



Assessment of atomistic coarse-graining methods

Young Chen^{a,*}, Jonathan Zimmerman^b, Anton Krivtsov^c, David L. McDowell^{d,e}

^a Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, FL 32611, USA

^b Mechanics of Materials Department, Sandia National Laboratories, Livermore, CA 94551, USA

^c Department of Theoretical Mechanics, St. Petersburg State Polytechnical University, St. Petersburg 199178, Russia

^d School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^e G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

ARTICLE INFO

Article history:

Received 11 October 2010

Accepted 24 March 2011

Available online 4 May 2011

Keywords:

Atomistic model

Coarse-graining

Statistical mechanics

Lattice dynamics

ABSTRACT

This paper reviews classical theories of coarse-graining and gives a short introduction to representative coarse-grained atomistic models that were developed based on structure reduction, an assumption of homogenous deformation, and field representation. The applicability and limitations of these coarse-grained models are analyzed on the basis of their theoretical frameworks as well as the coarse-graining methods they employ.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The increasing demands of engineering design to push the limits of current capabilities require predictive theories and simulation tools. The need for this predictive ability has enabled atomistic modeling and simulation to become an essential component for examining phenomena in molecular science, materials science, and engineering applications. Supplemented by quantum mechanical calculations of force fields that describe the interaction of atoms, atomistic simulations can predict properties and behavior of various molecular and material systems.

However, MD is limited by its characteristic length and time scales, and by the speed and storage constraints of available computers. Current state-of-the-art MD simulations on supercomputer can handle about 10^9 atoms, amounting to a volume of less than a cubic micron, for a short duration of time. It is unlikely, in the near future, for MD to solve engineering material systems or complex molecular processes that involve physical phenomena operating across large ranges of scale – 12 orders of magnitude in time scales as in the modeling of protein folding, or 10 orders of magnitude in spatial scales as in the design of advanced materials (Oden et al., 2006). These limitations have motivated efforts in the research and development of coarse-graining methods for study of complex phenomena that involve large length and time scales.

We define the process of representing a system with fewer degrees of freedom than those actually present in the system as coarse-graining (Espanol, 2004). Phenomenological theories, e.g., classical thermodynamics and macroscopic mechanics, are all coarse-grained (CG) models in which the majority of degrees of freedom is eliminated. These phenomenological CG models were usually constructed with a judicious balance of physical intuition, simplicity, and respect of material symmetries. They start from a few empirical observations, which are organized and axiomatized in the form of physical laws, and

* Corresponding author.

E-mail addresses: ypchen2@ufl.edu (Y. Chen), jzimmer@sandia.gov (J. Zimmerman), akrivtsov@bk.ru (A. Krivtsov), david.mcdowell@me.gatech.edu (D.L. McDowell).

arrive at a CG model with a few parameters. However, molecular information is usually absent in these phenomenological approaches of coarse-graining.

Many recent developments of CG models are based on atomistics, and hence we may call them CG atomistic models. By coarse-graining atomistic models, we expect to predict the properties and behavior of the systems from the interaction at atomic scale.

The objective of this paper is to analyze the applicability and limitations of coarse-graining methods from their mathematical and physical foundations. Therefore, it is not our intention to provide an extensive review of existing coarse-grained models. Following this introduction, classical theories of coarse-graining will be reviewed in Section 2, representative modern CG models will be introduced in Section 3, analyses of the CG models will be presented in Section 4, and a brief discussion will be given in Section 5.

2. Theoretical foundations of coarse-graining

2.1. Coarse graining through ensemble averaging – equilibrium statistical mechanical theory

The principles of statistical mechanics offer a molecular basis for the laws of phenomenological thermodynamics and provide a means to calculate macroscopic quantities from properties of molecules (Green, 1952). The most fundamental concept in statistical mechanics is coarse graining or averaging. Two important averaging processes in statistical mechanics are the “time average” and the “ensemble average”. From the standpoint of mechanics, macroscopically observable quantities in a thermodynamic system are simply the time averages over the molecular trajectories in phase space:

$$\langle A \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_{t_0}^{t+t_0} A(\mathbf{r}(t + \tau), \mathbf{p}(t + \tau)) d\tau. \quad (1)$$

Here $\langle A \rangle$ is the time-average of the $A(\mathbf{r}, \mathbf{p})$, where $(\mathbf{r}, \mathbf{p}) \equiv (\mathbf{R}^1, \mathbf{R}^2, \dots, \mathbf{R}^n, m^1 \mathbf{V}^1, m^2 \mathbf{V}^2, \dots, m^n \mathbf{V}^n)$, are the phase-space coordinates, i.e., the positions and momenta of atoms. The calculation of the time averages, however, was a very arduous task before the advent of digital computers. Gibbs, along with Maxwell and Boltzmann, made a great advance by suggesting that the average over a period of time for a given system at equilibrium is equivalent to the average over the ensemble at one instant of time. The equilibrium ensemble average of a dynamic phase function $A(\mathbf{r}, \mathbf{p})$ is defined as

$$\bar{A} \equiv \int_{\mathbf{p}} \int_{\mathbf{r}} A(\mathbf{r}, \mathbf{p}) f(\mathbf{r}, \mathbf{p}) d\mathbf{r} d\mathbf{p}, \quad (2)$$

where the probability density function

$$f(\mathbf{r}, \mathbf{p}) = \begin{cases} 1 & \text{if } E < H(\mathbf{r}, \mathbf{p}) < E + \Delta, \\ 0 & \text{otherwise,} \end{cases} \quad (3)$$

represents the microcanonical ensemble (NVE), with $H(\mathbf{r}, \mathbf{p})$ being the Hamiltonian, E is a constant, and

$$f(\mathbf{r}, \mathbf{p}) = e^{-H(\mathbf{r}, \mathbf{p})/kT}, \quad (4)$$

represents the canonical ensemble (NVT). According to the ergodic hypothesis, the time average defined by Eq. (1) should be the same as the ensemble average defined by Eq. (2). Eq. (2) thus replaces the mechanically well-posed but physically difficult task of integrating the classical many-body dynamics equations of motion by the somewhat more manageable task of averaging over *static phase-space states*. As mentioned by Maxwell and Boltzmann that laws of macroscopic physics can be deduced from the microscopic dynamics of a system at equilibrium, Gibbs' ensemble theory has successfully formulated and explained the fundamental laws of equilibrium thermodynamics through coarse-graining microscopic many-body dynamics.

2.2. Coarse-graining through field representation – Statistical mechanical theory of transport processes

Gibbs developed the statistical ensemble theory for analyzing equilibrium thermodynamic properties of macroscopic systems. When the conditions depart from thermodynamic equilibrium, transport processes occur. The most common transport processes are diffusion, heat transfer, fluid flow, and response to external forces that depend upon time. These transport processes are irreversible processes. The central problem of nonequilibrium statistical mechanics has thus been to derive the governing equations that describe the irreversible processes in coarse-grained systems from the reversible equations of motion in microscopic many-body dynamics (Montroll & Green, 1954).

The kinetic theory of rarefied gases of Boltzmann (1872) marked the beginning of the statistical mechanics formulation of irreversible processes, providing insight into the problem of how irreversible phenomena can be treated building on the concepts of reversible dynamics. Many fundamental developments in coarse-graining of nonequilibrium processes in dense fluids and solids have resulted from the fruitful and inspiring work of Kirkwood in the years 1946–1959, with a series of 14 articles bearing the thematic title of “statistical mechanical theory of transport processes” as a backbone.

In Kirkwood’s statistical mechanical theory of transport processes, the fundamental equation that defines the link between microscopic many-body dynamics and the macroscopic description is the definition of local densities in the three-dimensional physical space:

$$\bar{\mathbf{a}}(\mathbf{x}, t) = \sum_{k=1}^n \int_{\mathbf{r}} \int_{\mathbf{p}} \mathbf{A}(\mathbf{r}, \mathbf{p}) f(\mathbf{r}, \mathbf{p}, t) \delta(\mathbf{R}^k - \mathbf{x}) d\mathbf{r} d\mathbf{p}, \tag{5}$$

where $\mathbf{r} = \{\mathbf{R}^1, \mathbf{R}^2, \dots, \mathbf{R}^n\}$, and $\mathbf{p} = \{m^1\mathbf{V}^1, m^2\mathbf{V}^2, \dots, m^n\mathbf{V}^n\}$, are respectively the positions and momenta of *molecular centers*. The probability function $f(\mathbf{r}, \mathbf{p}, t)$ is time-dependent, and the delta function, $\delta(\mathbf{R}^k - \mathbf{x})$, is normalized with a unit of inverse volume. Following from Eq. (5), Kirkwood and his co-workers obtained the time evolution laws of the local densities of mass, linear momentum and energy, as exact consequence of laws of Newtonian mechanics that governs the dynamics of the microscopic many-body systems. Here, the ergodic hypothesis is not pursued and fully nonequilibrium behavior can be treated. These partial differential equations are identical in form with transport equations of hydrodynamics or the balance equations of continuum mechanics. In the process of the formulation, the formulas for calculations of fluxes (stress and heat flux) were derived and the parameters involved were determined from the underlying atomistic model.

It is worthwhile to mention that the statistical mechanical theories of CG nonequilibrium systems were also intensely studied by Green (1952), Kubo (1957), Zwanzig (1911), Mori (1965), and others. Among these statistical mechanical methods, Kirkwood’s field method is intended to apply to all states of aggregation. The formulation has also provided a method to investigate the limits of validity of the empirical laws of diffusion, heat conduction, and viscous flow, and a means to determine the coefficients of diffusion, thermal conductivity, and viscosity, from the structure of the system on the molecular scale. It has also provided a powerful technique to deepen understanding of Brownian motion and of the Boltzmann and Enskog equations for gas-phase kinetics. Furthermore, it led to derivation of the first autocorrelation function representation in transport theory, for the “friction coefficient,” in Langevin equations, anticipating the later Green–Kubo–Mori–Zwanzig results of the same generic form.

Kirkwood’s statistical mechanical theory of transport processes provides a coarse-grained description using field variables which have, in principle, an infinite number of degrees of freedom. Note that these fields are continuous in physical space. Since the continuum fields can be represented by a discretization on the length scale of interest, it becomes clear that the coarse-grained level of description indeed uses fewer degrees of freedom than the atomistic description. There seems to be a smallest length-scale for classical continuum field models, however, determined by the molecular or atomic structure. This characteristic length scale was studied and discussed by Alder and Alley (1984), whose analysis of simulation data shows that the classical continuum field representation works successfully from macroscopic down to the length of only a few inter-atomic distances.

2.3. Coarse-graining through assumptions of homogeneous deformation in crystals

Crystalline solids are distinguished from other states of matter by a periodic arrangement of the atoms; such a structure is called crystal lattice (Fig. 1). If we visualize a simple lattice as the periodic repetition of a single atom, we can look upon a general lattice or a multi-atom lattice as the repetition of the atoms in the basis as a group.

If a lattice is deformed such that the resulting structure remains a perfect lattice, according to Born and Huang (1954), the deformation is homogeneous. Under homogenous deformation, a particle in a simple lattice initially at \mathbf{r} is moved to \mathbf{r}' according to the affine mapping given by

$$r'_i - r_i = u_i = \sum_j F_{ij} r_j \quad (i, j = 1, 2, 3), \tag{6}$$

with u_i is the i th component of displacement, F_{ij} are called deformation parameters. Eq. (6) transforms the coordinates of all particles linearly and homogeneously and is generally referred to as Cauchy–Born hypothesis.

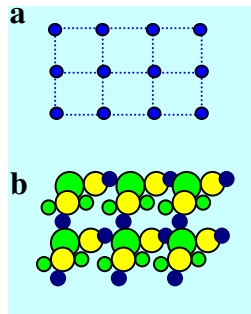


Fig. 1. (a) Simple lattice, (b) general lattice.

If there is more than one atom in the lattice cell, say N_a atoms, the total displacement of the α th atom in the k th lattice cell, denoted as $k\alpha$ atom, should then be expressed as

$$u_i^{k\alpha} = \xi_i^\alpha + \sum_j F_{ij} r_j^{k\alpha} \quad (i, j = 1, 2, 3, \alpha = 1, 2, \dots, N_a), \quad (7)$$

where the displacement of $k\alpha$ atom is decomposed as the displacement of the mass center of lattice cell k and of α th atom within the k th lattice cell, with ξ_i^α being the i th component of the internal displacement of the α th atom.

The quantities ξ_i^α and F_{ij} were respectively described as the internal and external deformation; the latter are identical with the macroscopic elastic deformation. As a body is elastically deformed, an internal strain is induced. If one assumes the internal strain minimize the energy density for the given external elastic deformation F_{ij} . The internal deformation can then be eliminated. The atomistic model of general crystals can then be coarse-grained to obtain a macroscopic elastic model. Using this homogeneous deformation assumption, [Born and Huang \(1954\)](#) derived the energy density, elastic constants, and mechanical stability of crystals subjected to homogenous deformation in which the particles interact with central forces.

3. Representative CG atomistic models

The fundamental process of coarse-graining is to eliminate degrees of freedom. The art of coarse-graining is hence to balance the reduction of CG variables so that the reduced order of representation of the system is amenable to simulation while the essential properties of interests can still be retained. Here we divide the methods that have been developed to reduce the degrees of freedom of an atomistic system into three categories:

- (1) Reducing the order of the particle representation of the molecular structure.
- (2) Assuming atomic-scale homogeneous deformation.
- (3) Using field representations.

3.1. CG models based on reduced-representation of molecular structures

Most of CG soft matter models are based on the reduced-structure method shown in [Fig. 2](#). This method consists of two steps: (1) grouping several atoms into one rigid CG particle so as to directly reduce the complexity of the structure, and (2) construct an effective force field for the CG model by matching the structure, or thermodynamic properties, or forces of the CG model with that of the underlying atomistic model. Popular models in this category include the earliest CG models: united-atom model ([Levitt, 1976](#); [Levitt & Warshel, 1975](#)), the super-atom model ([Reith, Meyer, & Müller-Plathe, 2001](#); [Tschöp, Kremer, Batoulis, Bürger, & Hahn, 1998](#)), the beads model ([Favrin, Irbäck, & Wallin, 2002](#)), the dissipative particle dynamics ([Español & Warren, 1995](#)), and recently developed the multiscale CG method ([Izvekov & Voth, 2005](#)).

(a) Super-atom model (united atom model, beads model)

The united-atom, the super-atom, and the beads model intend to reproduce the structural properties or to match thermodynamic properties such as energy or free energy of the underlying atomistic model by parameterization of a pre-selected analytical form of the CG potential. The analytical effective potentials are assumed to contain the intermolecular non-bonded potential and intramolecular bonded potentials. The energy-matching model has been useful for simulating processes where thermodynamic properties play a decisive role. The structure-matching model that aim to reproduce a target structure, often described by a set of radial distribution functions obtained from all-atom molecular simulations, on the other hand, has a distinct advantage that it facilitates “backmapping” to reinsert atomistic coordinates into the CG model after CG simulation. The general strategy is to use rigid all-atom chain fragments – which were taken from the all-atom chain structures. These fragments are fitted onto the CG structure. The resulting all-atom structure is then relaxed by energy minimization and a short equilibration. The combination of CG simulations with an efficient backmapping or inverse mapping capability has the promise to efficiently simulate long time scale and large length scale soft matter processes and in the end to obtain well-equilibrated atomistic structures and trajectories ([Peter & Kremer, 2010](#)).

(b) Multiscale coarse-grained method (MS-CG)

MS-CG is a new structure-reduction based CG method introduced by [Izvekov and Voth \(2005\)](#) for determining the effective interactions between CG sites using information from atomistic MD trajectories. The basis of the MS-CG

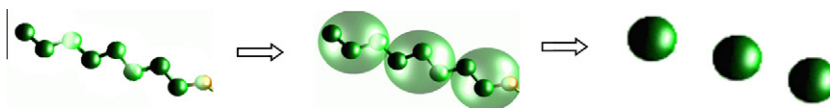


Fig. 2. Procedure to construct a super-atom model from the underlying atomistic model, (a) The atomistic model, (b) the atoms are grouped into 3 rigid particles, (c) the CG model.

approach is the force-matching method (Hone, Izvekov, & Voth, 2005; Izvekov, Parrinello, Burnham, & Voth, 2004) used to build effective empirical force fields from *ab initio* MD data. In distinction with the structure- or energy-based structure-reduction CG methods, MS-CG method aims to generate a CG model that is “consistent” with the atomistic model of the same system in that the equilibrium distribution function of the CG model is equal to the distribution determined by the specific CG mapping and the equilibrium distribution function of the atomistic model. The statistical mechanics foundation of the MS-CG force matching method was described by Noid et al. (2008a), who defined the CG potential $U(\mathbf{R}^N)$ in terms of the atomistic potential $u(\mathbf{r}^n)$, i.e.,

$$U(\mathbf{R}^N) = -k_B T \ln \left(\int d\mathbf{r}^n \exp[-u(\mathbf{r}^n)/k_B T] \delta(\mathbf{M}_R^N(\mathbf{r}^n) - \mathbf{R}^N) \right). \quad (8)$$

The CG force is given by

$$\mathbf{F}_I(\mathbf{R}^N) = -\frac{\partial U(\mathbf{R}^N)}{\partial \mathbf{R}_I}, \quad (9)$$

which is determined by variationally minimizing the residual

$$\chi_{MS}^2[\mathbf{F}^{MS}] = \frac{1}{3N} \left\langle \sum_{I=1}^N |\mathbf{f}_I(\mathbf{r}^n) - \mathbf{F}_I^{MS}(\mathbf{M}_R^N(\mathbf{r}^n))|^2 \right\rangle, \quad (10)$$

where $\mathbf{M}_R^N(\mathbf{r}^n) = \sum_{i=1}^N c_i \mathbf{r}_i$, $\mathbf{f}_I(\mathbf{r}^n) = \sum_{i \in I} \mathbf{f}_i(\mathbf{r}^n)$, n the number of atoms, and N is the number of CG particles.

There have been substantial efforts to numerically implement the MS-CG method. Current MS-CG developments are mainly based on simple potential functions, e.g., pairwise additive potentials (Das & Andersen, 2009; Noid et al. (2008a, 2008b)) and three-body potentials (Larini, Lu, & Voth, 2010). MS-CG simulations have been shown to reproduce well the structural properties of atomistic models (Das & Andersen, 2009; Izvekov & Voth, 2005; Larini et al., 2010).

(c) Dissipative particle dynamics (DPD)

DPD is a particle model that allows simulation of complex fluids at mesoscopic scales. The original phenomenological formulation was not linked to microscopic particle systems. Espanol (1995), Espanol and Warren (1995) derived the stochastic differential equations of DPD using the technique of projection operators. By considering not only effective conservative forces but also velocity-dependent frictional forces as those in the generalized Langevin equations for the CG variables, the resulting dynamic equations have the structure of DPD. Each particle in a DPD model can be regarded as a collection of molecules. The time evolution of the particles is governed by the Langevin equations of motion, i.e., the force acting on a particle has three parts:

$$\mathbf{f}_i = \mathbf{f}_i^C + \mathbf{f}_i^D + \mathbf{f}_i^R = \sum_j \mathbf{f}_{ij}^C + \xi_i \dot{\mathbf{r}}_i + \mathbf{f}_i^R(T, t). \quad (11)$$

Here \mathbf{f}^C is the conservative force, \mathbf{f}^D the velocity-dependent dissipative or dragging force, and \mathbf{f}^R the random force, and ξ_i is the friction constant. The amplitudes of these forces are dictated by the fluctuation–dissipation theorem. The DPD method in general has been shown to produce a correct NVT ensemble if the fluctuation–dissipation relation is satisfied. Recent developments have extended the DPD method from the constant temperature DPD to include constant pressure or constant surface tension (Jakobsen et al., 2005).

DPD currently is the most commonly used mesoscopic model for complex fluids. There is, however, no theory to link the atomic interaction and the DPD force fields and parameters, no direct connection between the friction coefficient and the viscosity of the solvent. The fluid particle has no physical size and the scale of the DPD particle is undetermined. The model is purely isothermal and, as a consequence of the absence of the internal energy of the fluid particles, energy is not conserved. Therefore, DPD is not an atomistically-consistent CG model.

3.2. CG models based on homogeneous deformation assumption

Assuming homogenous deformation, as in Eq. (6) (Born & Huang, 1954), is another approach to reduce the degrees of freedom of the systems. A special case is the Cauchy–Born rule based on the hypothesis introduced by Cauchy (1828) and Born (1915) to relate changes in atomic positions to macroscopic deformation. Two popular methods using this method are the quasi-continuum method and the coarse-grained molecular dynamics method.

(a) Quasicontinuum method (QC)

QC is an energy minimization technique developed by Tadmor, Ortiz, and Phillips (1996) and Knap and Ortiz (2001) for simulating mechanical response of crystalline materials at zero temperature. The essence of the method is to replace the atomistic model of N atoms by a CG model of N_h ($N_h < N$) representative atoms (or nodal points), and to replace the energy minimization of the atomistic model

$$\min \Phi(\mathbf{r}^1, \mathbf{r}^2, \dots, \mathbf{r}^N), \quad \text{or} \quad \mathbf{f}^i = 0, \quad i = 1, 2, \dots, N \quad (12)$$

with a reduced counterpart

$$\min \Phi_h(\mathbf{r}_h^1, \mathbf{r}_h^1, \dots, \mathbf{r}_h^{N_h}), \quad \text{or} \quad \mathbf{f}_h^i = \mathbf{0}, \quad i = 1, 2, \dots, N_h, \quad (13)$$

where the positions of the atoms $\mathbf{r} = \{\mathbf{r}^1, \mathbf{r}^2, \dots, \mathbf{r}^N\}$ are linked to and determined by the position of the nodal points or representative atoms $\mathbf{r}_h = \{\mathbf{r}_h^1, \mathbf{r}_h^1, \dots, \mathbf{r}_h^{N_h}\}$ through “Cauchy–Born rule” (see Fig. 3), and the displacements of the CG nodes \mathbf{r}_h are solved through Eq. (13) using conjugate gradients method.

The zero-temperature static QC has been widely used to study diverse problems and has attracted many researchers to follow. Recently, the method has been extended to treat nonequilibrium systems at finite-temperature by replacing the position-dependent interatomic potentials with position-temperature-dependent ones, and treating time-dependent phenomena as a sequence of incremental problems (Kulkarni, Knap, & Ortiz, 2008). This finite-temperature formulation, however, has lost the simplicity of that of the zero-temperature, and is no longer “consistent” with the atomistic model since macroscopic phenomenological laws, such as the law of heat conduction, have to be assumed. The energy to be minimized is the sum of Helmholtz free energy F and an external potential Φ^{ext} :

$$\Phi(\langle \mathbf{r}_h \rangle, T_h, \{\omega\}_h) = F(\langle \mathbf{r}_h \rangle, T_h, \{\omega\}_h) + \Phi^{ext}(\langle \mathbf{r}_h \rangle). \quad (14)$$

Here, $\langle \mathbf{r}_h \rangle$ are the mean positions of \mathbf{r}_h , T_h is the CG local temperature, $\{\omega\}$ is a measure of the standard deviation of atomic positions and momenta; the mean position, temperatures and $\{\omega\}$ of each atoms are linked to those of the representative atoms through piecewise interpolation functions.

Another attempt to extend QC to nonequilibrium systems (Marian et al., 2010) was based on the Langevin equation. The equations that govern the time evolution of the CG displacement \mathbf{r}_h were derive as

$$\mathbf{M}_h \ddot{\mathbf{r}}_h + \tau^{-1}(\mathbf{r}_h) \mathbf{M}_h \dot{\mathbf{r}}_h = \mathbf{f}_b(\mathbf{r}_h) + \mathbf{R}_h(t), \quad (15)$$

where \mathbf{M}_h is called mass matrix, $\mathbf{f}_b(\mathbf{r}_h)$ are the body forces, $\mathbf{R}_h(t)$ the instantaneous random forces, and $\tau^{-1}(\mathbf{r}_h)$ is a spatial variable describing a characteristic damping time. The governing equations of QC now have become stochastic differential equations (SDE) and have the same structure as that of the DPD.

(b) Coarse-grained molecular dynamics (CGMD)

CGMD is a procedure to derive the effective Hamiltonian for a set of coarse-grained variables from the Hamiltonian of the atomistic N -body system (Rudd & Broughton, 1998, 2004, 2005). The displacement of the mesh node j is a weighted average of the atomic displacements

$$\mathbf{u}_{CG}^j = \sum_{\alpha} W_{j\alpha} \mathbf{u}^{\alpha}, \quad (16)$$

where $W_{j\alpha}$ is a weighting function determined by FE shape function. The CG energy is defined as canonical ensemble averaged energy, and is expressed in terms of displacements \mathbf{u}_{CG} and momenta \mathbf{p}_{CG} of the FE nodes as

$$E_{CG} = E(\mathbf{u}_{CG}, \dot{\mathbf{u}}_{CG}) = \frac{1}{Z} \int_{\mathbf{r}} \int_{\mathbf{p}} H(\mathbf{r}, \mathbf{p}) f(\mathbf{r}, \mathbf{p}) \prod_j \delta\left(\mathbf{u}_{CG}^j - \sum_{\alpha} f_{j\alpha} \mathbf{u}^{\alpha}\right) \delta\left(\mathbf{p}_{CG}^j - \sum_{\alpha} f_{j\alpha} \mathbf{p}^{\alpha}\right) d\mathbf{r} d\mathbf{p}, \quad (17)$$

where $f(\mathbf{r}, \mathbf{p})$ is the canonical ensemble probability function in Eq. (4), and Z is the partition function given by

$$Z = \int_{\mathbf{r}} \int_{\mathbf{p}} f(\mathbf{r}, \mathbf{p}) \prod_j \delta\left(\mathbf{u}_{CG}^j - \sum_{\alpha} f_{j\alpha} \mathbf{u}^{\alpha}\right) \delta\left(\mathbf{p}_{CG}^j - \sum_{\alpha} f_{j\alpha} \mathbf{p}^{\alpha}\right) d\mathbf{r} d\mathbf{p}. \quad (18)$$

The CGMD governing equations can be written in the general form

$$M_{jk} \ddot{\mathbf{u}}_{CG}^k = -K_{jk} \dot{\mathbf{u}}_{CG}^k + \mathbf{F}_{ext}^j. \quad (19)$$

For monatomic harmonic crystals, the matrix M , K , and the CG energy E_{CG} can be analytically computed (Rudd & Broughton, 2005). CGMD then operates in a manner similar to conventional MD. Thermodynamic quantities are calculated in the usual

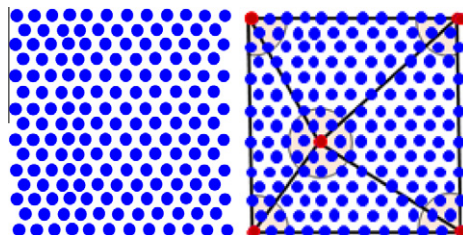


Fig. 3. Procedure to construct a QC model (a) an atomic model, (b) displacements of atoms are constrained by that of FE nodes.

way. In particular, temperature is defined in terms of the mean-squared velocity of the CG nodes. The CGMD is derived solely from the MD model, and has no continuum parameters. Currently its formulation is complete for monatomic harmonic crystals. The anharmonic potential is computed by perturbation theory about the harmonic Hamiltonian assuming quasi-harmonic or small anharmonic interaction.

3.3. CG models based on field representation

Most of phenomenological CG models are based on the invocation of a continuum field assumption. In this section we review two field theories that can be developed through coarse-graining of atomistic N -body dynamics.

(a) Micromorphic theory

Micromorphic theory is a continuum field theory originally introduced by Eringen and Suhubi (1964) and Eringen (1964) for material bodies that possess internal fine scale structures. The theory was further developed by Eringen (1970, 1972) and by Eringen and Kafadar (1976), revisited and closed by Eringen (1992), and presented with micropolar theory and microstretch theory on a unified foundation in the book *Microrcontinuum Field Theories* (1999). In micromorphic theory, a material body is considered as a continuous collection of a large number of deformable particles, called material particles. The material particle differs from that of classic continuum mechanics by possessing internal structure of finite size. A material particle, in the reference configuration, is identified by its centroidal \mathbf{X} and a director Ξ attached to it. The motion of the particle is then characterized by two sets of equations: the motion of the centroid \mathbf{X} and the motion of the director Ξ . As shown in Fig. 4a, a generic point P is represented by the vector sum of \mathbf{X} and Ξ in the reference state at time $t = 0$.

The motions that carry $P(\mathbf{X}, \Xi)$ to $P(x, \xi, t)$ in the deformed state at time t are governed by conservation equations of mass, microinertia, generalized spin, linear momentum, and energy. These equations were formulated by means of volume and surface averages applied to an element of the body (Eringen, 1964; Eringen & Suhubi, 1964), and were obtained again from the macroscopic energy balance equation (Eringen, 1992) by subjecting it to invariance under arbitrary, constant velocity rigid-body translations and arbitrary, constant-velocity rotations, as

$$\frac{\partial \rho}{\partial t} + \nabla_x \cdot (\rho \mathbf{v}) = 0, \tag{20}$$

$$\frac{\partial}{\partial t}(\rho \mathbf{i}) + \nabla_x (\mathbf{v} \otimes \rho \mathbf{i}) = \rho \boldsymbol{\varphi} + \rho \boldsymbol{\varphi}^T, \tag{21}$$

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla_x \cdot (\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{t}) = \mathbf{f}, \tag{22}$$

$$\frac{\partial}{\partial t}(\rho \boldsymbol{\varphi}) + \nabla_x \cdot (\mathbf{v} \otimes \rho \boldsymbol{\varphi} - \mathbf{m}) = \boldsymbol{\omega} \cdot \rho \mathbf{i} \cdot \boldsymbol{\omega}^T + \mathbf{t}^T - \mathbf{s} + \mathbf{l}, \tag{23}$$

$$\frac{\partial(\rho \varepsilon)}{\partial t} + \nabla_x \cdot (\mathbf{v} \rho \varepsilon - \mathbf{q}) = \mathbf{t} : \nabla \otimes \mathbf{v} + \mathbf{m} : \nabla \otimes \boldsymbol{\omega} + \boldsymbol{\omega} : (\mathbf{s} - \mathbf{t})^T + h, \tag{24}$$

where ρ , $\rho \mathbf{i}$, $\rho \mathbf{v}$ and $\rho \boldsymbol{\varphi} = \boldsymbol{\omega} \cdot \rho \mathbf{i}$ are the local densities of mass, moment inertia, linear momentum, and generalized spin, respectively; \mathbf{t} is the Cauchy stress, \mathbf{s} is the microstress average, and \mathbf{m} is high order moment stress; \mathbf{f} and \mathbf{l} are the densities of body force and body moment, respectively; h is the energy source.

Micromorphic theory was considered as a branch of continuum theories. Upon assumptions of small deformation and slow motion within the particle, micromorphic theory is shown (Chen, Lee, & Eskandarian, 2004) to reduce to Mindlin's Microstructure Theory (Mindlin, 1964). When the microstructure of the material is considered as rigid, micromorphic theory then reduces to the micropolar Theory (Eringen, 1965). Assuming a constant microinertia, micropolar theory is identical to the Cosserat Theory (1909). Eliminating the distinction of macromotion of the particle and the micromotion of its internal structure, it results in the couple stress theory (Mindlin & Tiersten, 1962; Toupin, 1962). When the particle reduces to a structure-less mass point, all the microcontinuum theories revert to classical continuum mechanics. These microcontinuum

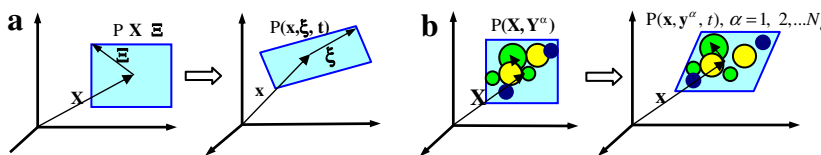


Fig. 4. Macro- and micro-motions of a material particle in (a) micromorphic theory and (b) AFT, left in (a) and (b) the reference state and (right) the deformed state at time t , where N_a is the number of atoms in a primitive unit cell.

formulations serve as successful CG models formulated via a top-down approach based on the principles of rational continuum mechanics.

The connection of micromorphic theory to atomistic model was studied by [Chen and Lee \(2003a, 2003b\)](#) and [Chen et al. \(2003c, 2004\)](#). Decomposing the atomic displacements into the lattice displacements and the relative internal displacements within each lattice cell, and also assuming the subscale internal deformation is continuous, [Chen and Lee \(2003a, 2003b\)](#) have derived the full set of balance equations of micromorphic theory from atomistic model and identified the connections between micromorphic variables and atomic variable, thus obtaining a CG model of micromorphic theory from the atomistics. By constructing a material frame-based formalism similar to the spatial frame-based formalism developed by [Hardy \(1982\)](#) and [Zimmerman et al. \(2010\)](#) have derived expressions for micromorphic theory variables based on atomic-scale quantities and obtained again the exact form of balance equations of micromorphic theory. These atomistic derivations have confirmed that micromorphic theory is on firm atomistic foundation, and can be framed as a CG atomistic model that does not involve continuum parameters.

(b) Atomistic Field Theory (AFT)

In the first one of the 14 classical papers on the statistical mechanical theory of transport processes, [Kirkwood \(1946\)](#) envisioned the extension of the formulation to molecules possessing internal degrees of freedom. In the book by [Born and Huang \(1954\)](#), the atomic deformation in a general lattice was expressed as the sum of the lattice and internal deformation. Motivated by Kirkwood's idea of molecule possessing internal degrees of freedom as well as the lattice dynamics description of internal deformation, [Chen and Lee \(2005\)](#) proposed a new approach for linking a local density $\mathbf{a}(\mathbf{x}, \mathbf{y}^\alpha, t)$ to atomic variables:

$$\mathbf{a}(\mathbf{x}, \mathbf{y}^\alpha, t) \equiv \sum_{k=1}^{N_l} \sum_{\xi=1}^{N_a} \mathbf{A}(\mathbf{r}, \mathbf{p}) \delta(\mathbf{R}^k - \mathbf{x}) \tilde{\delta}(\Delta \mathbf{r}^{k\xi} - \mathbf{y}^\alpha), \quad (25)$$

where \mathbf{R}^k are the mass center position of the k th unit cell, $\Delta \mathbf{r}^{k\xi}$ the internal positions of the α th atom relative to the unit cell k , and the first localization function, $\delta(\mathbf{R}^k - \mathbf{x})$, implies that over the entire physical space all the unit cells can be found; then, for each unit cell k , the second localization function, $\tilde{\delta}(\Delta \mathbf{r}^{k\xi} - \mathbf{y}^\alpha)$, identifies $\Delta \mathbf{r}^{k\xi}$ to be \mathbf{y}^α .

This new definition establishes a two-level correspondence between the phase space and physical space description of quantities, and leads to a concurrent two-scale representation of balance equations. Later, [Chen \(2009\)](#) derived Eq. (25) from the local density definition in Kirkwood's formulation, Eq. (5), by considering that there is group of atoms situated in each lattice cell, and proved that the atomic-scale local density defined in Eq. (25) is related to the unit-cell-averaged local density or Kirkwood's molecular-scale local density as

$$\bar{\mathbf{a}}(\mathbf{x}, t) = \sum_{\alpha=1}^{N_a} \mathbf{a}(\mathbf{x}, \mathbf{y}^\alpha, t). \quad (26)$$

[Chen \(2009\)](#) further showed that by including the subscale internal variable \mathbf{y}^α ($\alpha = 1, 2, \dots, N_a$), where N_a is the number of atoms in one molecule or one primitive unit cell, a multiscale representation of the balance equations of an atomistic system can be obtained:

$$\frac{\partial \rho^\alpha}{\partial t} = -\nabla_{\mathbf{x}} \cdot (\rho^\alpha \mathbf{v}) - \nabla_{\mathbf{y}^\alpha} \cdot (\rho^\alpha \Delta \mathbf{v}^\alpha), \quad (27)$$

$$\frac{\partial \rho^\alpha (\mathbf{v} + \Delta \mathbf{v}^\alpha)}{\partial t} = \nabla_{\mathbf{x}} \cdot (\boldsymbol{\tau}^\alpha - \rho^\alpha \mathbf{v} \otimes (\mathbf{v} + \Delta \mathbf{v}^\alpha)) + \nabla_{\mathbf{y}^\alpha} \cdot (\boldsymbol{\tau}^\alpha - \rho^\alpha \Delta \mathbf{v}^\alpha \otimes (\mathbf{v} + \Delta \mathbf{v}^\alpha)) + \mathbf{f}^\alpha, \quad (28)$$

$$\frac{\partial}{\partial t} (\rho^\alpha \mathbf{e}^\alpha) = \nabla_{\mathbf{x}} \cdot (\mathbf{q}^\alpha + \mathbf{t}^\alpha \cdot (\mathbf{v} + \Delta \mathbf{v}^\alpha) - \mathbf{v} \rho^\alpha \mathbf{e}^\alpha) + \nabla_{\mathbf{y}^\alpha} \cdot (\mathbf{j}^\alpha + \boldsymbol{\tau}^\alpha \cdot (\mathbf{v} + \Delta \mathbf{v}^\alpha) - \Delta \mathbf{v}^\alpha \rho^\alpha \mathbf{e}^\alpha) + \mathbf{f}^\alpha \cdot (\mathbf{v} + \Delta \mathbf{v}^\alpha). \quad (29)$$

The decomposition of the atomic displacement into a smooth-varying displacement field and a rapidly-varying internal atomic displacement enables description of an atomic-scale local property to be continuous in \mathbf{x} while discontinuous in α , with \mathbf{y}^α being internal variables. Consequently, fluxes consist of two parts: the homogeneous parts resulted from the distortions of lattice cells (denoted as $\boldsymbol{\tau}^\alpha$ and \mathbf{q}^α , respectively), and the inhomogeneous parts caused by the rearrangement of atoms within each lattice cell (denoted as $\boldsymbol{\tau}^\alpha$ and \mathbf{j}^α , respectively). The formulation, called atomistic field theory (AFT), has thus extended Kirkwood's formulation to include the internal degrees of freedom of a molecule or a unit cell, and is consistent with Born and Huang's crystal dynamics description of general lattice. The formulation possesses a similar framework of rational continuum mechanics in that it views a material as a continuous collection of material points, but departs from classical continuum mechanics description of materials in that embedded within each material point there is a group of discrete atoms.

AFT is derived solely from atomistic model and does not have continuum parameters for static, dynamic, zero or finite temperature systems. Its goal is therefore not to achieve a reduced order of continuum model but rather an atomistic field representation. In the process of the derivation, the fluxes are determined in terms of atomic displacements and local temperature. In AFT, a material can be discretized into finite elements; each contains a collection of primitive unit cells, with

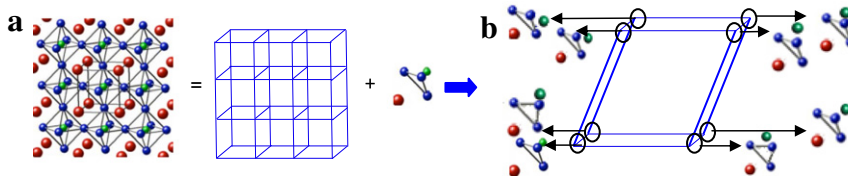


Fig. 5. Procedure to construct a CG-AFT model by FE method: (a) an undeformed atomistic model, (b) the deformed CG-AFT model in which each FE node corresponds to a primitive unit cell.

each FE node corresponding to a primitive unit cell that contains a group of atoms (Fig. 5). Coarse-grained AFT by finite element method can be mapped back to the underlying atomistic model. AFT can also be seamlessly linked to atomistic particle models.

4. Comparisons and analyses

4.1. Theoretical framework

- (1) The governing equations of the reduced-structure based methods, including the united-atom method, super-atom method, MS-CG, etc., is Newton's law for each CG particle, i.e., the same as for MD equations of motion. In a viscous medium like water, these equations of motion are then replaced by Langevin equations, as also the case for constant-temperature MD or DPD. The CG methods in this category thus fall within the theoretical framework of N -body dynamics. The CG equivalent force field and parameters are, therefore, keys to such CG models.
- (2) The equilibrium positions in static zero-temperature QC are obtained by minimizing total potential energy of the CG model, or equivalently, by force equilibration at each nodal point, with the interatomic potential being the sole empirical input. The QC formulations for nonequilibrium systems, however, involve assumptions of phenomenological law or parameters that require extra empirical assumptions or pre-assigned coefficients as that in DPD. Although the local properties are piecewise continuously distributed assuming Cauchy–Born rule or continuous interpolation function, both QC and CGMD are essentially particle models, i.e., they are coarse-grained molecular mechanics or molecular dynamics models.
- (3) Fundamentally different from that in CG particle models, the governing equations in micromorphic theory and AFT are expressed in terms of local densities. The evolution of these local densities in space and time is governed by the conservation equations of mass, linear momentum, and energy. In both micromorphic and AFT, there is an analytical link between the continuum quantities and the atomic variable. The independent field variables to be solved are the local temperature and displacement field. The later is a sum of the homogeneous displacement field and the subscale internal displacements embedded within the material particles. Note that the balance equations in AFT have a similar structure to that in micromorphic theory. The main difference is that micromorphic theory assumes the structure of the material particle to be a continuum, while AFT considers that there is a group of discrete atoms embedded within each material particle (see Fig. 4). AFT can be reduced to micromorphic theory assuming continuous subscale internal deformation (Chen, Lee, & Xiong, 2009). While micromorphic theory is a two-scale continuum-continuum theory, AFT provides a concurrent atomistic-continuum methodology.

4.2. Applicability and limitations

- (1) By eliminating fine details of the molecular structure, reduced-structure methods (Super-Atom, MS-CG, etc.) simultaneously reduce the degrees of freedom and eliminate high frequency-vibration modes of the systems, which in turn increase simulation time steps and reduce the range of interactions. As a consequence, the computational speed can be increased by several orders of magnitude. This is the most efficient CG method. However, the cost of parameterization for the CG effective potential can be intimidating. Currently, reduced-structure models obtained by matching structural or thermodynamic properties of the atomistic model can reproduce structural properties or thermodynamic properties, but not both. MS-CG aims to derive its force field by matching the force field with that of the atomistic model. Its applicability in reproducing both structural and thermodynamic properties is yet to be demonstrated. There are considerable efforts that aim to design CG models to be thermodynamically and structurally consistent with an underlying atomistic simulation model. This consistency has to be achieved before the CG models to be used in a multiscale concurrent simulation framework (Peter & Kremer, 2010).

DPD is also essentially a molecular dynamics simulation technique, but the particles interact through both direct conservative potentials and dissipative Brownian dashpots. The macroscopic behavior of Brownian dynamics simulations is diffusive as the only conserved quantity is the total mass of the system. In DPD, on the other hand, not only the mass but also momentum is conserved. However, the energy is not conserved. Therefore, DPD is applicable to studies of hydrodynamic behavior but not those involving energy transport (Espanol, 1995).

Although it is tempting for the structure-reduction based CG methods to model dynamic processes and phenomena, such an effort, as pointed out by Izvekov and Voth (2005), would be seriously misguided. The simple equivalent structural representation averages out the fine details of the molecular structure and high frequency vibrations of the systems. Using classical MD method with such CG particle models based on an equivalent potential that was fitted to reproduce force or energy or structure may not be able to yield the real microscopic dynamic information (e.g., phonon transport processes, heat conduction). The actual dynamics of the systems as would be seen in a fully resolved atomistic MD simulation is essentially lost through the structural reduction.

- (2) The CG models of QC and CGMD were constructed based on the assumption of atomic-scale homogeneous deformation following Eq. (6). Different from the reduced-structure methods, the atomic deformation is constrained, but the atomic-level structure can be preserved in both QC and CGMD. Therefore, the same interatomic potential can be used for the CG model. The reduction of the interaction sites is proportional to the reduction of the degrees of freedom. Since the site energy is computed through atomic interaction, the computational time step in such CG simulations cannot be increased. Methods in this category are less efficient than reduced-structure approaches and the efficiency is also dependent on the numerical method. From Eq. (6), we see that the Cauchy–Born rule is only valid for Bravais lattices; the static QC is thus only applicable to static analysis of simple lattice. It should be noted that, however, the focus of QC is not on the CG region, but the atomic region or the overall behavior of the combined atomic + CG region. The applicability of QC, therefore, may better be considered from that perspective.

In many aspects, QC is similar to CGMD. They represent an effective technique for construction of a concurrent multiscale particle model. Compared with QC, CGMD was developed to reproduce NVT MD, but its theoretical formulation for materials other than monatomic harmonic crystals becomes very complicated or incomplete, which may have hindered the application of CGMD to more challenging problems than have been reported in the literature. Unlike CGMD, the finite-temperature QC needs additional empirical assumption or parameterization. The advantage of static QC and CGMD is that both the atomistic and the CG regions are governed by the same theoretical framework and in the atomic limit both QC and CGMD can be reduced to the atomistic model.

Applicability of the dynamic QC and CGMD to nonequilibrium processes is unclear since the key step in CGMD is the definition of a Hamiltonian and that of dynamic QC is a Hamiltonian or a Lagrangian. The Hamiltonian plays a central role in Gibbs' equilibrium statistical mechanics. Nevertheless, one new element in the statistical mechanics of nonequilibrium systems is the abandonment of Hamiltonian dynamics, and the key theme of nonequilibrium thermodynamics becomes the time-evolution equations. Like DPD, QC and CGMD conserve mass and momentum, however, the lack of an energy transport equation in their methodologies makes the current versions of QC and CGMD inapplicable to nonequilibrium processes involving energy transport. Also, QC and CGMD both are constructed by constraining atomic deformation and/or motion. As a consequence, they may not be applicable to systems involving large thermally driven fluctuations such as soft matter systems.

- (3) Field theories are the earliest theoretical models that provide CG descriptions of macroscopic properties and material behavior. For numerical simulation, a field theory has to be represented by a discretization on the length scale of interest. The applicability of a field theory thus not only depends on the theoretical formulation but also the numerical implementation. By including subscale micro-motion and micro-deformation, micromorphic theory extends the application of classical field theories to microscopic space and time scales. However, the continuum assumption of the internal structure of the particles give rises to fundamental limitations in the applications to complex crystalline materials, in particular, to crystalline materials that have more than two atoms in the primitive unit cell. Chen et al. (2003c, 2004) have examined the physical foundation of microcontinuum or generalized continuum theories by comparing the predictions of phonon dispersion relations from each of those theories with real experimental measurements, and concluded that while micromorphic theory overlaps a large application region of atomistic dynamics, the applicability of those microcontinuum theories is limited because of the continuum assumption of the microstructure and micromotion of the material particles.

AFT extends Kirkwood's formulation to molecules possessing internal degrees of freedom. Different from Kirkwood's formulation or classical continuum mechanics, the balance equations solve for both the homogeneous deformation of lattice cells and the rearrangement of atoms within the lattice cells, thus extending the application region of a continuum field theory to atomic scale. AFT has been shown to be able to generate the complete set of phonon dispersion relations of BiScO₃ (Chen, 2006), and with the majority of degrees of freedom being reduced, to reproduce the phenomenon of phase transformation (Xiong & Chen, 2009a, 2009b), dislocation nucleation and migration (Xiong, Tucker, McDowell, & Chen, 2010), and also dynamic crack initiation, propagation and branching (Deng, Xiong, & Chen, 2010). The representation of the complete conservation laws makes AFT applicable to dynamic and nonequilibrium processes involving mass, momentum and/or energy transport. Discretization of AFT at primitive unit cell level yields the underlying atomistic model. Assuming homogeneous deformation of unit cells, the majority of degrees of freedom of an atomistic system can be eliminated. It reproduces the full set of phonon modes; however, phonons with wavelength smaller than the size of a finite element will be cut off if linear FE shape function is used. This is a problem facing any continuum as well as structure-reduction or motion-constrain based CG models.

Reducing the representation of an atomistic model can increase the length/time scales of the computational models. Eliminating degrees of freedom, on the other hand, necessarily gives rise to models which reproduce fewer features of the atomistic systems. Main features and applicability of discussed CG models are summarized in Table 1.

Table 1
Summary and comparisons of representative CG atomistic models.

	Super-atom	MS-CG	DPD	Static QC	Dynamic QC	CGMD	Micro-morphic	AFT
Publication year	1975	2005	1992	1996	2010	1998	1964	2005
Route to CG	Structure reduction	Structure reduction	Structure reduction	Cauchy–Born rule	Cauchy–Born rule	Shape function	Field representation	Field representation
Theoretical framework	Particle mechanics	Particle mechanics	Particle mechanics	Particle mechanics	Particle mechanics	Particle mechanics	Continuum mechanics	Continuum mechanics
Governing laws	Newton's 2nd law	Newton's 2nd law	Langevin dynamics	Energy minimization	Langevin Dynamics	Newton's 2nd law	Balance Laws	Balance laws
Information passing	Structure or energy	Atomic Force	Atomic interaction	Atomic interaction	Atomic Interaction	Atomic interaction	Atomic interaction	Atomic interaction
Additional empirical laws	No	No	Yes	No	Yes	No	No	No
Parameter fitting	Yes	Yes	Yes	No	Yes	No	Yes	No
Backmapping to atoms	Yes	Yes	No	Yes	Yes	Yes	No	Yes
Interfacing with atomic model	Not yet	Not yet	No	Yes	Yes	Yes	Not seamlessly	Yes
Energy transport	No	No	No	No	No or assumed	No	Yes	Yes
Phonon branches	Reduced	Reduced	Reduced	N/A	3	3	Up to 12	All
Critical behavior	Phase transition	Not clear	No	Not in CG region	Not in CG region	Not in CG region	Partially	Yes

5. Summary and discussion

In this paper, we have reviewed the theoretical foundations of coarse graining methods and analyzed several representative CG models. CG method promises to enable a direct comparison between predictive simulation and a variety of experimental techniques and to project itself beyond the realm of physical experiments and observations. Current CG methodologies are still not as predictive as all-atom simulations. There is a clear need for more accurate representations of the systems, more rigorous parameterization methodologies, and better validation procedures.

Simulation of soft matter means dealing with large spatial and conformational fluctuations, making equilibration very difficult. The locally relevant length scale can be from a few angstroms to a few nanometers (Peter & Kremer, 2010). From this perspective, the reduced-structure model is currently the most effective method to reproduce structure properties of soft matter. In single crystalline materials, on the other hand, the lattice is homogeneous and continuous, and in the high temperature limit the magnitude of atomic displacement measured is only tenths of angstroms (Dove, 1993). Therefore, the assumption of homogeneous lattice deformation in the particle models as well as the continuous assumption of lattice-level local properties in field representations is appropriate. For static or zero-temperature equilibrium phenomena, the CG particle models is simple and straight, and may be easier to numerically implement compared with continuum field methods. Upon discretization, a field theory may become similar to a particle model for zero-temperature equilibrium problems.

The fundamental difference between the discussed particle models and field representations is the treatment of dynamic and nonequilibrium phenomena. Engineering processes by definition involve nonequilibrium systems. For this reason, there has been a growing need for nonequilibrium models. However, for most nonequilibrium problems there are at present no well-established MD methods. Thus, construction of a nonequilibrium CG particle model through coarse-graining MD or MM models faces fundamental and foundational challenges. A field representation may be more advantageous for modeling of transport phenomena if the dynamic equations of the transport processes, i.e., balance equations, can be fully formulated from the underlying atomistic model. One of the difficulties lies in that well-established numerical methods were developed for single length/time scale models, and hence, for simulation based on multiscale field representation there is a need for new numerical methods.

Acknowledgment

This paper is dedicated to the memory of Professor Eringen. The material is based upon the work supported by the National Science Foundation under Award Numbers CMMI-0758265 (McDowell), CMMI-0824688 and CMMI-0855795, and DARPA under Award Number N66001-10-1-4018 (Chen). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

References

- Alder, B. J., & Alley, W. E. (1984). Generalized hydrodynamics. *Physics Today*, 37(1), 56.
- Boltzmann, L. (1872). Weitere Studien über das Warmegleichgewicht unter Gasmolekülen. *Wiener Berichte*, 66, 275–370.
- Born, M. (1915). *Dynamik der Kristallgitter (Dynamics of Crystal Lattices)*. Leipzig und Berlin: B.G. Teubner.
- Born, M., & Huang, K. (1954). *Dynamical theory of crystal lattices*. Oxford: Clarendon Press.
- Cauchy, A. L. (1828). Sur l'équilibre et le mouvement d'un système de points matériels sollicités par des forces d'attraction ou de répulsion mutuelle. *Exercices de Mathématique*, 3, 227–252, 253–277, 278–287.
- Chen, Y. (2006). Local stress and heat flux in atomistic systems involving three-body forces. *Journal of Chemical Physics*, 124, 054113-1–054113-6.
- Chen, Y. (2009). Reformulation of microscopic balance equations for multiscale materials modeling. *Journal of Chemical Physics*, 130, 134706.
- Chen, Y., & Lee, J. D. (2003a). Connecting molecular dynamics to micromorphic theory. Part I: Instantaneous mechanical variables. *Physica A*, 322, 359–376.
- Chen, Y., & Lee, J. D. (2003b). Connecting molecular dynamics to micromorphic theory. Part II: Balance laws. *Physica A*, 322, 377–392.
- Chen, Y., & Lee, J. D. (2005). Atomistic formulation of a multiscale theory for nano/micro physics. *Philosophical Magazine*, 85, 4095–4126.
- Chen, Y., Lee, J. D., & Eskandarian, A. (2003c). Examining physical foundation of continuum theories from viewpoint of phonon dispersion relations. *International Journal of Engineering Science*, 41, 61–83.
- Chen, Y., Lee, J. D., & Eskandarian, A. (2004). Atomistic viewpoint of the applicability of microcontinuum theories. *International Journal of Solids and Structures*, 41, 2085–2097.
- Chen, Y., Lee, J. D., & Xiong, L. (2009). A generalized continuum theory and its relation to micromorphic theory. *Journal of Engineering Mechanics*, 149–155.
- Cosserat, E. & Cosserat, F. (1909). *Theorie des corps déformable*, Hermann, Paris.
- Das, A., & Andersen, H. C. (2009). The multiscale coarse-graining method. III. A test of pairwise additivity of the coarse-grained potential and of new basis functions for the variational calculation. *Journal of Chemical Physics*, 131, 034102.
- Deng, Q., Xiong, L., & Chen, Y. (2010). Coarse-graining atomistic dynamics of brittle fracture by finite element method. *International Journal of Plasticity*, 26(2010), 1402–1414.
- Dove, M. T. (1993). *Introduction to lattice dynamics*. Cambridge University Press.
- Eringen, A. C. (1964). Simple microfluids. *International Journal of Engineering Science*, 2, 205–217.
- Eringen, A. C. (1965). *Theory of micropolar continua. Developments in mechanics*. New York: Wiley.
- Eringen, A. C. (1970). Balance laws of micromorphic mechanics. *International Journal of Engineering Science*, 8, 819–828.
- Eringen, A. C. (1972). Theory of thermomicrofluids. *Journal of Mathematical Analysis and Applications*, 38, 480–496.
- Eringen, A. C. (1992). Balance laws of micromorphic continua revisited. *International Journal of Engineering Science*, 30, 805–810.
- Eringen, A. C. (1999). *Microcontinuum field theories. I: Foundations and solids*. Springer-Verlag.
- Eringen, A. C., & Kafadar, C. B. (1976). Polar field theories. In A. C. Eringen (Ed.), *Continuum physics* (Vol. 4, pp. 1–73). New York: Academic Press.
- Eringen, A. C., & Suhubi, E. S. (1964). Nonlinear theory of simple micro-elastic solids – I. *International Journal of Engineering Science*, 2, 189–203.
- Espanol, P. (1995). *Physical Review E*, 52, 1734.
- Espanol, P. (2004). Statistical mechanics of coarse-graining. *Lecture Notes in Physics*, 640, 69–115.
- Espanol, P., & Warren, P. (1995). Statistical mechanics of dissipative particle dynamics. *Europhysics Letters*, 30(4), 191–196.
- Favrin, G., Irbäck, A., & Wallin, S. (2002). Folding of a small helical protein using hydrogen bonds and hydrophobicity force. *Proteins*, 47, 99–105.
- Green, S. (1952). Markoff random processes and the statistical mechanics of time-dependent phenomena. *Journal of Chemical Physics*, 20, 1281–1290.
- Hardy, R. J. (1982). Formulas for determining local properties in molecular-dynamics simulations: Shock waves. *Journal of Chemical Physics*, 76(1), 622–628.
- Hone, T., Izvekov, S., & Voth, G. A. (2005). Fast centroid molecular dynamics: A force-matching approach for the predetermination of the effective centroid forces. *Journal of Chemical Physics*, 122, 54105.
- Izvekov, S., Parrinello, M., Burnham, C. J., & Voth, G. A. (2004). Effective force fields for condensed phase systems from ab initio molecular dynamics simulation: A new method for force-matching. *Journal of Chemical Physics*, 120, 10896.
- Izvekov, S., & Voth, G. A. (2005). A multiscale coarse-graining method for biomolecular systems. *Journal of Physical Chemistry B*, 109(7), 2469–2473.
- Jakobsen, A. F. (2005). Constant-pressure and constant-surface tension simulations in dissipative particle dynamics. *Journal of Chemical Physics*, 122, 124901.
- Kirkwood, J. G. (1946). The statistical mechanical theory of transport processes. I: General theory. *Journal of Chemical Physics*, 14, 180.
- Kirkwood, J. G. (1967). In I. Oppenheim (Ed.), *Selected topics in statistical mechanics*. New York: Gordon & Breach.
- Knap, J., & Ortiz, M. (2001). An analysis of the quasicontinuum method. *Journal of the Mechanics and Physics of Solids*, 49, 1899.
- Kubo, R. (1957). Statistical-mechanical theory of irreversible processes. I: General theory and simple applications to magnetic and conduction problems. *Journal of Physical Society of Japan*, 12, 570–586.
- Kulkarni, Y., Knap, J., & Ortiz, M. (2008). A variational approach to coarse graining of equilibrium and non-equilibrium atomistic description at finite temperature. *Journal of the Mechanics and Physics of Solids*, 56, 1417–1449.
- Larini, L., Lu, L., & Voth, Gregory A. (2010). The multiscale coarse-graining method. VI: Implementation of three-body coarse-grained potentials. *Journal of Chemical Physics*, 132, 164107.
- Levitt, M. (1976). A simplified representation of protein conformations for rapid simulation of protein folding. *Journal of Molecular Biology*, 104, 59–107.
- Levitt, M., & Warshel, A. (1975). Computer simulation of protein folding. *Nature*, 694–698.
- Mariani, J., Venturini, G., Hansen, B. L., Knap, J., Ortiz, M., & Campbell, G. H. (2010). Finite-temperature extension of the quasicontinuum method. *Modelling and Simulation in Materials Science and Engineering*, 18, 015003.
- Mindlin, R. D. (1964). Microstructure in linear elasticity. *Archive for Rational Mechanics and Analysis*, 16, 51–78.
- Mindlin, R. D., & Tiersten, H. F. (1962). Effects of couple stresses in linear elasticity. *Archive for Rational Mechanics and Analysis*, 11, 415–448.
- Montroll, E. W., & Green, M. S. (1954). Statistical mechanics of transport and nonequilibrium processes. *Annual Review of Physical Chemistry*, 5, 449–476.
- Mori, H. (1965). Transport, collective motion, and Brownian motion. *Progress of Theoretical Physics*, 33, 423.
- Noid, W. G., Chu, J. W., Ayton, G. S., Krishna, V., Izvekov, S., Voth, G. A., et al. (2008a). The multiscale coarse-graining method. I. A rigorous bridge between atomistic and coarse-grained models. *Journal of Chemical Physics*, 128, 244114.
- Noid, W. G., Liu, P., Wang, Y., Chu, J. W., Ayton, G. S., Izvekov, S., et al. (2008b). The multiscale coarse-graining method. II. Numerical implementation for coarse-grained molecular models. *Journal of Chemical Physics*, 128, 244115.
- Oden, J. T., Belytschko, T., Fish, J., Hughes, T. J. R., Johnson, C., & Yip, S. (2006). Simulation-based engineering science, revolutionizing engineering science through simulation. *Report of the National Science Foundation Blue Ribbon Panel on Simulation-Based Engineering Science*.
- Peter, C., & Kremer, K. (2010). Multiscale simulation of soft matter systems. *Faraday Discuss*, 144, 9–24.
- Reith, D., Meyer, H., & Müller-Plathe, F. (2001). *Macromolecules*, 34, 2235.
- Rudd, R. E. (2004). Concurrent simulation at finite temperature: Coarse-grained molecular dynamics. *Handbook of Materials Modeling Methods*.
- Rudd, R. E., & Broughton, J. Q. (1998). *Physical Review*, B58, R5893.
- Rudd, R. E., & Broughton, J. Q. (2005). Coarse-grained molecular dynamics: Nonlinear finite elements and finite temperature. *Physical Review B*, 72, 144104.
- Tadmor, E. B., Ortiz, M., & Phillips, R. (1996). Quasicontinuum analysis of defects in solids. *Philosophical Magazine A*, 73, 1529–1563.
- Toupin, R. A. (1962). Elastic materials with couple-stresses. *Archive for Rational Mechanics and Analysis*, 11, 385–414.
- Tschöp, W., Kremer, K., Batoulis, J., Bürger, T., & Hahn, O. (1998). Simulation of polymer melts. I: Coarse-graining procedure for polycarbonates. *Acta Polymerica*, 49, 61.
- Xiong, L., & Chen, Y. (2009a). Multiscale modeling and simulation of single-crystal MgO through an atomistic field theory. *International Journal of Solids and Structures*, 46, 1448–1455.

- Xiong, L., & Chen, Y. (2009b). Coarse-grained simulations of single-crystal silicon. *Modelling and Simulation in Materials Science and Engineering*, 17, 035002:1–035002:17.
- Xiong, L., Tucker, G., McDowell, D. L., & Chen, Y. (2010). Coarse-Grained Atomistic Simulation of Dislocations. *Journal of Mechanics and Physics of Solids*, 59, 160–177.
- Zimmerman, J. A., Jones, R. E., & Templeton, J. A. (2010). A material frame approach for evaluating continuum variables in atomistic simulations. *Journal of Computational Physics*, 229, 2364–2389.
- Zwanzig, R. (1911). Memory effects in irreversible thermodynamics. *Physical Review*, 124, 983.