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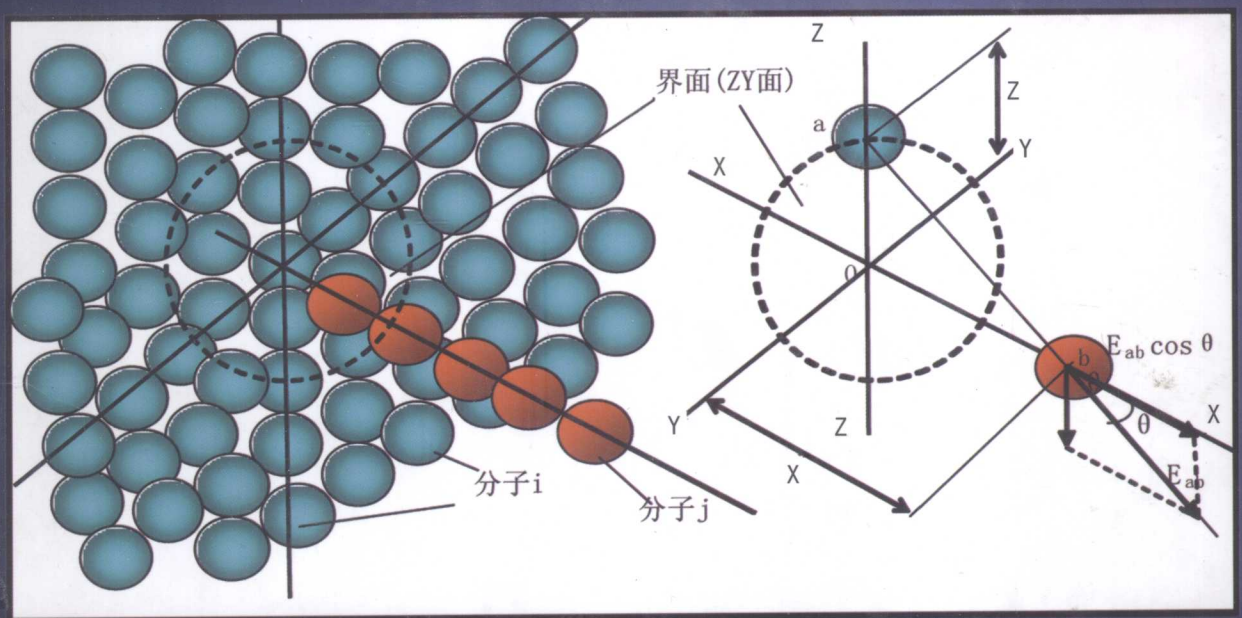
Basis and Calculation

张福田 著

宏观分子相互作用理论

基础和计算



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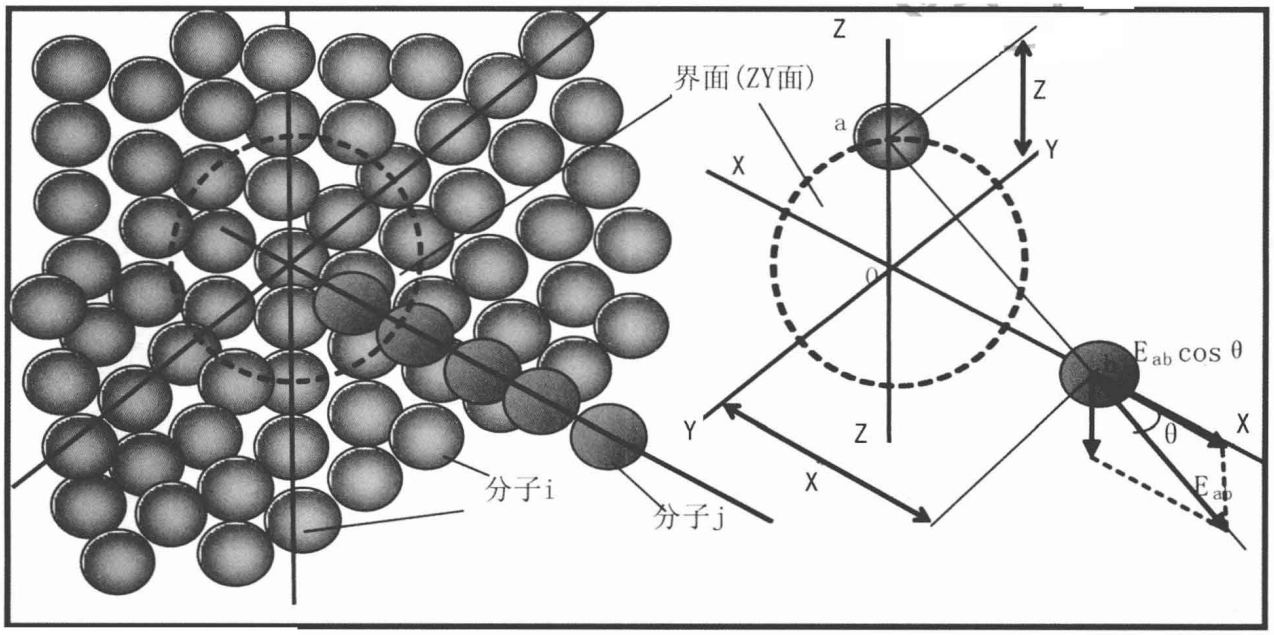

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内 容 简 介

宏观分子间相互作用理论是讨论大量粒子体系中分子间相互作用，由此在微观分子间相互作用理论基础上，找出宏观性质的统计规律性，即找出宏观性质的微观结构，作为分析、解释、改变宏观性质的微观依据。本书以宏观性质压力为讨论主线，集聚了众多实际数据，制成图、表对理论讨论作了明确说明，将本书理论观点与实际数据结合起来，成为具有特色的分子间相互作用理论专著。

全书共八章，前两章介绍微观的和宏观的分子间相互作用理论，第三章讨论分子间相互作用与宏观性质的统计力学关系。后五章是分子压力理论，介绍分子压力的导出，分子压力与宏观性质“压力”的关系，分子压力理论在纯物质、气体和液体混合物的应用。提出了分子压力分为分子动压力和分子静压力两种概念，在液体混合物——溶液讨论中提出溶液条件以区别不同类型的溶液，并以物理界面相平衡理论明确地解释溶液成为理想溶液的微观因素。

本书可作为高等院校理工科（如物理、化学、化工、能源、生物、药学、材料、冶金、等）有关专业的大学教师、高年级大学生和研究生的教、学参考书，也可供有关科研人员、工程技术人员参考。

前　言

物质的宏观性质与物质内部的各种分子间的相互作用密切相关。目前用于描述物质内分子间相互作用的方法有两种：

第一种方法为微观分子间相互作用研究法。即研究分析两个分子间的相互作用。

第二种方法为宏观分子间相互作用研究法。即研究宏观状态下大量微观粒子集体运动的规律性，在统计力学中叫做统计规律性。

这两个研究领域对于促进科学技术的发展所起的作用应该是异曲同工的。

微观分子间相互作用研究方法是从微观信息出发，例如分子的微观性质、分子的移动、转动、振动能阶和分子间作用力等。这些微观信息经过统计力学处理，用于预测体系的宏观性质。

胡英教授指出，这里的“预测”专指的是由微观结构预测宏观性质。

宏观分子间相互作用研究方法是从宏观性质出发，经过统计力学处理，找出相适应的统计规律性，以达到了解、分析、解释、改变这个宏观性质及其变化规律。

这里的“找出”应该是由宏观性质找出其统计规律性。

这两种方法在当前统计力学理论中均有应用。简单举例来讲，就是计算一个平衡体系的内能。微观分子间相互作用研究方法是计算每个分子在每个瞬时的能量，然后将所有分子瞬时的能量加和起来，用以预测宏观体系的内能。

宏观分子间相互作用研究方法认为每个粒子在每一瞬间时的能量虽然不同，但在平衡状态时其平均能量却是一定的。故而采用统计力学的方法，如统计、分布、涨落等法，从宏观性质内能找出粒子的平均能量，然后由体系粒子数目，得到体系的内能值。因此这个方法是采用所讨论的宏观性质的统计规律性找出该宏观性质的微观结构。

比较而言，宏观分子间相互作用研究方法与宏观性质联系更紧密些，亦就是与实际现象联系更紧密些，理论上可能遇到的困难会少一些，数学上的难题亦可能少一些。

这两种讨论分子间相互作用方法在现有统计力学、统计物理和分子热力学中都有涉及，并已做了很多有意义的工作。微观分子间相互作用理论从其目的——预测宏观性质来看，应有一定的实际意义。但其出发点是微观结构，很自然地会较偏重于理论性的探讨；

而宏观分子间相互作用理论的出发点是宏观性质，其目的是找出宏观性质的统计规律性，用于解释、分析和改变宏观性质，应有可能与实践结合得更紧密些。为此，作者认为值得将宏观分子间相互作用理论进行较系统地总结、归纳、整理，以介绍给读者。

本书将以宏观性质中的压力和微观性质中的各种分子压力为主线，将宏观分子间相互作用研究中涉及的宏观性质、统计规律性、微观结构对宏观性质及其变化规律的影响等相关内容串联起来，从而使本书内容不仅是单纯的理论探讨，而且使理论与实践联系起来。书内列有很多计算实例与图表，便于读者阅读与理解。

本书主要内容由三个部分八章组成：首先介绍宏观分子间相互作用理论与微观分子间相互作用理论间不同之处，由此讨论宏观分子间相互作用的特性；其次对关联宏观性质—微观性质的统计力学一些相关概念作简单的介绍，并说明选择压力作为讨论的宏观性质的原因；最终对压力的微观结构中的分子压力进行了较全面的分析讨论。

第一章简单介绍微观下分子间相互作用的基本特性、长程力和不同物质间分子作用力等基本概念，为下一步讨论作铺垫。

第二章主要内容为讨论分析大量粒子间相互作用的一些基本特性、大量分子相互作用下的长程性质作用力、多种分子体系中分子间的相互作用和系统中与移动分子相关的分子动压力与定居分子相关的分子静压力等。

第三章分析讨论宏观分子间相互作用统计力学基础。由于宏观分子间相互作用与宏观性质密切相关，本书讨论的微观性质为各种分子压力，故与微观性质中分子动压力相关的宏观性质中的压力是着重讨论的对象。

第四章提出分子压力概念，并以状态方程、统计力学理论计算和讨论分子压力。

第五章讨论气态纯物质的分子压力。内容有不同热力学过程下气体分子压力的特性、影响气相分子压力的各种因素、经典热力学中代表分子间相互作用影响的逸度与分子压力的关系。

第六章讨论理想气体和真实气体混合物的分子压力规律，由此讨论在气体混合物中分子压力的混合规则及气体 Virial 系数的微观特征。

第七章讨论液态纯物质的分子动压力和分子静压力。着重讨论分子动压力的特性和各种影响因素。此外，依据宏观分子间相互作用观点，对液态物质引入了 Virial 方程，讨论了 Virial 方程对液体的适用性和液体 Virial 系数与分子压力的关系，并对气体与液体 Virial 系数进行了比较。

第八章以经典热力学理论、相平衡理论、统计力学理论讨论溶液——液态物质混合物中多分子间相互作用和液体结构对溶液——液态物质混合物中分子压力的影响。并依据溶液条件不同，讨论完全理想溶液、近似理想溶液和实际溶液的分子压力特点及其混合规则。

本书中宏观分子间相互作用理论可归纳成以下理论结果：其一是提出了宏观性

质的压力和微观组成结构中分子压力的关系；其二是提出了气态和液态纯物质与混合物的各种分子压力的计算原理和方法；其三是提出分析了形成不同类型溶液的溶液条件和溶液特性；其四是通过分子压力，有可能将分子间相互作用微观信息（分子间吸引作用和排斥作用）用于定量地分析和讨论宏观物质热力学过程。相信这些理论结果将有助于冶金、化学、化工、石油化工、医药科学、生命科学等领域的研究，为改进生产工艺参数，提高产品质量、产量，发展新技术和新材料、新产品提供一些理论思路。

因此本书的读者对象为物理、化学、物理化学、冶金、焊结、胶接、化工、生化、医药、金属和非金属材料等专业的大学生、硕士生、博士生、教师和研究人员，以及在各种高新技术和各个工业技术领域中从事与生产工艺有关的技术人员和研究人员。

分子间相互作用理论是近代开始发展起来的，特别是当分子间相互作用理论与统计力学相结合，发展为分子热力学时更涉及众多的新知识。如上所述，其中理论难点必定很多，限于作者的能力与水平，书中的缺点、错误等一定在所难免，对于此，希望读者能给予指正和谅解。

此外，作者向关心与支持宏观分子间相互作用理论、分子压力概念的读者和研究人员表示感谢，对于在本书编写过程中给予支持和帮助的老一辈专家李正邦教授、刘友梅教授和陈国邦教授等表示衷心感谢；华东理工大学刘洪来教授审阅了本书，提出了许多宝贵意见，在此亦表示衷心感谢。

张福田

2011.4.20 于上海

附注：作者的 Email 地址：zftzq2@yahoo.com.cn，欢迎大家就本书内容进行交流和提供意见和建议。

Preface

The macroscopical properties of a substance are related closely with the interactions between the molecules in the substance. At present time, there are two ways for describing the molecular interactions, they are:

The first is the microscopical molecular interactions method, that is to research the interactions between two molecules.

The second is the macroscopical molecular interaction method, that is to research the regularity of collective movements under the condition of large quantities of molecules in macroscopical state, which is called as statistical regularity in statistical mechanics.

The approaches of the two research fields are different, but both play the same role to promote the development of science and technology.

The research method of microscopical molecular interactions is to start from the microscopical information, such as the microscopical characteristics of molecules, translation and turning of molecules, energy order of vibration and molecular interactions etc. The above information can be used to predict the macroscopical properties of system through the treatments of statistical mechanics.

The professor Hu Ying points out that the "prediction" here is indicated specially as the prediction of macroscopical properties according to the microstructure.

The research method of macroscopical molecular interactions starts out from macroscopical properties, and by means of statistical mechanics, find out appropriate statistical regularity to be used to understand, analyze, explain, and change the macroscopical properties and the laws of its variation.

Here "find out" is indicated specially as the finding of statistical regularity from the macroscopical properties.

The both methods have applications in the current statistical mechanics theory. For instance, if you want to calculate the internal energy of a system, the research method of microscopical molecular interactions is to calculate the instantaneous energy of each

molecule, then the instantaneous energies of all molecules are added up to predict the internal energy of the macroscopical system.

The research method of macroscopical molecular interactions thinks although the energy of each particle in every moment is different, but in equilibrium state its average energy is certain. Namely, it is possible to use statistical mechanics methods, such as statistics, distribution, fluctuation etc., to found out the average internal energy of particle from the internal energy properties in macroscopical state, and then according to the particle numbers of system, the internal energy value of the system is obtained. Therefore this method is to use the statistical regularity of discussed macroscopical properties, to found out the microstructure of the discussed macroscopical properties.

By comparison, the research methods of macroscopical molecular interactions are more closely contact with the macroscopical properties, also more closely linked with the practice phenomenon, therefore, the possible difficulties will be relatively less in the theory research, and mathematical problems also may be less.

The discussion methods of the two kinds of molecular interactions all have been involved on the existing statistical mechanics, statistical physics and molecular thermodynamics, and already possess a lot of meaningful work. But microscopical molecular interaction theory, from its purpose is to predict macro properties, should has certain practical significance, however, because its starting point is the microstructure, naturally more focus on theoretical discussion. While the starting point of macroscopical molecular interaction theory is macroscopical property, its purpose is to find the statistical regularity of the macroscopical property, and it can be used to explain, analysis and change the macroscopical properties, therefore, may be combined more closely with practice. Therefore, we think: it is rewarding that the macroscopic molecular interaction theory systematically is summarized, summed up and sorted out, and is introduced to readers.

The mainline of this book is macro properties — pressure and microscopical properties — molecular pressures, this mainline is used to string together the macroscopical molecular interactions, statistical regularity, the influence of microstructure on macroscopical properties as well as the variation rules and other related contents. Thus it is made that the contents of this book is not only single theoretic discussions, but also association between the theory and practice. There are many calculating examples and charts in the book to facilitate readers' reading and understanding.

The main content of this book consists of three parts eight chapters: the first part introduces the difference between macro and micro molecular theories of interaction, thus discusses the characteristics of macroscopical molecular interactions, the second part is the simple introduction to some concepts of statistical mechanics related with macro properties — microscopical nature, and explains why pressure is selected as the macroscopical properties discussed. Finally, the third part comprehensively goes about the analysis and discussion of microscopical structure of pressure — molecules pressure.

The first chapter introduces the basic characteristics of the interactions between molecules in microscopical state, the basic concepts of long-distance forces and the molecular acting forces between various substances etc., which foreshadows the further discussion.

The main contents of second chapter are the discussion and analysis about the basic characteristics of interactions between large quantity of particles, long-distance forces of mass molecular interactions, molecular interactions in multicomponent system and dynamic molecular pressure related with moving molecules and static molecular pressure related with settled molecules in system, etc.

The third chapter discusses the foundations of statistical mechanics for macroscopical molecular interactions. Because the macroscopical molecular interactions closely relate with the macroscopical properties, and the microscopical properties discussed in this book are various kinds of the molecular pressure, so the macroscopical property — pressure related with dynamic molecular pressure in micro properties is discussed emphatically.

The fourth chapter put forwards the concept of molecular pressure, and calculations and discussions of molecular pressure by using state equation and statistical mechanics theory.

The fifth chapter discusses the molecular pressure of pure gas substances. In its content there are the characteristics of the molecular pressures of gas under different thermodynamics process, the influence factors of the molecular pressures of gas, and the relations of the fugacity which represents the influence of the molecular interactions in classical thermodynamics with the molecular pressure.

The sixth chapter discusses the rules of molecular pressures for real and ideal gas mixture, thereof discusses the mixed rules of molecular pressures in a mixture of gas and the microscopical characteristics of Virial coefficient for gas.

The seventh chapter discusses dynamic molecular pressure and static molecular pressure. This chapter gives emphasis to discuss the properties and the influence factors

of the dynamic pressure of liquid. In addition, according to the viewpoint of the macroscopical molecular interactions, Virial equation is led in the liquid substances, the applicability of Virial equation for liquid and the relations of Virial coefficient of liquid with the molecular pressures are discussed, and the Virial coefficient of liquid is compared with the Virial coefficient of gas.

The eighth chapter discusses the influences of multimolecular interactions and liquid structure on the molecular pressures in solution — mixtures of liquid substances by using classical thermodynamics theory, phase equilibrium theory and statistical mechanics theory, and discussed the characteristics of molecular pressures and mixed rules of perfectly ideal solution, approximate ideal solution and practical solution according to different solution conditions.

The macroscopical molecular interaction theory of this book can be concluded as the following theoretical results: The first, the relations between macroscopical properties — the micro structure of pressure — molecular pressures are proposed. The second, the principle and the methods of the molecular pressures of pure substance and mixtures in the state of gas or liquid are proposed. The third, the solution conditions and the solution characteristics of different types of solution are proposed and expounded. The fourth, with the aid of molecular pressure, the microcosmic information of molecular interactions (attractions and repulsion between molecules) can be used quantitatively to analyze and discuss the thermodynamics processes of macroscopical matter. It is believe that above molecular information will be helpful to provide some theoretical ideas about the improvement of parameters of production process, the improvement of quality and quantity of products and the development of new technology and new materials and new products for the researchers in metallurgy, chemistry, chemical engineering, petroleum chemical industry, medical science, life science and other areas.

Therefore, the suitable readers of this book are students, master or doctors, teachers and researchers in physics, chemistry, physical chemistry, metallurgy, welding, glued joint, chemical engineering, biochemistry, medicine, metallic and non-metallic materials, technicists and researchers related with manufacturing technique in the fields of high and new technology and various industrial technology.

Molecular interaction theory is developed in modern times, which involves new numerous knowledge especially when the molecular interactions theory was combined with statistical mechanics and developed into molecular thermodynamics. As above mentioned, there exists many theoretical difficulties, therefore, the shortcomings and

errors in the book must be unavoidable due to the limit of author's ability and level, for these, hope readers can give to correct and understanding.

In addition, author greatly appreciates readers and researchers' concern and support to the macroscopical molecular interactions theory and molecular pressures conception, sincerely thanks Professor Li Zheng Bang, Professor Liu You Mei, and Professor Chen Guo Bang those experts of the older generation for their support and help during the preparation of this book, and sincerely thanks Professor Liu Hong Lai at East China University of Science and Technology, who checks and approves the contents of this book and gives many precious suggestions.

Zhang Fu Tian

2011. 4. 20 in Shanghai

Nate: The author's Email address: zftzq2@yahoo. com. cn. The author welcomes any comments for future revisions.

目　录