

# Symmetry-Consistent Expansion of Interaction Kernels Between Rigid Molecules

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**Abstract.** We discuss the expansion of interaction kernels between anisotropic rigid molecules. The expansion decouples the correlated orientational variables, which is the crucial step to derive macroscopic free energy. It is at the level of kernel expansion, or equivalently the free energy, that the symmetries of the interacting rigid molecules can be fully recognized. Thus, writing down the form of expansion consistent with the symmetries is significant. Symmetries of two types are considered. First, we examine the symmetry of an interacting cluster, including the translation and rotation of the whole cluster, and label permutation within the cluster. The expansion is expressed by symmetric traceless tensors, with the linearly independent terms identified. Then, we study the molecular symmetry characterized by a point group in  $O(3)$ . The proper rotations determine what symmetric traceless tensors can appear. The improper rotations decompose these tensors into two subspaces and determine how the tensors in the two subspaces are coupled. For each point group, we identify the two subspaces, so that the expansion consistent with the point group is established.

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## 1 Introduction

In a system consisting of many rigid molecules, the interactions between the molecules depend not only on the relative position, but also on the relative orientation. Such interactions can lead to nonuniform orientational distribution. As a result, even in an infinitesimal volume, local anisotropy can be formed and further correlated spatially, which is the typical mechanism for liquid crystals. An example that many are familiar with is

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the (uniaxial) nematic phase formed by rod-like molecules, where no positional order is observed but an optical axis can be identified. If layer structure further arises, the smectic phases could appear. The concept of liquid crystals has been expanded to a great extent since rigid molecules of other shapes, such as bent-core molecules, have proved to possess richer phase behaviors experimentally [16,29].

In mathematical theory, to identify liquid crystalline phases, one needs to construct free energy about some order parameters describing the local anisotropy. A simple approach is to construct phenomenological macroscopic models, typically a polynomial of the order parameters and their derivatives. For rod-like molecules, the order parameter can be chosen as a second order symmetric traceless tensor, based on which the Landau-de Gennes theory is built and has been successfully applied to both stationary and dynamic problems [2,10,25]. When discussing other types of liquid crystalline phases, including polar, biaxial or tetrahedral order, people also attempted to construct phenomenological models with different tensor order parameters [11,12,14,26,27,30]. In these models, the terms are usually kept as minimum to describe specific phenomena.

Macroscopic theories can also be built upon molecular theories. Such an approach dates back to the derivation of the equations of state for gases, where a homogeneous system consisting of spherical molecules is considered [19,21]. Inhomogeneous systems, without considering the anisotropy of the molecule, have also been discussed, leading to theories for modulated phases that can describe various materials such as amphiphilic systems and block copolymers [7,13,24]. Molecular theories are characterized by interaction kernel functions of several molecules, in which the variables representing the positions of these molecules are correlated. To derive a macroscopic theory, it is necessary to separate these variables, which can be done by expanding the kernel functions. After the expansion is done, each term in the expansion corresponds to a term in the free energy, so that the macroscopic theory is established.

When non-spherical rigid molecules are put into consideration, extra variables are introduced for the orientation of the molecule. Most theories developed from molecular interactions focus on the orientational variables only and are built for spatially homogeneous systems. In this case, the kernel functions are independent of spatial variables, and the expansion decouples the orientational variables. Theories of this kind possibly start from Maier-Saupe [20] for rod-like molecules. Other rigid molecules, including cuboid, bent-core, triangular and cross-like [4,5,28,35,36], have also been discussed.

Recently, the expansion has been extended to spatially inhomogeneous cases, where both spatial inhomogeneity and orientational anisotropy are included. This approach combines the techniques for spatially inhomogeneous systems of spherical molecules and for spatially homogeneous systems of non-spherical molecules. It was first proposed for rod-like molecules [15], for which a tensor model was established for both nematic and smectic phases. Later, it has been successfully applied to bent-core molecules [34], resulting in a tensor model for modulated nematic phases.

Despite the success of these works, they still cannot describe the majority of exotic liquid crystalline phases exhibited by non-spherical rigid molecules [18,29,39]. This is