

GRAPH THEORY AND NETWORKS IN THE PHYSICS OF MICROSCOPIC DISPERSION FORCES IN AND BETWEEN MATERIALS.

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Abstract—Dispersion forces or as widely known van der Waals forces, play an important role at different scales of the physical world from the visible macroscopic through the nanometric to the microscopic molecular level, and this makes them important in various domains such as biology, physics and chemistry. At the microscopic level in material sciences, these forces present an important factor in the process of modelling materials' properties and behavior. Several theories throughout the last decades have been developed; such as the Coupled Dipole Method and similar approaches derived from the fluctuation-dissipation theorem. For more direct derivation and calculation of these interactions and Inspired by and based on the previous works that simplified these interactions at the microscopic level using simple graphical representations such as the work of A.Jones and J.Crain (2013), we propose in this study a novel representation of the phenomena using graph theory and networks, where we will lay the foundations and write the fundamental theorems that will construct such a promising technique. the connection between these theorems and these graphs with the physical aspects of dispersion forces and the pre-existing models are clearly stated, and the different modes of the involved many-body interactions are presented and their energies are derived from and through this mathematical representation.

Index Terms—Dispersion forces, Graph theory, Networks, Many-body interactions, van der Waals forces.

I. INTRODUCTION

THE graph theory is one of the key methods used in various domains especially in computer sciences, social sciences, communication, and biology [1-4]. this mathematical tool offers a powerful technique to simplify real problems into a combination of dots and lines and solve them remarkably using the mathematical properties of these graphs. Graphical representations in physics are not a new trend but an old one, however a rare one, and the famous Feynman diagrams are the most famous example of this [5, 6]. The Feynman diagrams proved to be a powerful technique in QED, with its simplicity and clarity to describe the different modes of interaction between particles, however these graphs are somewhat different from the graphs encountered in the mathematical

theory of graphs and networks. Moreover, this mathematical tool has been used in other branches, especially in statistical physics where combinatorial problems are encountered when studying certain systems [7, 8].

Motivated by the fact that an accurate description of long-range van der Waals (vdW) dispersion interactions, is a challenging task when modelling molecules and materials [9]. In the last two decades, there has been growing interest in studying dispersion long range van der Waals interactions at the microscopic level [10]. The importance of these interactions comes from the fact that, even though the methods used in first-principles modelling of molecules and materials such as density functional theory (DFT), prove to capture most of the total energy of the system (up to 99%) [10], however, the remaining missing fraction can be crucial for various observables and properties of interest, such as relative energies, binding properties, and structural features as well as the mechanical, thermodynamic, kinetic, and electronic signatures of a given system [11]. And main phenomena responsible for this lost fraction comes from the vdW long-range interactions [10, 11]. Thus, It has been shown that an accurate vdW correction can improve significantly these first-principles calculations [9]. The vdW forces arise from the interaction of quantum-mechanical instantaneous charge fluctuations in molecules [12]. the first description of these forces was accomplished by London second-order perturbation theory [13], where he found that the dispersion energy between two identical particles is proportional to r^{-6} [14, 15]. this model has a fundamental limitation related to the physical assumption he made when making the calculations, he considered the interaction to be instantaneous disregarding thus the finite speed of electromagnetic waves communicated between the interacting atoms [16, 17]. We will keep the same assumption of instantaneity for our study in this paper. When dealing with a system of many particles, even though these forces are non-local and non-additive in nature, the conventional method is to assume the additivity of the dispersion forces and sum all pairwise interactions [11], excluding thus the screening effect coming from many body interactions and other complex phenomena.

There has been many theories proposed for accurate calculations of dispersion forces which went beyond the pairwise summation approach, among those we recognise the

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adiabatic-connection fluctuation-dissipation theorem formulation[10], or the coupled dipole method where a system of Quantum harmonic oscillator are coupled through a dipole-dipole potential [18, 19]. The first appearance of the coupled dipole method (CDM) was in a successive three articles by bij Renne and Nijboer [20-22]. Lately it had resurfaced as Kim et al. reintroduced this approach with applications to the interaction between spherical nanoparticles and the calculation of static polarizabilities of nanoclusters [23-25]. The CDM is an atomistic approach which has the unique property of accounting for all many body interactions contributing to the dispersion energy between two objects [24, 25]. This model has been used to demonstrate the limitation of the pairwise summation approach as well as the DLP theory especially for extremely small nanoparticles [24]. Furthermore, A less computationally expensive method has been derived from the standard CDM denoted the Trace Couple dipole method which helped the solve efficiently the eigen problem encountered in the CDM approach[14]. Our mathematical representation is based on this formulism although it can be readily generalized and adapted to be used in different frameworks, which makes it an important tool for those attempting to study many-body dispersion interactions at a microscopic level.

II. GRAPH THEORY LANGUAGE

A graph G is defined as any ordered pair $(V(G), E(G))$ consisting of a set $V(G)$ of vertices(points) and a set $E(G)$ of (lines)edges. We call the numbers of vertices $m(G)$ and edges $n(G)$ in G ; the order and size of G [26, 27]. Each edge has a set of one or two vertices associated to it, which are called its endpoints. An edge is said to join its endpoints [27]. An edge with identical endpoints is called a loop, and an edge with distinct ends a link. Two or more links with the same pair of ends are said to be multi-edges. A graph is simple if it has no loops or parallel edges. The edge-multiplicity between a pair of vertices u and v is the number of edges between them [26]. A multigraph is a loopless graph that might contain multi-edges. The dipole D_n is a loopless graph with two vertices and n edges joining them [26].

Graphs can be assigned other features which can be useful in developing mathematical models for certain applications. These attributes can be assigned to edges and vertices, where an edge attribute is defined as a function from the edge-set to some set of possible values, and similarly any a function from the vertex-set to some set of possible attribute values is a vertex attribute. An example of these attributes are; edge direction, edge weight and color for both edges and vertices[27]. A directed graph (digraph) is a graph consisting of directed edges, where the latter is any edge whose one of its endpoints is designated as a head and the other as a tail. Vertices and adges can be assigned with colors where a edge/vertex-coloring of a graph G is a function from its edge/vertex-set $E(G)/V(G)$ to a set CE/CV whose elements are called colors [26].

III. GRAPH THEORY LANGUAGE

To simplify the graphical representation of the interaction modes, a schematic representation can be given in an innovative way using the concept of isomorphism of graphs from graph theory. The representation proposed does not consider distances or boundaries of objects. Only atoms presented by vertices and the interaction between each two atoms represented as edges; we distinguish between particles by assigning a different color for vertices. Using at first the the Feynman diagram representing the Contribution of static dipole-dipole interaction to dispersion potential at second-order of perturbation theory, where the solid vertical lines represent the state of the interacting species, time flows upward, and the dashed horizontal lines depicts the instantaneous interaction. We then replace the vertical lines representing the atoms (molecules) with dots which signify in the framework of CDM an instantaneous dipole (QHO). This representation allows to embody the interaction between n -atom contrary to the Feynman diagrams which can become challenging for a large system of atoms. However, they assume a constant point in time which means that no relativistic effects are included in this representation yet. This means that all studied interactions in this paper are non-retarded dispersion interactions. Furthermore, for two interacting microscopic systems, each color presents a vertex from a certain cluster. edge coloring on other hand is given to signify the screening effects causes by internal interactions within the systems (inter-vdW forces).

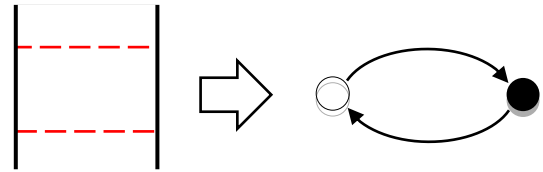


Fig. 1. The transition from a Feynman diagram of two interacting atoms to a graph theory network.

In order to develop a complete mathematical theory of the graphs corresponding to these interactions, we will start by laying the basic theorems regarding the nature of these networks. Most of these mathematical results come from the existing models such as trace-CDM.

Theorem 1: All graphs corresponding to the interacting between m species are cyclic multi-edge graphs of order $n \geq m$.

Theorem 2: let d be the degree (number of incident edges) of any vertex $v \in G$, such that:

$$\sum_{v \in V} d(v) = 2m \quad (1)$$

This is physically explained as each vertex (atom/molecule) interacts in a two-way manner, such that it sends and receives the electromagnetic signal produced by the instantaneous dipole.

Corollary 2.1: In any cyclic graph, the number of vertices of odd degree is odd. and the number of vertices of even degree is even.

Theorem 3: A map (F) is a map from the set (E^m) of all graphs $G(m, n)$ with order 'm' to the set (E^{m-1}) of graphs $G(m-1, n)$ with order 'm-1'. consider v_i^α and $v_j^\alpha \in G(m, n)$ are two non-adjacent vertices with same coloring (α); $F[v_i^\alpha, v_j^\alpha]$ is an operation merging these two vertices:

$$F[G(m, n)] \equiv G(m-1, n) \quad (2)$$

Where the size of the graph is conserved under this operation.

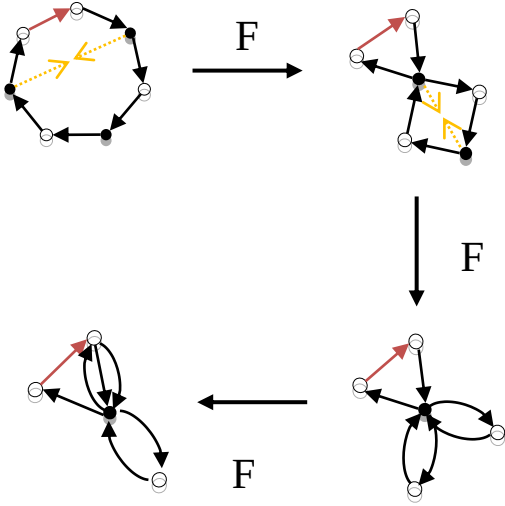


Fig. 2. an example of a merging operation series acting on $G(7,7)$.

Theorem 4: Let G_0 be an irreducible graph under the operation F. F_N is the composition of an "N" operation F:

$$F_N \equiv \underbrace{F \circ F \circ \dots \circ F}_N \quad (3)$$

Such that

$$F_N[G(m, n)] \equiv G_0 \quad (4)$$

Corollary 4.1: The number N for any graph G is odd, and is equal to m-1 if m is even and m-2 if m is odd.

Corollary 4.2: All graphs G reduce exactly two types of graphs such that for any graph $G(m, n)$:

$$F_N[G(m, n)] \equiv G_0 \equiv \begin{cases} D_n & \text{if } m \text{ is even} \\ T_n & \text{if } m \text{ is odd} \end{cases} \quad (5)$$

Where the triplet T_n is an irreducible graph of degree 3 and size n. At a physical level this can be understood that within the framework of the TCDM, the 2-body and 3-body interactions are found within all nth contribution to the energy, which shows that these are fundamentally the most important

interactions with in the m-body description of the dispersion forces

Theorem 5: All graphs G are Eulerian graphs. Where a digraph is Eulerian if it contains a closed trail that contains all of the edges in G. This closed trail is known as an Eulerian Trail [26].

Corollary 5.1: At any given vertex the number of in-edges (in-degree) is the same as the number of out-edges (out-degree)

$$\text{Ind}(v) = \text{outd}(v) \quad (6)$$

Corollary 5.2: Each graph has only a single trail (S) with a length L equals to the size "n" of the graph:

$$L(S) = n \quad (7)$$

Theorem 6: Each edge with ends i and j is attributed with a weight tensor T_{ij} where :

$$w_{ij} = \alpha_i T_{ij} = \alpha_i \nabla_i \nabla_j \left(\frac{1}{R} \right) \quad (8)$$

The energy associated with a single graph (graph-weight) is calculated as the product of the weights of all edges combined as follows:

$$E[G(m, n)] = \frac{\hbar \omega_0}{2} c_n \prod_{ij} w_{ij} \quad (9)$$

where the coefficient c_n from the development of the Trace-CDM, where it is attributed to each nth order contribution to the total energy. And $\hbar \omega_0$ comes from the fact that each mode of interaction in the system of coupled QHOs contributes an energy of an order $\hbar \omega_0/2$. Furthermore, to calculate m-body interaction energies separately using the model proposed in this work, the graphs are used. the m-body interaction energy can be calculated from the sum of the energies (weights) of all possible graphs of order (m).

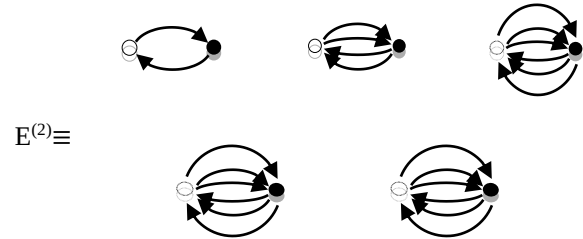


Fig. 3. Graphical representations of the first 2-body interaction modes.

The 2-body interaction energy is represented by a group of graphs which can be algebraically interpreted as a power series of the form:

$$E^{(2)} = \frac{\hbar\omega_0}{2} c_2 \sum_{s=1}^{\infty} (\alpha_i T_{ij} \otimes \alpha_j T_{ji})^{n/2} \quad (10)$$

This interaction can be written with respect to the dipole-dipole dispersion coefficients C_{6i} :

$$E^{(2)}(\vec{r}_i, \vec{r}_j) = \sum_{i=s}^{\infty} C_{3n} \cdot r_{ij}^{-3n} \quad (11)$$

And the coefficients C_{3n} are defined as follows:

$$C_{3n} = c_n (1 - (-2)^{n-1}) \hbar\omega_0 (\alpha_i \alpha_j)^{n/2} \quad (12)$$

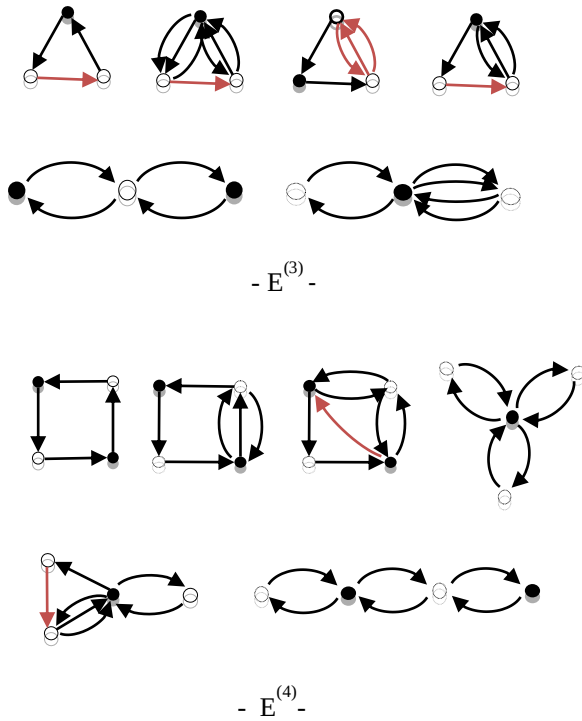


Fig. 4. First representative graphs of the 3-body and 4-body interaction modes.

We notice that the first term of the series (Eq.11) is exactly the same as the formula proposed by London for 2-body interactions using perturbation theory [1, 2]. The 3-body interaction energy is derived from the graphical presentation also in the same manner, and it is given as follows:

$$E^{(3)} = \frac{\hbar\omega_0}{2} \sum_{l,s,p=0}^{\infty} c_{3(l+s+p+1)} \text{Tr} \left[\alpha_i^{3l+1} T_{ij}^{3l+1} \otimes \alpha_j^{3s+1} T_{jk}^{3s+1} \otimes \alpha_k^{3p+1} T_{ki}^{3p+1} \right] + \frac{\hbar\omega_0}{2} \sum_{l,s,p=1}^{\infty} c'_{6(l+s)} \text{Tr} \left[(\alpha_i T_{ij} \otimes \alpha_j T_{ji})^l \otimes (\alpha_j T_{jk} \otimes \alpha_k T_{kj})^s \right] \quad (13)$$

The first term when studied is found to depend on the geometry of the triplet, and the first term of the resulting series is the Axilrod-Teller-Muto (ATM) potential for a 3-body

problem[3, 4]. The second term however does not depend on the geometry but just the distance between particles. Similar calculations can be done using the proposed mathematical presentation, where any m-body interaction can be deduced from the corresponding graphs in the form of an infinite summation that can be overcome by considering the fact that this sum is convergent. Moreover, keeping forth in developing a more rigorous mathematical theory of these graphs can lead to numerous possibilities in studying the behaviour of these many body interactions.

IV. CONCLUSION

In this paper we have developed a graph theory-based presentation of dispersion many body interactions at a microscopic level. The basic theorems and mathematical foundations have been laid keenly to study these interactions within the framework and with the language of graph and network theory. A method has been demonstrated on how to deduce any m-body interaction energy, with a demonstrative example of the case of 2-body and 3-body interactions.

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