cap M_2$. By Theorem 2.4 and Lemma 2.6, we have $af(H_n, M) = af(H_1, M_1) + af(H_{n-1}, M_2)$. According to Eqs. (14)

and (15), we have

$$\begin{aligned}\sum_{M\in Y_4} x^{af(H_n,M)} &= \sum_{M_1\in\mathcal{M}_d(H_1),M_2\in\mathcal{M}_d(H_{n-1})} x^{af(H_1,M_1)+af(H_{n-1},M_2)}\\ &= \Big(\sum_{M_1\in\mathcal{M}_d(H_1)} x^{af(H_1,M_1)}\Big)\Big(\sum_{M_2\in\mathcal{M}_d(H_{n-1})} x^{af(H_{n-1},M_2)}\Big)\\ &= (2x^3+2x^2+x)(Af(H_{n-1},x)-xAf(H_{n-2},x))\\ &= (2x^3+2x^2+x)Af(H_{n-1},x)-(2x^4+2x^3+x^2)Af(H_{n-2},x).\end{aligned} \tag{16}$$

By Eqs. (11), (12), (13) and (16), we obtain a recursive relation as below:

$$\begin{aligned}Af(H_n,x) &= \sum_{M\in\mathcal{M}(H_n)} x^{af(H_n,M)}\\ &= \sum_{M\in Y_1} x^{af(H_n,M)} + \sum_{M\in Y_2} x^{af(H_n,M)} + \sum_{M\in Y_3} x^{af(H_n,M)} + \sum_{M\in Y_4} x^{af(H_n,M)}\\ &= (2x^3+2x^2+x)Af(H_{n-1},x)+(x^4-x^3)Af(H_{n-2},x)+xAf(G_{n-1},x).\end{aligned} \tag{17}$$

Similar as above, we can prove the following recursive formula for the auxiliary graph G_n (see Fig. 1(b)),

$$Af(G_n,x)=(x^3+3x^2)Af(H_{n-1},x)+(x^4-x^3)Af(H_{n-2},x)+xAf(G_{n-1},x). \tag{18}$$

Eq. (17) subtracts Eq. (18), we have

$$Af(G_n,x)=Af(H_n,x)-(x^3-x^2+x)Af(H_{n-1},x),$$

so

$$Af(G_{n-1},x)=Af(H_{n-1},x)-(x^3-x^2+x)Af(H_{n-2},x).$$

Substituting this expression into Eq. (17), we can obtain the Eq. (10), the proof is completed. ■

By theorem 4.1, we can obtain an explicit expression as below.

Theorem 4.2. Let H_n be the pyrene system with n pyrene fragments. Then

$$Af(H_n,x)=x^n\sum_{l=0}^{2n}\sum_{i=\lceil\frac{l+2n}{4}\rceil}^{n}\sum_{j=\lceil\frac{l}{2}\rceil}^{l}(-1)^{n-i}2^{2i-n}\binom{i}{2i-n}\binom{2i-n}{j}\binom{j}{l-j}x^l. \tag{19}$$

Proof. Let $A_n := Af(H_n, x)$, then the generating function of sequence $\{A_n\}_{n=0}^{\infty}$ is

$$\begin{aligned} G(t) &= \sum_{n=0}^{\infty} A_n t^n = 1 + (2x^3 + 2x^2 + 2x)t + \sum_{n=2}^{\infty} A_n t^n \\ &= 1 + (2x^3 + 2x^2 + 2x)t + \sum_{n=2}^{\infty}((2x^3 + 2x^2 + 2x)A_{n-1} - x^2 A_{n-2})t^n \\ &= 1 + (2x^3 + 2x^2 + 2x)t \sum_{n=0}^{\infty} A_n t^n - x^2 t^2 \sum_{n=0}^{\infty} A_n t^n \\ &= 1 + (2x^3 + 2x^2 + 2x)tG(t) - x^2 t^2 G(t). \end{aligned}$$

So

$$\begin{aligned} G(t) &= \frac{1}{1 - ((2x^3 + 2x^2 + 2x)t - x^2t^2)} = \sum_{i=0}^{\infty}((2x^3 + 2x^2 + 2x)t - x^2t^2)^i \\ &= \sum_{i=0}^{\infty}\sum_{j=0}^{i}\binom{i}{j}(2x^3 + 2x^2 + 2x)^j t^j (-x^2t^2)^{i-j} \\ &= \sum_{i=0}^{\infty}\sum_{n=i}^{2i}(-1)^{n-i}2^{2i-n}\binom{i}{2i-n}(x^2 + x + 1)^{2i-n}x^n t^n \\ &= \sum_{n=0}^{\infty}\sum_{i=\lceil \frac{n}{2} \rceil}^{n}(-1)^{n-i}2^{2i-n}\binom{i}{2i-n}(x^2 + x + 1)^{2i-n}x^n t^n, \end{aligned}$$

we have

$$\begin{aligned} Af(H_n, x) &= x^n \sum_{i=\lceil \frac{n}{2} \rceil}^{n}(-1)^{n-i}2^{2i-n}\binom{i}{2i-n}(x^2 + x + 1)^{2i-n} \\ &= x^n \sum_{i=\lceil \frac{n}{2} \rceil}^{n}(-1)^{n-i}2^{2i-n}\binom{i}{2i-n}\sum_{j=0}^{2i-n}\binom{2i-n}{j}x^j\sum_{k=0}^{j}\binom{j}{k}x^k \\ &= x^n \sum_{i=\lceil \frac{n}{2} \rceil}^{n}(-1)^{n-i}2^{2i-n}\binom{i}{2i-n}\sum_{j=0}^{2i-n}\sum_{l=j}^{2j}\binom{2i-n}{j}\binom{j}{l-j}x^l \\ &= x^n \sum_{l=0}^{2n}\sum_{i=\lceil \frac{l+2n}{4} \rceil}^{n}\sum_{j=\lceil \frac{l}{2} \rceil}^{l}(-1)^{n-i}2^{2i-n}\binom{i}{2i-n}\binom{2i-n}{j}\binom{j}{l-j}x^l. \end{aligned}$$

■

According to Theorem 4.2, the following corollary is immediate.

Corollary 4.3. Let H_n be a pyrene system with n pyrene fragments. Then

1. $af(H_n) = n$;
2. $Af(H_n) = 3n$;

3. $\mathrm{Spec}_{af}(H_n) = [n, 3n]$.

In the following, we will calculate the sum over the anti-forcing numbers of all perfect matchings of H_n, and investigate its asymptotic behavior.

Theorem 4.4. The sum over the anti-forcing numbers of all perfect matchings of H_n is

$$\begin{aligned}\frac{d}{dx}Af(H_n,x)\big|_{x=1} &= \frac{3\sqrt{2}}{64}(3-2\sqrt{2})^n + \frac{17-12\sqrt{2}}{16}n(3-2\sqrt{2})^n - \frac{3\sqrt{2}}{64}(3+2\sqrt{2})^n \\ &+ \frac{17+12\sqrt{2}}{16}n(3+2\sqrt{2})^n. \end{aligned} \tag{20}$$

Proof. By Theorem 4.1,

$$\begin{aligned}\frac{d}{dx}Af(H_n,x) &= (6x^2+4x+2)Af(H_{n-1},x) + (2x^3+2x^2+2x)\frac{d}{dx}Af(H_{n-1},x) \\ &\quad -2xAf(H_{n-2},x) - x^2\frac{d}{dx}Af(H_{n-2},x). \end{aligned} \tag{21}$$

For convenience, let $\Phi_n := \Phi(H_n)$ and $AF_n := \frac{d}{dx}Af(H_n,x)\big|_{x=1}$, by Eq. (21), we have

$$AF_n = 6AF_{n-1} - AF_{n-2} + 12\Phi_{n-1} - 2\Phi_{n-2}. \tag{22}$$

By Eq. (5), $\Phi_n = 6\Phi_{n-1} - \Phi_{n-2}$, so $AF_n = 6AF_{n-1} - AF_{n-2} + 2\Phi_n$, which implies $2\Phi_n = AF_n - 6AF_{n-1} + AF_{n-2}$. Therefore $2\Phi_{n-1} = AF_{n-1} - 6AF_{n-2} + AF_{n-3}$ and $2\Phi_{n-2} = AF_{n-2} - 6AF_{n-3} + AF_{n-4}$, substituting them into Eq. (22), we obtain the following recurrence formula

$$AF_n = 12AF_{n-1} - 38AF_{n-2} + 12AF_{n-3} - AF_{n-4}. \tag{23}$$

Note that recurrence formulas (8) and (23) have the same homogeneous characteristics equation, so the general solution of Eq. (23) is $AF_n = \lambda_1(3-2\sqrt{2})^n + \lambda_2 n(3-2\sqrt{2})^n + \lambda_3(3+2\sqrt{2})^n + \lambda_4 n(3+2\sqrt{2})^n$. By the initial values $AF_5 = 70956$, $AF_6 = 496794$, $AF_7 = 3380640$ and $AF_8 = 22531256$, we have $\lambda_1 = \frac{3\sqrt{2}}{64}$, $\lambda_2 = \frac{17-12\sqrt{2}}{16}$, $\lambda_3 = -\frac{3\sqrt{2}}{64}$ and $\lambda_4 = \frac{17+12\sqrt{2}}{16}$, so Eq. (20) holds for $n \geq 5$. We can check that Eq. (20) also holds for $n = 0, 1, 2, 3, 4$, the proof is completed. ■

By Eq. (6) and Eq. (20), we can prove the following corollary.

Corollary 4.5. Let H_n be a pyrene system with n pyrene fragments. Then

$$\lim_{n\to\infty}\frac{AF_n}{n\Phi_n} = 1 + \frac{3\sqrt{2}}{4}.$$

References

[1] P. Adams, M. Mahdian, E. S. Mahmoodian, On the forced matching numbers of bipartite graphs, *Discr. Math.* **281** (2004) 1–12.

[2] P. Afshani, H. Hatami, E. S. Mahmoodian, On the spectrum of the forced matching number of graphs, *Australas. J. Comb.* **30** (2004) 147–160.

[3] Z. Che, Z. Chen, Forcing on perfect matchings – A survey, *MATCH Commun. Math. Comput. Chem.* **66** (2011) 93–136.

[4] Z. Che, Z. Chen, Conjugated circuits and forcing edges, *MATCH Commun. Math. Comput. Chem.* **69** (2013) 721–731.

[5] S. J. Cyvin, I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer, Berlin, 1988.

[6] H. Deng, The anti–forcing number of hexagonal chains, *MATCH Commun. Math. Comput. Chem.* **58** (2007) 675–682.

[7] H. Deng, The anti–forcing number of double hexagonal chains, *MATCH Commun. Math. Comput. Chem.* **60** (2008) 183–192.

[8] K. Deng, H. Zhang, Anti–forcing spectra of perfect matchings of graphs, *J. Comb. Optim.* **33** (2017) 660–680.

[9] K. Deng, H. Zhang, Anti–forcing spectrum of any cata-condensed hexagonal system is continuous, *Front. Math. China* **12** (2017) 19–33.

[10] K. Deng, H. Zhang, Extremal anti–forcing numbers of perfect matchings of graphs. *Discr. Appl. Math.* **224** (2017) 69–79.

[11] P. Hansen, M. Zheng, Bonds fixed by fixing bonds, *J. Chem. Inf. Comput. Sci.* **34** (1994) 297–304.

[12] F. Harary, D. Klein, T. Živković, Graphical properties of polyhexes: perfect matching vector and forcing, *J. Math. Chem.* **6** (1991) 295–306.

[13] W. He, W. He, P–V matrix and enumeration of Kekuklé structures, *Theor. Chim. Acta* **75** (1989) 389–400.

[14] H. K. Wang, H. Lei, Y. Yeh, H. Zhang, Distribution of forcing and anti–forcing numbers of random perfect matchings on hexagonal chains and crowns (preprint, 2015). http://140.109.74.92/hk/?p=873

[15] X. Jiang, H. Zhang, On forcing matching number of boron–nitrogen fullerene graphs, *Discr. Appl. Math.* **159** (2011) 1581–1593.

[16] X. Jiang, H. Zhang, The maximum forcing number of cylindrical grid, toroidal 4-8 lattice and Klein bottle 4-8 lattice. *J. Math. Chem.* **54** (2016) 18–32.

[17] D. Klein, M. Randić, Innate degree of freedom of a graph, *J. Comput. Chem.* **8** (1987) 516–521.

[18] S. Kleinerman, Bounds on the forcing numbers of bipartite graphs, *Discr. Math.* **306** (2006) 66–73.

[19] F. Lam, L. Pachter, Forcing number for stop signs, *Theor. Comput. Sci.* **303** (2003) 409–416.

[20] H. Lei, Y. Yeh, H. Zhang, Anti–forcing numbers of perfect matchings of graphs, *Discr. Appl. Math.* **202** (2016) 95–105.

[21] X. Li, Hexagonal systems with forcing single edges, *Discr. Appl. Math.* **72** (1997) 295–301.

[22] C. L. Lucchesi, D. H. Younger, A minimax theorem for directed graphs, *J. Lond. Math. Soc.* **17** (1978) 369–374.

[23] L. Pachter, P. Kim, Forcing matchings on square grids, *Discr. Math.* **190** (1998) 287–294.

[24] M. Randić, D. J. Klein, Kekulé valence structures revisited. Innate degrees of freedom of π-electron couplings, in: N. Trinajstić (Ed.), *Mathematical and Computational Concepts in Chemistry*, Wiley, New York, 1985, pp. 274–282.

[25] M. Randić, D. Vukičević, Kekulé structures of fullerene C_{70}, *Croat. Chem. Acta* **79** (2006) 471–481.

[26] M. E. Riddle, The minimum forcing number for the torus and hypercube, *Discr. Math.* **245** (2002) 283–292.

[27] L. Shi, H. Zhang, Forcing and anti–forcing numbers of (3,6)-fullerenes, *MATCH Commun. Math. Comput. Chem.* **76** (2016) 597–614.

[28] L. Shi, H. Wang, H. Zhang, On the maximum forcing and anti–forcing numbers of (4,6)-fullerenes, *Discr. Appl. Math.* **233** (2017) 187–194.

[29] L. Shi, H. Zhang, Tight upper bound on the maximum anti–forcing numbers of graphs, *Discr. Math. Theor. Comput. Sci.* **19** (2017) #9.

[30] D. Vukičević, I. Gutman, M. Randić, On instability of fullerene C_{72}, *Croat. Chem. Acta* **79** (2006) 429–436.

[31] D. Vukičević, M. Randić, On Kekulé structures of buckminsterfullerene, *Chem. Phys. Lett.* **401** (2005) 446–450.

[32] D. Vukičević, N. Trinajstié, On the anti–forcing number of benzenoids, *J. Math. Chem.* **42** (2007) 575–583.

[33] D. Vukičević, N. Trinajstié, On the anti–Kekulé number and anti–forcing number of cata-condensed bezenoids, *J. Math. Chem.* **43** (2008) 719–726.

[34] H. Wang, D. Ye, H. Zhang, The forcing number of toroidal polyhexes, *J. Math. Chem.* **43** (2008) 457–475.

[35] L. Xu, H. Bian, F. Zhang, Maximum forcing number of hexagonal systems, *MATCH Commun. Math. Comput. Chem.* **70** (2013) 493–500.

[36] Q. Yang, H. Zhang, Y. Lin, On the anti-forcing number of fullerene graphs, *MATCH Commun. Math. Comput. Chem.* **74** (2015) 681–700.

[37] F. Zhang, X. Guo, R. Chen, Z-transformation graphs of perfect matchings of hexagonal systems, *Discr. Math.* **72** (1988) 405–415.

[38] F. Zhang, X. Li, Hexagonal systems with forcing edges, *Discr. Math.* **140** (1995) 253–263.

[39] H. Zhang, K. Deng, Forcing spectrum of a hexagonal system with a forcing edge, *MATCH Commun. Math. Comput. Chem.* **73** (2015) 457–471.

[40] H. Zhang, D. Ye, W. C. Shiu, Forcing matching numbers of fullerene graphs, *Discr. Appl. Math.* **158** (2010) 573–582.

[41] H. Zhang, F. Zhang, Plane elementary bipartite graphs, *Discr. Appl. Math.* **105** (2000) 291–311.

[42] H. Zhang, S. Zhao, R. Lin, The forcing polynomial of catacondensed hexagonal systems, *MATCH Commun. Math. Comput. Chem.* **73** (2015) 473–490.

[43] H. Zhang, X. Zhou, A maximum resonant set of polyomino graphs, *Discuss. Math. Graph Theory* **36** (2016) 323–337.

[44] Q. Zhang, H. Bian, E. Vumar, On the anti–Kekulé and anti–forcing number of catacondensed phenylenes, *MATCH Commun. Math. Comput. Chem.* **65** (2011) 799–806.

[45] S. Zhao, H. Zhang, Forcing polynomials of benzenoid parallelogram and its related benzenoids, *Appl. Math. Comput.* **284** (2016) 209–218.

[46] S. Zhao, H. Zhang, Anti–forcing polynomials for benzenoid systems with forcing edges, *Discr. Appl. Math.* **250** (2018) 342–356.

[47] S. Zhao, H. Zhang, Forcing and anti–forcing polynomials of perfect matchings for some rectangle grids, *J. Math. Chem.* **57** (2019) 202–225.

[48] X. Zhou, H. Zhang, Clar sets and maximum forcing numbers of hexagonal systems, *MATCH Commun. Math. Comput. Chem.* **74** (2015) 161–174.

[49] X. Zhou, H. Zhang, A minimax result for perfect matchings of a polyomino graph, *Discr. Appl. Math.* **206** (2016) 165–171.