

Chapter 1

Modern Physics at a Glance

The progress of humankind has always been in parallel with our improved understanding and the consequent mastery of the natural elements around us. In particular, our ability to engineer natural materials into useful tools and devices of desirable properties — be they mechanical, electrical, or chemical — is paramount to the advancement of our own civilization. This tandem march towards overall societal progress is so recognizably intrinsic that early milestones of human civilization are named after the characteristic natural materials that were mastered by our progenitors during the specific time periods. For instance, the stone age and the bronze age have been so named for our ancestral achievement in mastering the tool-making techniques based on stone and bronze, respectively, for the first time in history. Fast forwarding to modern times, the industrial revolution would not have been possible without the tremendous progress in our firm grasp of metallurgy, of the principles of *thermodynamics* that spawned the steam engine and later the internal combustion engine, and of *electromagnetism* that preceded electrical power regeneration — in conjunction with all other social factors at the time including the institutional movement from feudalism to imperialism in Europe as well as the creation of financial markets. Of course, we are presently in the midst of a revolution of our times in information technology. The ramifications thereof are still wide open to determination. Of the most important progeny of our current IT revolution is the World Wide Web, which owes its existence largely to our technical know-hows of semiconductors making use of such materials as silicon, germanium, and gallium arsenide. In this instance, our understanding of semiconductors stems from the fundamental theory of *quantum mechanics*.

Thus, we see that in the prior examples that with each breakthrough in our understanding of materials and matter comes the corresponding step forward in the quality of our daily life. Historically, new understanding of materials and matter has been driven by novel experimental results requiring new theoretical explanations as well as new directions taken by theorists in modeling and predicting properties. In what follows, we will define a *theoretical model* generally as an abstraction of aspects of a physical system for which we are interested in explaining their inner working and properties. Some theoretical models yield predictions that are so encompassing in scope and revolutionary in paradigm that we call them *fundamental theories*. The aforementioned example of quantum mechanics would be one such instance: with the advent of quantum mechanics at the turn of the twentieth century, our understanding of matter and materials advanced to an unprecedented level. As a result of the revolutionary thinking made by the likes of Max Planck, Neil Bohr, Louis de Broglie, Max Born, Werner Heisenberg, Erwin Schrödinger, Wolfgang Pauli, Paul Dirac and others, chemistry has since progressively turned from a field of empirical science to one whose basis can be, in principle, rigorously understood in terms of the quantum physics of atoms and molecules.

It turns out that the discovery of quantum mechanics is only the tip of an iceberg. When we further consider interaction of matter with light (photons) that underlies the foundation of spectroscopy, the theory of *quantum electrodynamics* (QED) comes into play, which merges non-relativistic quantum mechanics with special relativity and electromagnetism. As we probe further into the finer structure of the atom and its nucleus, we reach the domain of *quantum chromodynamics* (QCD) which describes the strong interaction binding the quarks and gluons together that make up the protons and neutrons inside the nucleus of an atom, as well as other types of hadrons. Together with the unified description in terms of the *electroweak theory* of electromagnetism and the weak nuclear force, the latter of which is responsible for radioactivity, we have outlined the *standard model* which underlies the foundation of modern physics. In principle, these theories should encode all information pertaining to all systems to which they are applicable, or equivalently, we should be able to derive the fundamental properties of all such systems from these theories. However, the complexity of such calculations involved often precludes such possibility at the practical level.

Consequently, numerical methods and approximate analytical models continue to be of value in our quest for further understanding of many

physical systems in nature, in spite of the already available “cracked codes” — in the guise of the aforementioned fundamental theories — to the inner working of Nature firmly in our hands. In what follows, we will define an *analytical* model as a theoretical model that allows for the explicit evaluation of the relevant quantities pertaining to the physical properties of a system in closed analytical forms. In particular, to distinguish from fundamental theories, we refer to an *approximate* model whose main purpose is to serve as an effective description of the phenomenology of a system in certain useful or interesting limits. These approximate models are also sometimes referred to as *phenomenological models* or *effective models* to emphasize their very specific range of applicability.

On the other hand, *numerical methods* to theoretical modeling comprises analytical models whose predictions of relevant physical parameters can only be obtained through computational algorithms or expressible in numerics. *Simulations* would by construction fall into this category of numerical modeling. Numerical methods are essential as there are only very few classes of problems, pertaining mostly to highly idealized systems, which can be directly cast and solved entirely within the tight constraints imposed by *classical analysis* in mathematics. In fact, both numerical methods and approximate theoretical models are necessary in scientific research due to the computational complexity and often the resulting practical impossibility to deriving everything from fundamental theories; the pursuit of the continual refinement of these numerical methods as well as of approximate analytical models in understanding Nature comprises the bulk activity of the present-day enterprise of scientific research.

As a concrete illustration of the necessity of approximate models and numerical methods in science, we point out the fact that the issue of computational difficulty is already present at the level of *classical mechanics* in the study of three-body systems. This seemingly innocuous three-body problem is already not amenable to a closed-form analytic solution. More generally, for the problem of an N -body system, one can only resort to numerics to plot out the trajectories of motion carried out by the system when the total number of bodies exceeds three, notwithstanding the facts that Newton’s laws of motion and gravity are well founded and understood in the language of classical differential equations as well as that the formulation of the N -body problem can be straightforwardly presented in analytical form. With limitations, the existence of an analytical solution in the form of a slowly converging series was eventually established by the Sundman theorem for the three-body problem, but the complexity involved in extending

this result to the general N -body problem exemplifies the unfortunate fact that elegance and generality do not always go in tandem in analysis.

Consequently, given the complexity found in real systems, the reductionist approach of the physical sciences, wherein we abstract what we deem as the defining features of a system and strip down to its bareboned ideal analogue that still preserves these features, is a rather necessary and pragmatic philosophy. The prominent roles of numerical methods and approximate models in modern science demonstrate the constant struggle between practical idealism and the seemingly impenetrable reality. Striking a compromise between the two realities, one can go about it in two ways: firstly, to invent more-efficient algorithms in obtaining numerical solutions that would allow us to model, by computational brute force, a more accurate abstraction of the real systems that must necessarily include more complex details; alternatively, one can develop better approximate analytical models that would allow for more accurate or detailed predictions using existing computational tools.

What precisely makes for an improved model over established ones now warrants further attention. While the qualifier for a more efficient algorithm is unequivocal — one that does the same job in less time and/or using less computational resource — the criteria for improved approximate analytical models merit broader consideration. At the most obvious level, an improved approximate model would, as described earlier, provide a new and more efficient computational route for theoretical scientists to produce falsifiable results that can be verified against experimental findings, just like its numerical counterpart. Achieving this goal requires the insights from scientists in discerning which subset of the underlying degrees of freedom for a system contributes most crucially to certain observed properties for the system.

Consider the Brownian motion of a particle in a fluid with constant friction. The erratic trajectory of the Brownian particle is due to the collisions it makes with other fluid particles. There are two dual descriptions of this problem. The first approach is that of the Langevin equation, which is an example of stochastic differential equation. The Langevin equation for this Brownian particle is simply the Newton's equation, with the addition of a source term encapsulating the overall effect of constant collisions that describes the time evolution the particle's position and velocity. On the other hand, the approach of Fokker-Planck equation, which delineates the velocity probability function for the diffusing particle (the generalization to the probability function for displacement and other variables is called

the Smoluchowski equation), focuses on a different set of quantities and provides an alternative description to Langevin equation. While one can utilize the Langevin equation to derive the many interesting results of the system without a direct solution (by means of the fluctuation-dissipation theorem), obtaining the direction solution is itself computationally intensive; the Fokker-Planck equation is often used instead. Thus, whichever model would work better depends, in general, on what one's main goals and interests are for the system under study. Of course, these dual descriptions are possible due in large part to their phenomenological nature satisfying a few rather general assumptions about the underlying dynamical systems not far from equilibrium. In addition, we note that numerical methods also exist for this problem with the use of Monte Carlo simulations.

In addition to seeking a minimal set of degrees of freedom that would most directly characterize a desired set of properties for a physical system, another useful approach in constructing good approximate analytical models involves smartly integrating out degrees of freedom that are non-essential; we would then consider the resulting *effective* or *coarse-grained* models, the latter of which refers specifically to models with microscopic degrees of freedom integrated out. For example, *thermodynamics* provides a description for the equilibrium states of systems that contain many degrees of freedom in terms of a few macroscopic system variables such as temperature, internal energy, or magnetization. These macroscopic quantities are, in general, much more useful characterization of a thermal equilibrium system than the knowledge of all colliding trajectories or all microstates associated with either the underlying particles or elementary excitations of the system. When we consider small perturbations to this ideal homogeneous equilibrium at all point in space, in the long-wavelength and low-frequency limit, we turn to the framework of *hydrodynamics* in terms of, again, a given set of macroscopic field variables. In this regard, both thermodynamics and hydrodynamics constitute coarse-grained theories concerning the static and dynamical properties, respectively, of the underlying physical systems with microscopic constituents.

In this work, we will mainly be concerned with the static aspects of two particular condensed-matter systems: colloidal crystals and loop polymers. By *statics*, we refer to such system properties as phase stability and other properties that do not have general time-dependence. In contrast, we refer to *dynamics* the study of all time- or frequency-dependent phenomena such as kinetics and coarsening not far from equilibrium. The main focus of this work is on the phenomena of phase transitions in colloidal crystals as well

as in polymers that are subjected to the constraints of non-trivial topology such as loops and knots. We will make connections with various ideas from geometry and topology to derive a new theoretical model in understanding the first-order colloidal phase transitions between the different lattices, in particular the exotic $A15$ lattice that has defied reasonable explanations thus far based on conventional wisdom. We will also make connections with geometry and topology in performing renormalization-group analysis on the second-order polymeric phase transitions and discovering a new scaling regime and new universality class for topologically constrained polymers.

In general, colloids can be classified according to their microscopic interactions between constituents. The intermolecular potential can either be long-range or short-range in nature. Charged colloids are the prototypical colloidal system with long-range constituent interaction: the particles interact via the screened-Coulomb potential, which is also known as the *Yukawa potential*. Previously, many experimental studies provided a wealth of data in regard to the stability of various phases, notably the disordered phase, the face-centered cubic phase (FCC) and the body-centered cubic phase (BCC). These experimental systems consisted typically of aqueous suspension of uniform, charged-polystyrene spheres with variable salt concentration, the latter being a control parameter for the degree of screening of the underlying electrostatic Coulomb interaction.

For prototypical colloidal systems with short-range interactions, we consider colloids of the *fuzzy* kind. Fuzzy systems are made of molecules with long, flexible alkyl chains attached to centers of rigid, aromatic rings. The interparticle potential for these systems may be approximated fairly well by a simple hardcore dressed with a repulsive short-range interaction of finite strength.

On the other hand, polymers are large molecules consisting of repeating chemical units. Each repeating unit, known as monomers, is typically made of more than five and fewer than 500 atoms, while a polymer is qualified by having more than 500 monomers linked together in various topologies — the most familiar one being long-chained linear polymers. Polymers have important industrial applications such as plastics and drug delivery and constitutes the basis of molecular biology.

In probing the stability of various colloidal phases, molecular dynamics (MD) simulations are generally used in addition to experiments. Qualitative corroborations exist between MD and experimental findings. Though it is encouraging that such qualitative agreement exists, one is hard-pressed for similar quantitative convergence between existing experimental data

and simulation results. Further complicating the matter is the lack of analytical calculations from which either experimental or simulation findings can be definitively derived. Methods like the *density-functional theory* does not provide an intuitive understanding of the phase behaviors and other thermodynamical properties of these colloidal systems. This difficulty thus strongly necessitates formulation of theoretical models that are not only computationally simple enough to yield insightful solutions but also general enough to have great applicability to a range of diverse systems.

Theoretically, the free energy of a system completely determines its equilibrium thermodynamics. The stable phases of a physical system for a given range of parameters correspond to the minima of its free energy for the respective range. This is in accordance with the *de facto* standard in modern physics that the rigorous formulation of a problem should involve the extremization of some relevant quantities with respect to certain set of constraints that characterize the system. This fact, along with another fact that physics is mostly about the study of *structures* of various systems (the universe, spin lattices, superconductors, *etc.*) might together explain the unusual effectiveness of mathematics as a language in describing the material world, as encapsulated by the *Wigner's Puzzle*.

At the mean-field level where we do not take into account the effects of correlation between the various components or constituents within a physical system, the Landau theory has proven remarkable success in modeling the phenomenology of a variety of systems near transitions between phases, under very simple assumptions based on the symmetry of order parameters. In this regard, Landau theory stands out as one of the most remarkable examples of coarse-grained models that we have first defined earlier.

To further elaborate on the details of Landau theory and coarse-graining, we return to discussing some of the general features of coarse-grained models, now with the specific context of thermodynamics of colloidal and polymeric systems in mind. The rigorous bridge between the microscopic degrees of freedom and the macroscopic field variables is formally established by the subject of *statistical mechanics*, wherein statistical methods are often utilized to extract useful information and characterization of systems approaching the *thermodynamic limit*, in which the total number of degrees of freedom, N , of these systems approach infinity ($N \rightarrow \infty$). Within statistical mechanics, the physical concept of coarse-graining has been made rigorous by the mathematics of *renormalization group*, which is perhaps one of the deepest and most beautiful insights arising from modern physics. The theory of renormalization group relates

effective models of different scales (such as length, momentum, or energy) in terms of how various interaction parameters and correlation functions change or *renormalize* with respect to these scales. It turns out that the relations of how these interaction parameters, coupling constants, and correlation functions scale with respect to length or energy (renormalization group flows) actually reveal unexpected and deep physics between the different phenomenological models, such as the origin of *universality classes* in *critical phenomena*.

Mathematically, phase transitions occur when non-analyticity develops for the free energy of a system for some choice of thermodynamic variables. It is shown in statistical mechanics that this non-analyticity is only a consequence of taking the system to its thermodynamic limit. Historically, phase transitions were classified according to the *Ehrenfest classification*: the various solid/liquid/gas transitions are deemed *first-order transitions* because they exhibit a discontinuity in the first derivative of the free energy with respect to a thermodynamic variable. On the other hand, the example of ferromagnetic/paramagnetic phase transition is considered a *second-order transition* because of a discontinuity in the second derivative of its free energy. The Ehrenfest classification is incomplete since it is based on the mean-field understanding of phases. The modern classification relies on whether these phase transitions involve *latent heat* (first-order) or not (continuous or second-order).

In general, second-order phase transitions are easier to study than first-order transitions due to the presence of latent heat in the latter processes. A whole host of machinery has been devised to the investigation of critical phenomena, so called because of their association with critical points in the free-energy description. Critical phenomena can be characterized by *critical exponents*, the index associated with the power law by which certain thermodynamic variables, such as the heat capacity, diverge. Remarkably, the phenomenon of universality is observed for continuous phase transitions across systems of wildly different microscopic physics that nevertheless exhibit the same set of critical exponents, thus reflecting a common characteristic long-distance critical behavior. As such, we classify second-order transitions into different *universality classes* as characterized by different sets of these critical exponents. And the method of renormalization group provides a systematic computational tool for the evaluation of these critical exponents, based upon the physical concept of coarse-graining and scaling, once we specify the free energy expression for a system. Therefore, our main challenge in physics and in this particular work is to come up with

reasonable free-energy expressions for various systems of interest that would capably capture the physical features underlying these systems to the level of accuracy that we desire.

Historically, physics has always drawn inspirations from development of mathematics. When it comes to modeling real-life physical systems, such as the construction of a suitably chosen free-energy expression, it is no exception. For example, as a first-order approximation, we often approximate microscopic particles as spheres when the specific properties of a system do not explicitly depend on the shape anisotropy of its constituents. Correspondingly, interactions between these microscopic particles are mapped to interactions between geometrical spheres. For more complicated systems such as liquid-crystalline mesogens whose macroscopic phase properties actually depend crucially on the shape anisotropy found in their inter-molecular interactions, we can idealize the constituent molecules with other appropriately chosen geometrical objects — cylinders in the case of liquid crystals. One of the major pillar of twentieth-century modern physics — Einstein's theory of *general relativity* — arose from Einstein's successful elucidation of gravitation upon combining the rigorous mathematical framework of *non-Riemannian geometry* and the physical idea behind the conceptually elegant *correspondence principle*.

Thus, geometry has played a central role in the development of modern physics. Conventional wisdom dictates that formulation of problems, when rooted in a properly chosen geometrical setting, becomes simple and meaningful. For example, Maxwell's equations and more generally the phenomenon of electromagnetism, in the context of gauge symmetry, is the unique consequence of the abelian $U(1)$ -gauge field. Furthermore, the strong and weak nuclear forces found in the standard model of particle physics are but physical consequences of the extended non-abelian gauge groups $SU(2)$ and $SU(3)$, respectively. In addition, such symmetry principle as *general covariance* serves as the prerequisite to all properly formulated fundamental models of Nature and expresses the fact that the physics of any system should be independent of any chosen mathematical description in terms of a particular coordinate system. As the main goals of this work, we use concepts from geometry in studying and understand a class of first-order phase transitions between the different lattice phases (FCC, BCC, and A15) found in colloidal crystals, and we apply geometric and topological concepts to studying a class of second-order phase transitions in closed-loop polymeric systems. In particular, we propose a geometrical way of understanding the thermodynamic and elastic properties of

colloidal crystals based on what we term as the *foam model*, and we perform a renormalization-group analysis to confirm a new universality class for long polymers with non-trivial topologies.

This monograph is organized as follows. In Chapter 2, we further pursue the general theory of phase transitions. We will illustrate with examples the pervasiveness of phase transitions as a theme in our understanding of Nature within the paradigm of modern physics. We will provide the common classifications of the different types of phase transitions. In particular, we will survey some of the most important concepts pertaining to both first-order and second-order phase transitions. We will conclude the chapter with an important exposition to the concept of renormalization group and the mathematical background behind the conceptual framework.

In Chapter 3, we will provide an account of density-functional theory, one of the main tools available to soft-condensed matter theorists in studying phase transitions. We will discuss density-functional theory both in its original context of electronic many-body problems as well as its adaptation to the classical study of macroscopic phase transitions of statistical systems.

In Chapter 4, we will survey some of the important concepts from solid geometry and topology pertaining to our main results of the foam model in describing phase stability of various lattice structures as well as our renormalization-group analysis applied towards studying phase transitions associated with closed-loop polymers. We will see on a practical level how symmetry can be used in the classification of a plethora of lattice phases found in two- and three-dimensional spaces. We will demonstrate both the Hermann-Mauguin crystallographic notation and the orbifold notation for labeling the different lattice phases. In particular, we will put emphasis on the three cubic lattice structures: namely, the face-centered cubic (FCC) lattice, the body-centered cubic (BCC) lattice, and the β -Tungsten A15 lattice. Structures with these three types of geometry have been found in colloidal systems, and we will see how the foam model can be used to understand their origins. After presenting the conceptual framework of our foam model, we will conclude the chapter by discussing the closely related mathematical problems of the Kelvin problem and of the Kepler conjecture.

In Chapter 5, we will apply our foam model in the direct construction of various free-energy expressions for the different phases of both charged and fuzzy colloidal crystals, in terms of their geometry and interparticle dynamics. Instead of the usual point approximation, we will consider the opposite limit of mapping these spherical colloidal particles as flat surfaces under appropriate experimental conditions.

In Chapter 6, we will present our main result of reproducing an experimental phase diagram [*Phys. Rev. Lett.* **62**, 1524 (1989)] with only one adjustable parameter of experimentally inaccessible surface-charge density of the colloidal particles. We will also discuss our results in the context of existing knowledge on phase properties regarding charged colloids.

In Chapter 7, we apply our foam analogy to studying elastic properties of colloidal crystals. We will construct the elastic free energy expressions for the FCC, BCC, and A15 lattices in both fuzzy colloids and charged colloids and derive the various elastic constants from first principles. We will present a thorough discussion on our main results, including instabilities of the BCC and A15 lattices with respect to certain shear modes.

In Chapter 8, we study the phase transitions of topologically-constrained polymers. Closed-loop polymers (such as DNA) obey the topological constraint given by Fuller's theorem between the Linking number Lk , twist Tw , and writhe Wr : $Lk = Tw + Wr$. To investigate the scaling behavior of these polymers in solution, the thermal fluctuation of system can be systematically handled by the casting the problem in a field-theoretic language. We will first introduce the Chern-Simons gauge field in order to implement the aforementioned Fuller topological constraint for these polymers. The model of interest will be the abelian Chern-Simons theory. We consider the fluctuation effect on the critical exponent associated with the radius of gyration up to two-loop order via the method of renormalization group analysis. We will demonstrate a new universality class for the class of closed-loop polymers. We will show that the critical exponent characterizing the onset of this phase transition depends on the chemical potential for writhe, and it gives way to a first-order transition induced by fluctuation.

We will conclude our survey of geometry and phase transitions in colloids and polymers with a few final thoughts in Chapter 9.