Multiscale Materials Modeling

Lecture 08

Pair Correlation Functions as Multiscale Messengers

Fundamentals of Sustainable Technology

These notes created by David Keffer,
University of Tennessee, Knoxville, 2012.

Outline

Pair Correlation Functions as Multiscale Messengers

I. Introduction
II. Failure of the Local Equilibrium Approximation
III. Enter the Pair Correlation Function
IV. Conclusions

Continuum (Macroscopic) Equations

equation	Name	#	unknowns	parameters
$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v})$$	total mass balance	1	ρ	-
$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A + \sum_{i=1}^{N_R} r_{i,A}$$	component mass balance	n_c	w_A	j_A, $r_{i,A}$
$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla (\mathbf{v}) - \nabla p - \nabla \cdot \boldsymbol{\tau} - \rho \nabla \hat{\Phi}$$	momentum balance	3	$\mathbf{v}$	p, τ, Φ
$$\frac{\partial \rho \left(\frac{1}{2} v^2 + \hat{U} + \hat{\Phi} \right)}{\partial t} = -\nabla \cdot \rho \left(\frac{1}{2} v^2 \mathbf{v} + \hat{U} \mathbf{v} + \hat{\Phi} \mathbf{v} \right) - \nabla \cdot \mathbf{q} - \nabla \cdot p \mathbf{v} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v})$$	energy balance	1	T	U, $\mathbf{q}$

Continuum (Macroscopic) Equations

the parameters are divided into

external fields – Φ, e.g. gravitational
thermodynamic parameters – p and U
transport fluxes – $\mathbf{j}_A$, $k_{i,A}$, τ and $\mathbf{q}$

External fields are typically inputs into the problem, because you know the strength of the external field.

Traditionally, thermodynamic properties come from mechanical or chemical equations of state.

Transport fluxes come from some constitutive equation.

Thermodynamic Properties

Thermodynamic properties come from equations of state

Example: pressure from the multicomponent van der Waals equation of state:

$$p(x_i, V_m, T) = \frac{k_B T}{V_m - b_{mix}} - \frac{a_{mix}}{V_m^2}$$

where the composition dependence of the mixture vdW parameters are given in terms of pure component vdW parameters

$$a_{mix} = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j a_{ij} \qquad b_{mix} = \sum_{j=1}^{N_c} x_j b_j$$

and where the mole fractions and molar volume can be related to mass fraction and density

$$x_i = \frac{w_i / MW_i}{\sum_{j=1}^{n_c} w_j / MW_j} \qquad V_m = \frac{1}{\rho \sum_{j=1}^{n_c} w_j / MW_j}$$

Thermodynamic Properties

Thermodynamic properties come from equations of state

Example: internal energy from the pure component heat capacities. Frequently one may be able to find data for pure component heat capacities, perhaps expressed as an empirical polynomial expansion in temperature

$$C_V(x_i, T) = \sum_{k=0}^{3} a_{i,k} T^k$$

This expression neglects all density dependence in the heat capacity. For an ideal mixture, the total internal energy is then

$$U(x_i, T) = \sum_{i=1}^{n_c} x_i U_i = \sum_{i=1}^{n_c} x_i \left[\int_{T_{ref}}^{T} C_V(x_i, T') dT' + U_{i,ref}(T_{ref}) \right]$$

To the extent that this physical property data is available and that the assumptions in it, such as ideal mixtures and independence of the internal energy on the density (or equivalently the pressure), expressions such as these may be used.

Constitutive Equations

Constitutive equations typically provide information regarding fluxes due to nonequilibrium gradients.

Fick's Law for isothermal, binary systems	$\mathbf{j}_A = -\rho D \nabla w_A$
Newton's Law of viscosity for purely shear flow	$\tau_{xy} = \mu \frac{\partial v_x}{\partial y}$
Fourier's Law	$\mathbf{q} = -k_c \nabla T$
elementary rate laws	$r_{i,A} = \nu_i k_{o,i} \exp\left(-\frac{E_{a,i}}{RT}\right) C_A^{\lvert\nu_A\rvert} C_B^{\lvert\nu_B\rvert}$

The constitutive equations provide functional forms to relate fluxes in terms of unknowns, but also require transport properties, like the diffusivity, viscosity, thermal conductivity, or reaction rate constants and activation barriers.

Issues with this Conventional Approach

There are two main issues associated with applying this conventional approach to the modeling of novel (potentially nanostructured) materials.

First, if the materials are new, there are likely no available thermodynamic and transport properties.

> The continuum equations only provide the framework describing the physics in the system. They say nothing about material properties, which still must be supplied.

Second, these expressions that have been derived for bulk materials may not apply for nanostructured materials.

For example, in any bulk equation of state, the pressure is a function only of the composition, density, and temperature at its local point. This is the local equilibrium approximation. Each point is at thermodynamic equilibrium given the local thermodynamic state of that point. In nanostructured materials, the local equilibrium approximation can fail.

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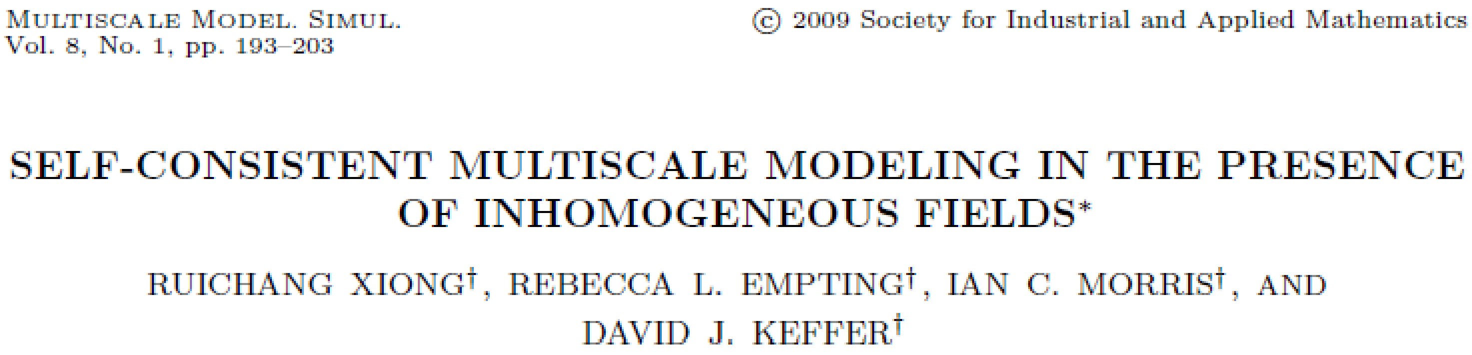
Failure of the Local Equilibrium Assumption



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SELF-CONSISTENT MULTISCALE MODELING IN THE PRESENCE OF INHOMOGENEOUS FIELDS*

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DAVID J. KEFFER†

Show that MD simulations should satisfy “continuum level” descriptions of conservation of mass, momentum and energy, only if the Local Equilibrium approximation is not invoked.

Failure of the Local Equilibrium Assumption

Single component, isothermal system
Mass and momentum balances

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho v), \tag{1a}$$

where ρ is the mass density, $\mathbf{v}$ is the center-of-mass velocity, and t is time, and a momentum balance,

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla(\mathbf{v}) - \nabla p - \nabla \cdot \boldsymbol{\tau} - \rho \nabla \hat{\Phi}, \tag{1b}$$

Simplify system, equations reduce to a relation between the pressure, the density and the external field:

$$\frac{dp}{dz} = -\rho \frac{d\hat{\Phi}}{dz}.$$

Failure of the Local Equilibrium Assumption

External field was a sin function, created an inhomogeneous fluid. Density is a function of position. It is a nanostructured fluid, since the variation in the density occurs over the nanometer length scale.

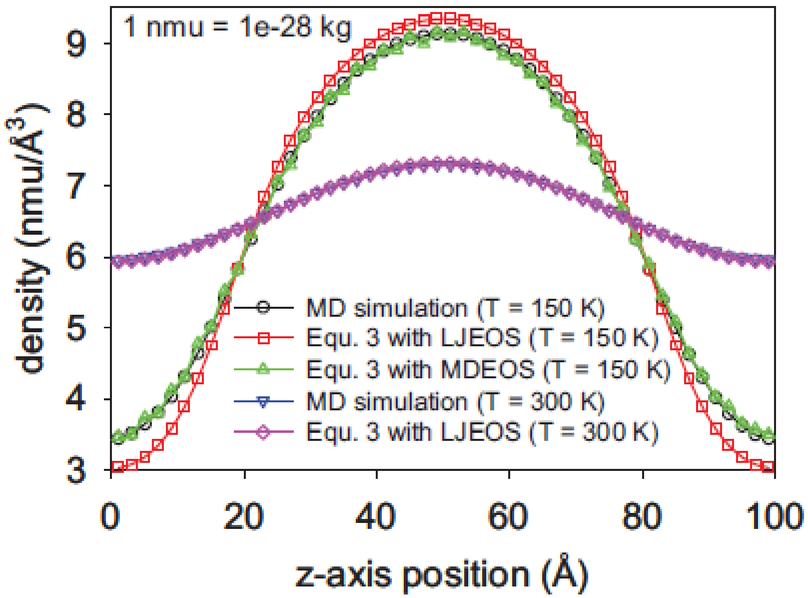

FIG. 4. *Spatial density profiles of the Lennard–Jones fluid from MD simulations using TS3 at 300 K and 150 K, respectively. Also shown are the profiles from the continuum description with a pressure given by the LJEOS and by* (3)*, compared with the profile from the continuum description with MDEOS and* (3).

Failure of the Local Equilibrium Assumption

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The "equation of state" that relates pressure to the density is obtained through direct evaluation in the MD simulation. Any "bulk" equation of state, like the Lennard-Jones equation of state, gives a different pressure, which cannot generate the density distribution observed in the MD simulation.

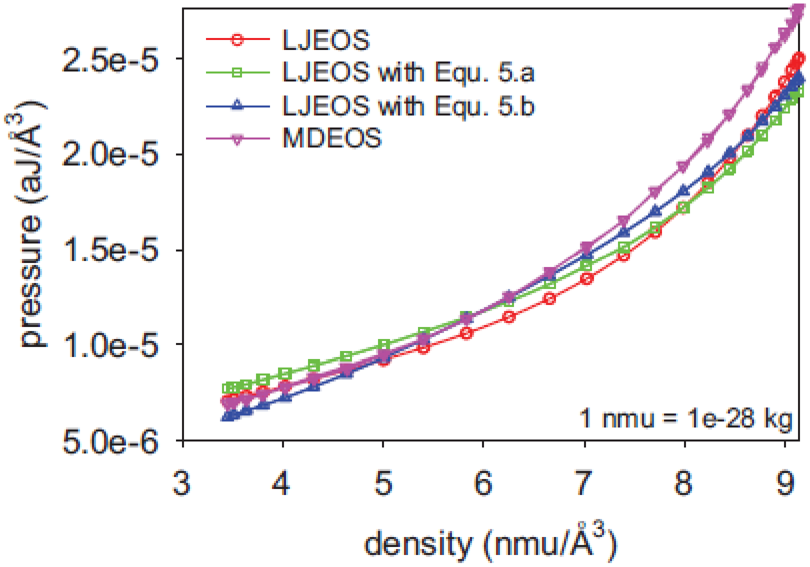

FIG. 6. *Four different equations of state profiles at 150 K: LJEOS, locally averaged LJEOS with (5a), locally averaged LJEOS with (5b), and normal pressure calculated from MDEOS.*

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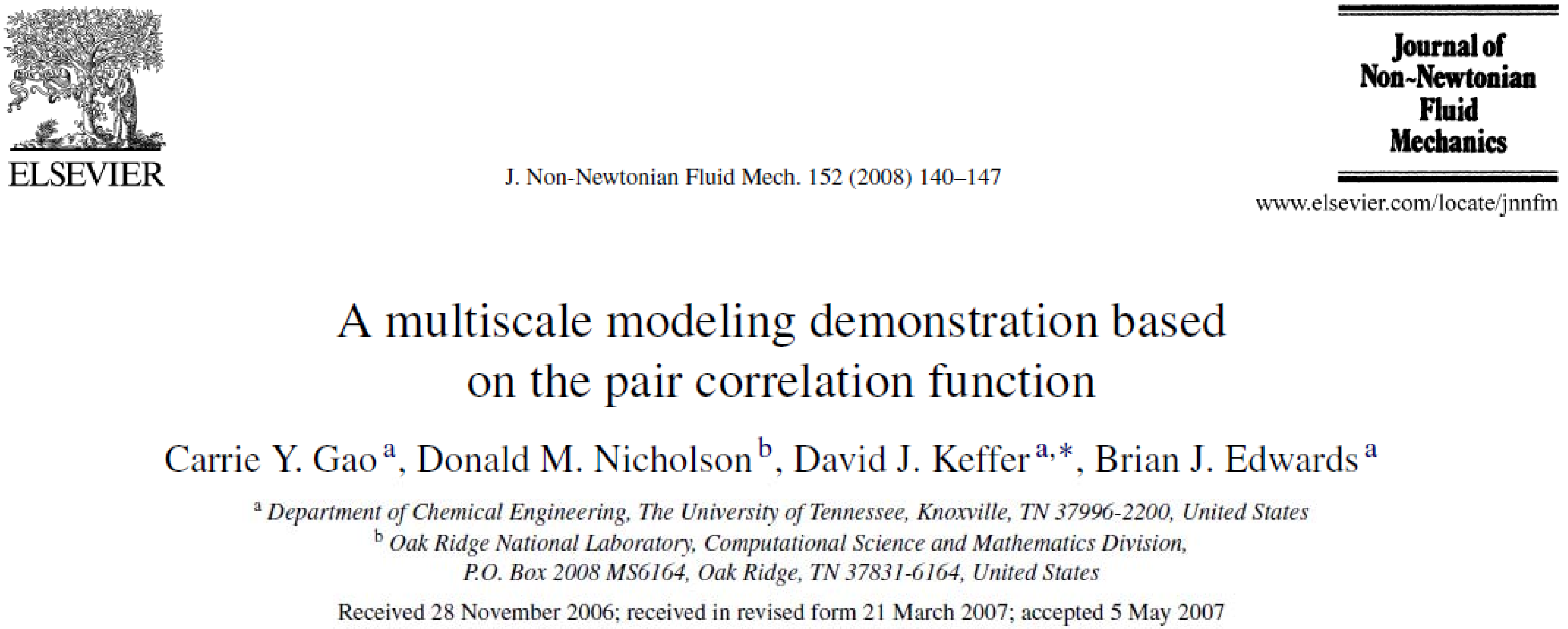
Pair Correlation Function as Messenger



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J. Non-Newtonian Fluid Mech. 152 (2008) 140–147

Journal of
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A multiscale modeling demonstration based on the pair correlation function

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This paper provided an example as to how pair correlation functions could act as messengers between simulations of different time and length scales.

Pair Correlation Function as Messenger

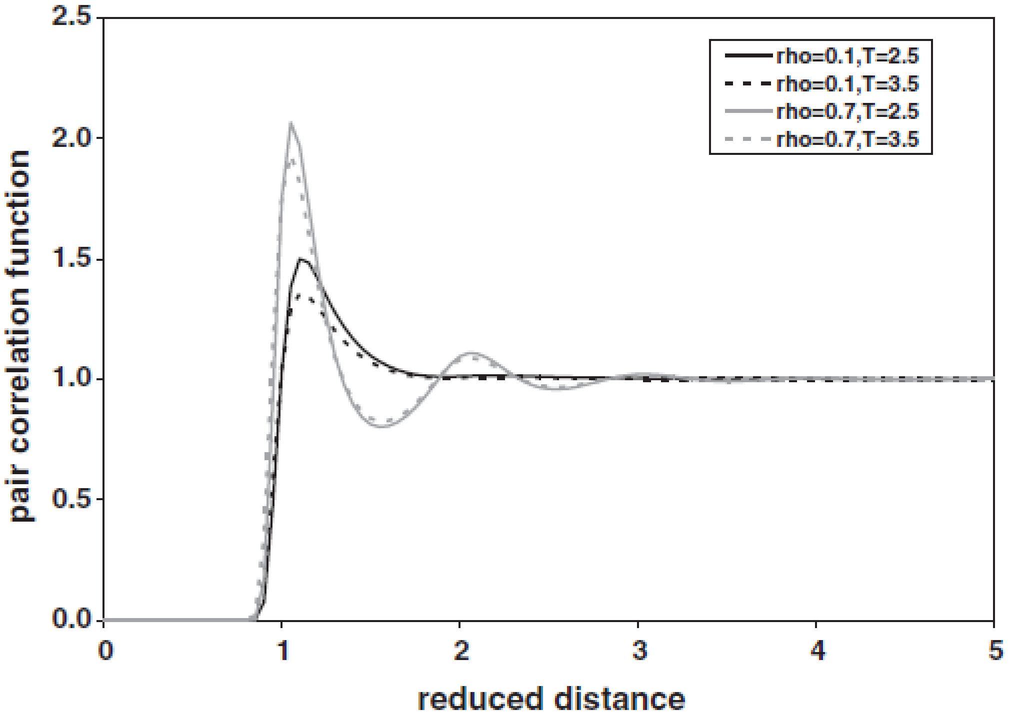


Fig. 1. PCF at the extremes of the density and temperature ranges.

For a simple Lennard-Jones fluid, we have seen that the PCFs of liquid and gases are functions of temperature and density. The x-axis is separation between particles, but let's take a step back.

Pair Correlation Function as Messenger

Pair Correlation functions can really be considered as functions of the positions of two particles in three dimensional space, **r** and **r**'.

In a homogeneous, bulk system, all points, **r**, are the same, so we drop it and, are interested in only the difference in positions, **r** - **r**'. We further assume there is no angular dependence and look at only the magnitude of the separation,
r = **r** - **r**'. That's how we obtain the PCF on the previous slide.

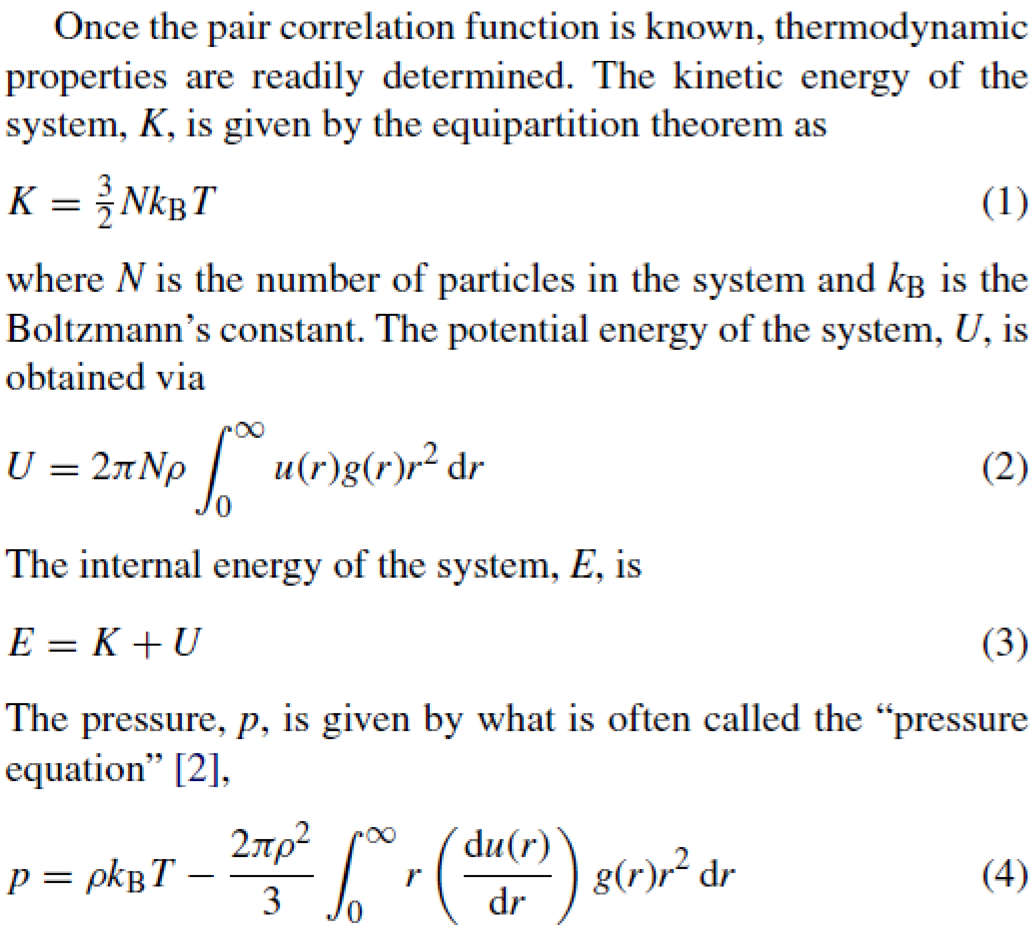
However, if the system is inhomogeneous, then all properties, including the pair correlation function, are functions of global position, x, as well as separation, r.

Thus we can write g(x,r) for an inhomogeneous system and have it reduce to g(r) for a homogeneous system.

Thus we see that the PCF is an instrinsically multiscale function, since x could be macroscopic position (meters) and r is intermolecular separation (Angstroms).

Pair Correlation Function as Messenger

Thermodynamic properties can be obtained from the PCF.



Once the pair correlation function is known, thermodynamic properties are readily determined. The kinetic energy of the system, K, is given by the equipartition theorem as

$$K = \tfrac{3}{2} N k_{\mathrm{B}} T \tag{1}$$

where N is the number of particles in the system and k_{B} is the Boltzmann's constant. The potential energy of the system, U, is obtained via

$$U = 2\pi N \rho \int_0^{\infty} u(r) g(r) r^2 \, \mathrm{d}r \tag{2}$$

The internal energy of the system, E, is

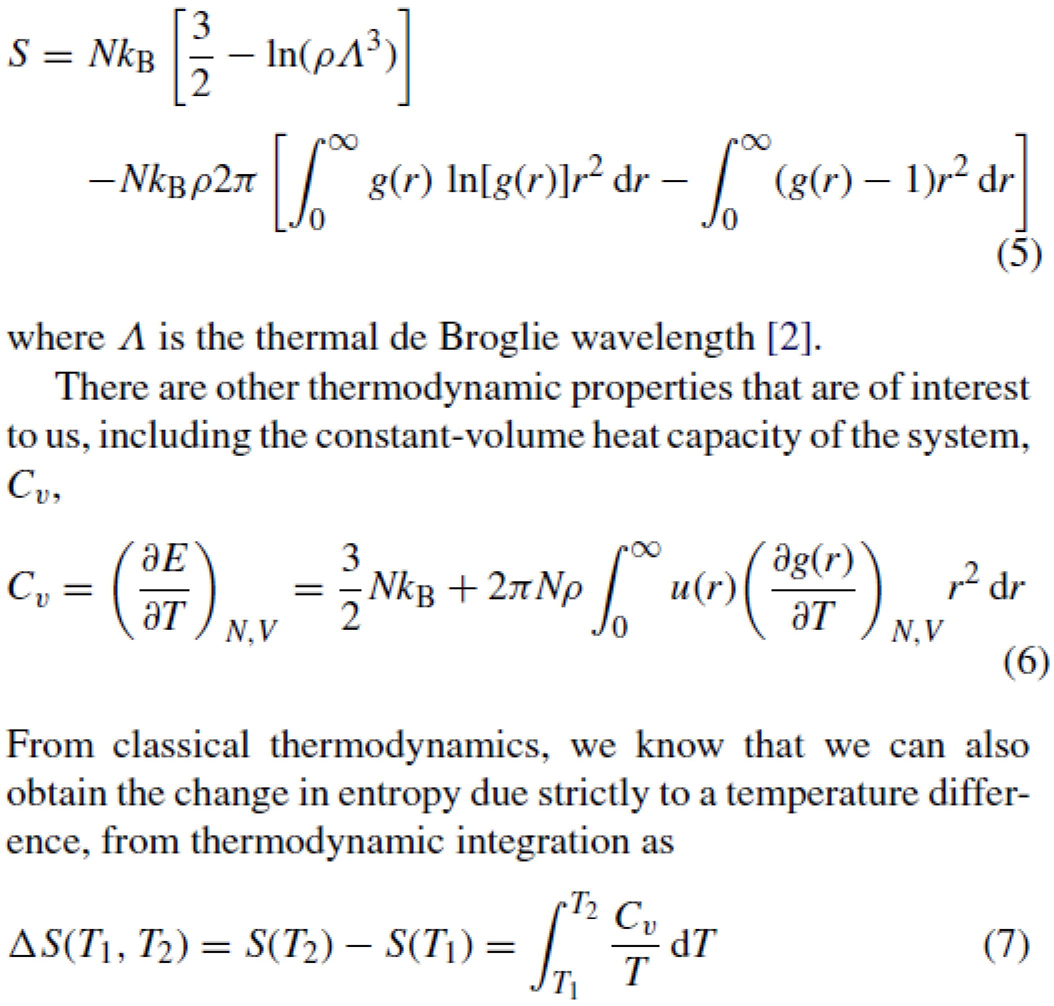
$$E = K + U \tag{3}$$

The pressure, p, is given by what is often called the "pressure equation" [2],

$$p = \rho k_{\mathrm{B}} T - \frac{2\pi\rho^2}{3} \int_0^{\infty} r \left(\frac{\mathrm{d}u(r)}{\mathrm{d}r} \right) g(r) r^2 \, \mathrm{d}r \tag{4}$$

Pair Correlation Function as Messenger

Entropy can be obtained approximately from the PCF.



$$S = Nk_{\mathrm{B}}\left[\frac{3}{2} - \ln(\rho\Lambda^3)\right] - Nk_{\mathrm{B}}\rho 2\pi\left[\int_0^\infty g(r)\ln[g(r)]r^2\,\mathrm{d}r - \int_0^\infty (g(r)-1)r^2\,\mathrm{d}r\right] \tag{5}$$

where Λ is the thermal de Broglie wavelength [2].

There are other thermodynamic properties that are of interest to us, including the constant-volume heat capacity of the system, C_v,

$$C_v = \left(\frac{\partial E}{\partial T}\right)_{N,V} = \frac{3}{2}Nk_{\mathrm{B}} + 2\pi N\rho\int_0^\infty u(r)\left(\frac{\partial g(r)}{\partial T}\right)_{N,V} r^2\,\mathrm{d}r \tag{6}$$

From classical thermodynamics, we know that we can also obtain the change in entropy due strictly to a temperature difference, from thermodynamic integration as

$$\Delta S(T_1, T_2) = S(T_2) - S(T_1) = \int_{T_1}^{T_2}\frac{C_v}{T}\,\mathrm{d}T \tag{7}$$

Pair Correlation Function as Messenger

Entropy can be obtained approximately from the PCF.

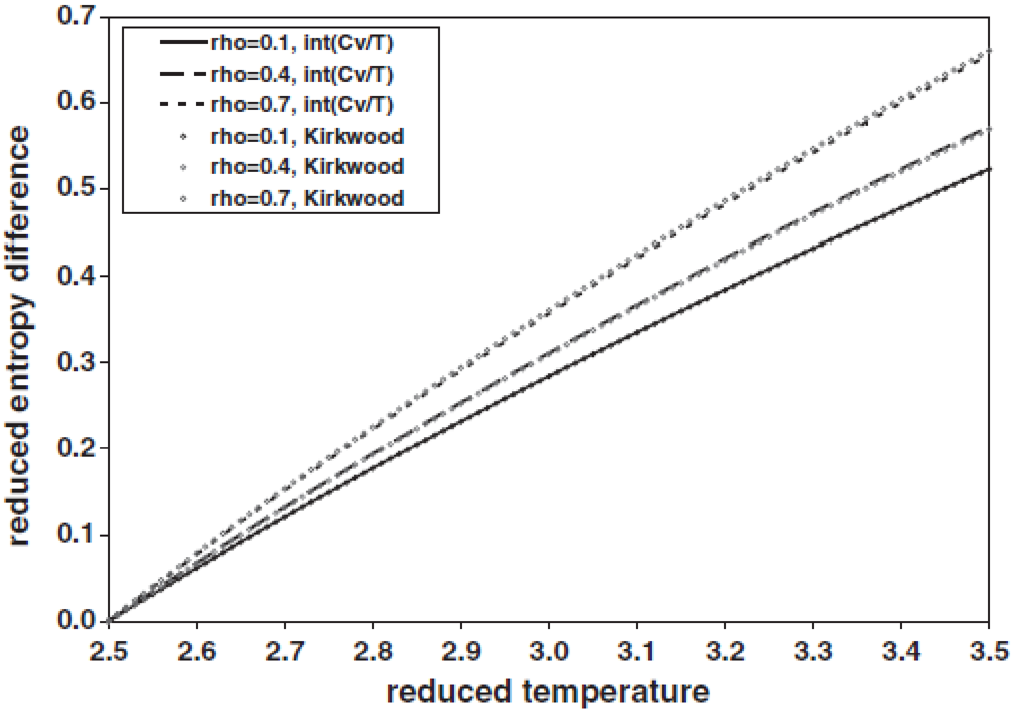
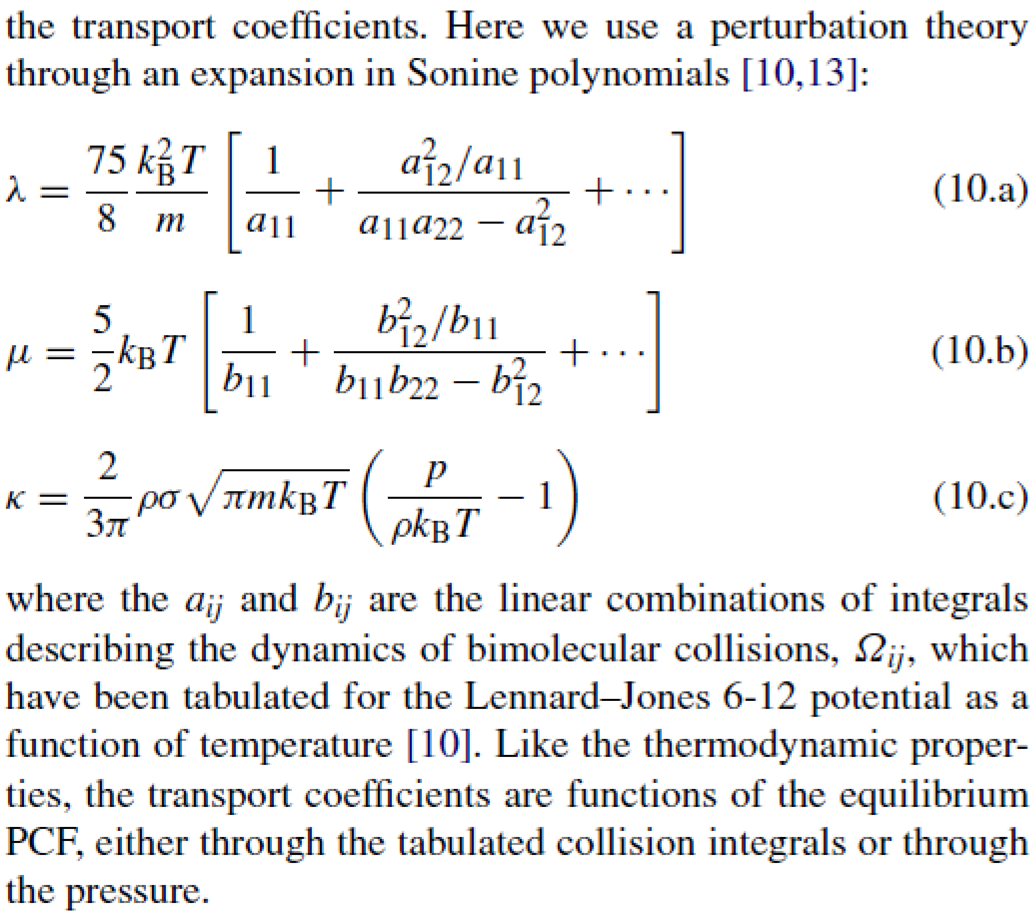


Fig. 2. The entropy difference as calculated from Eq. (5) (Kirkwood superposition approximation) and Eq. (7) (integral of C_v/T).

Pair Correlation Function as Messenger

Transport coefficients can be estimated from collision integrals and the PCF.



the transport coefficients. Here we use a perturbation theory through an expansion in Sonine polynomials [10,13]:

$$\lambda = \frac{75}{8}\frac{k_B^2 T}{m}\left[\frac{1}{a_{11}} + \frac{a_{12}^2/a_{11}}{a_{11}a_{22} - a_{12}^2} + \cdots\right] \qquad (10.a)$$

$$\mu = \frac{5}{2}k_B T\left[\frac{1}{b_{11}} + \frac{b_{12}^2/b_{11}}{b_{11}b_{22} - b_{12}^2} + \cdots\right] \qquad (10.b)$$

$$\kappa = \frac{2}{3\pi}\rho\sigma\sqrt{\pi m k_B T}\left(\frac{p}{\rho k_B T} - 1\right) \qquad (10.c)$$

where the a_{ij} and b_{ij} are the linear combinations of integrals describing the dynamics of bimolecular collisions, Ω_{ij}, which have been tabulated for the Lennard–Jones 6-12 potential as a function of temperature [10]. Like the thermodynamic properties, the transport coefficients are functions of the equilibrium PCF, either through the tabulated collision integrals or through the pressure.

Pair Correlation Function as Messenger

The macroscopic problem has a familiar form:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \tag{18.a}$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla(\mathbf{v}) - \nabla p - \nabla \cdot \boldsymbol{\tau} - \rho \nabla \hat{\Phi} \tag{18.b}$$

$$\rho \frac{\partial((1/2)v^2 + \hat{E} + \hat{\Phi})}{\partial t} = -\rho \mathbf{v} \cdot \nabla \left(\frac{1}{2} v^2 + \hat{E} + \hat{\Phi} \right) - \nabla \cdot \mathbf{q} \\ -\nabla \cdot p\mathbf{v} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \tag{18.c}$$

We can add to this a macroscopic evolution equation for the PCF. As an example, if the PCF is only a function of global density and temperature, then

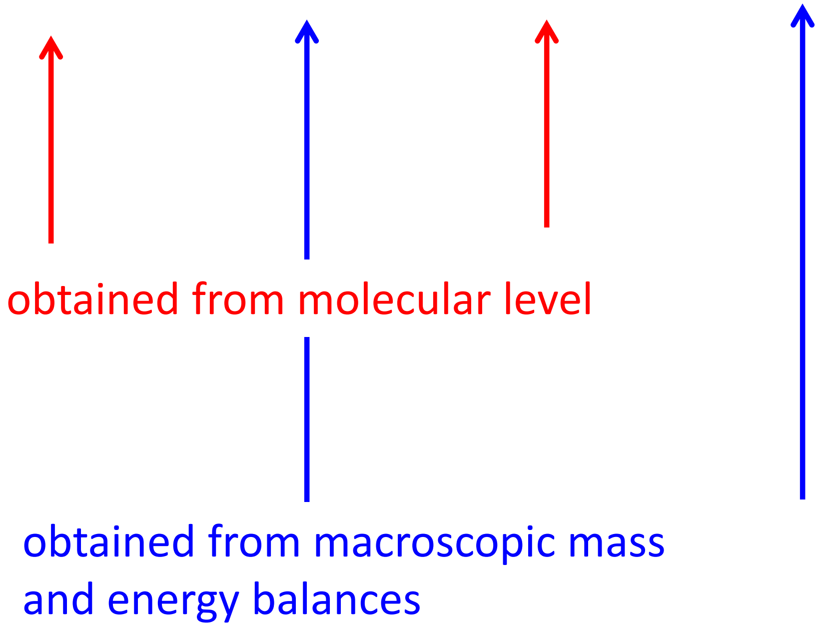
$$g(z,r) = f(z,r,\rho(z),T(z))$$

$$\frac{\partial g(z,r)}{\partial t} = \left(\frac{\partial g(z,r)}{\partial \rho} \right)_z \left(\frac{\partial \rho}{\partial t} \right) + \left(\frac{\partial g(z,r)}{\partial T} \right)_z \left(\frac{\partial T}{\partial t} \right)$$

Pair Correlation Function as Messenger

The evolution of the PCF at any global point z and separation r is given by

$$\frac{\partial g(z,r)}{\partial t} = \left(\frac{\partial g(z,r)}{\partial \rho}\right)_z \left(\frac{\partial \rho}{\partial t}\right) + \left(\frac{\partial g(z,r)}{\partial T}\right)_z \left(\frac{\partial T}{\partial t}\right)$$



obtained from molecular level

obtained from macroscopic mass and energy balances

Knowing the PCF at any point, allows one to determine pressure, internal energy, entropy and transport properties at any point.

Pair Correlation Function as Messenger

Example with a Lennard-Jones fluid.
Solution to the mass, momentum and energy balances:

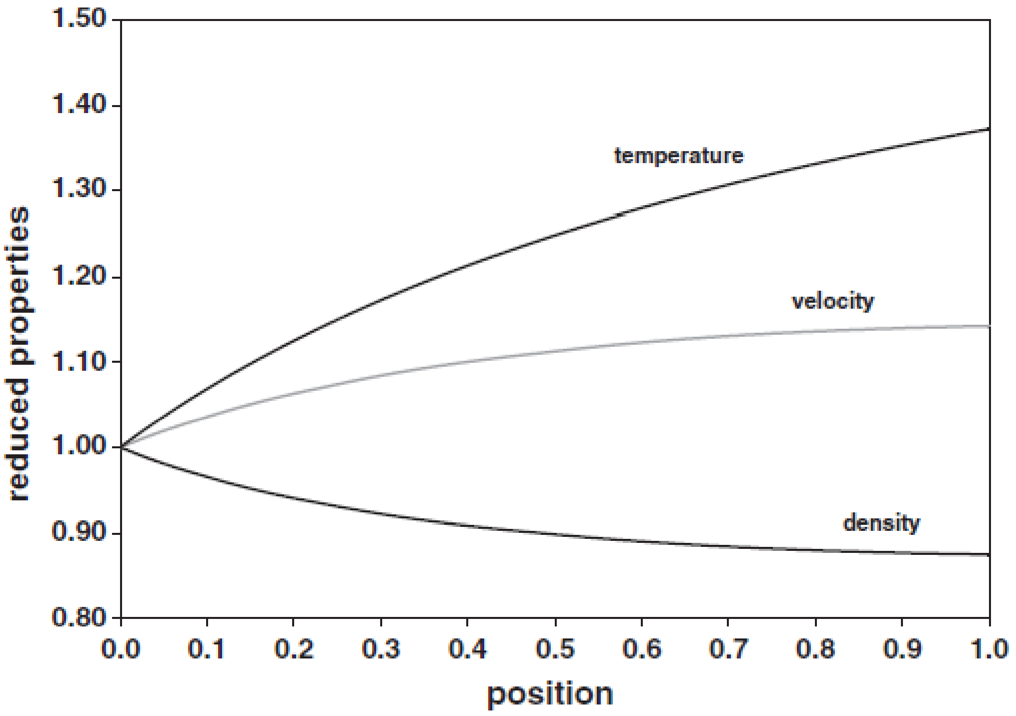


Fig. 3. Density, velocity and temperature profiles from the multiscale simulation.

Pair Correlation Function as Messenger

Example with a Lennard-Jones fluid.
Pieces of the solution of g(z,r) shown at three different values of z and at three different values of r.

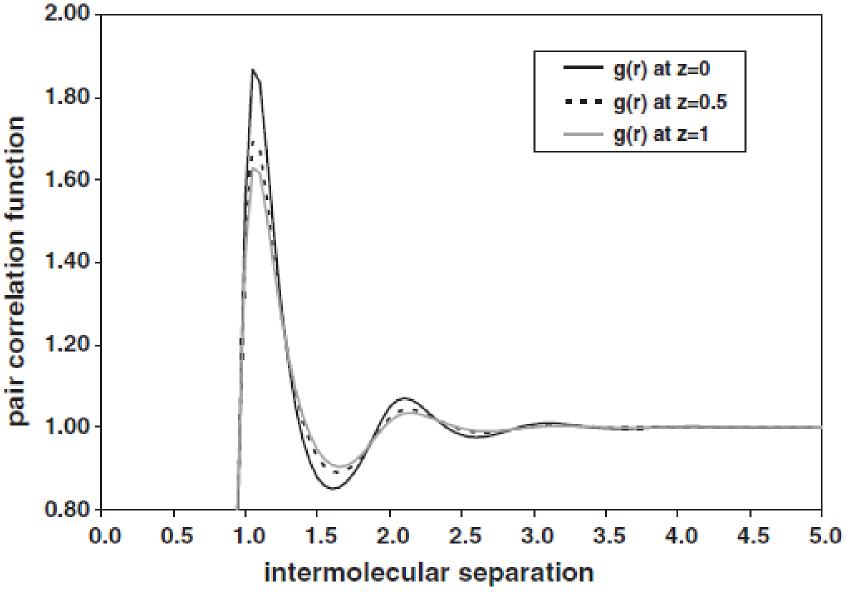


Fig. 5. Pair correlation functions at three different positions in the multiscale simulation.

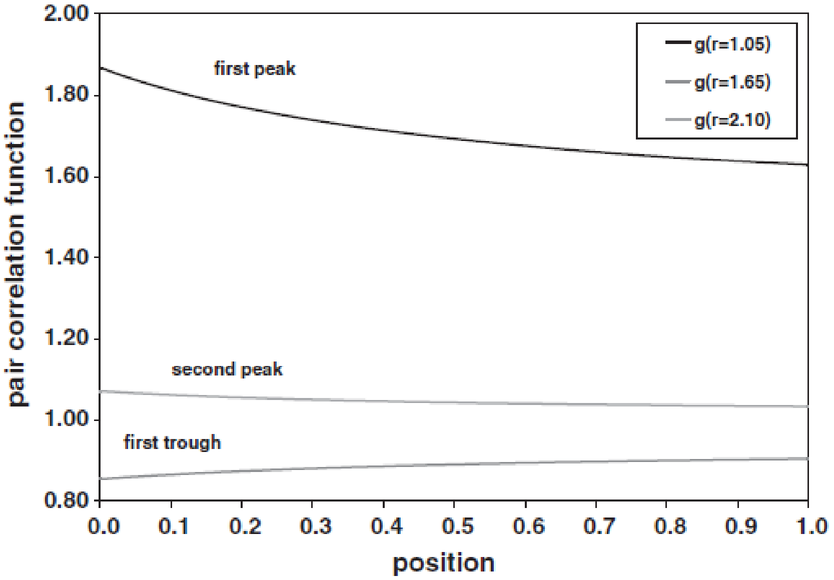


Fig. 6. Pair correlation peak and trough profiles from the multiscale simulation.

Pair Correlation Function as Messenger

Example with a Lennard-Jones fluid.
Properties obtained from g(z,r).

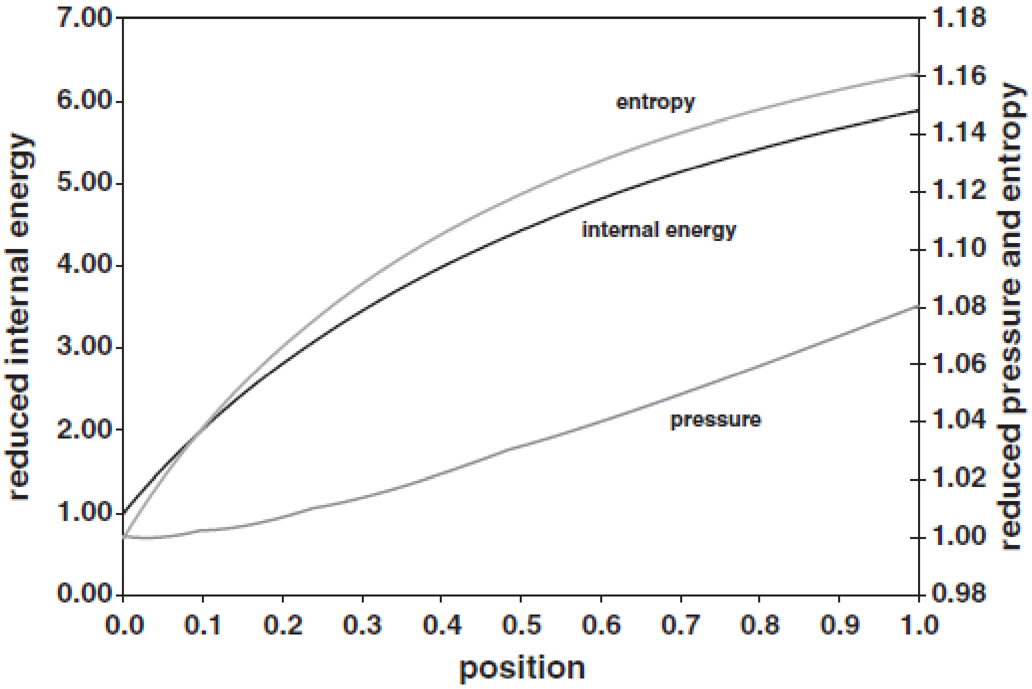


Fig. 4. Internal energy, pressure, and entropy profiles from the multiscale simulation.

Pair Correlation Function as Messenger

This example was possible because we generated a table of pair correlation functions as a function of density and temperature from some molecular-level theory or simulation.

$$\frac{\partial g(z,r)}{\partial t} = \left(\frac{\partial g(z,r)}{\partial \rho}\right)_z \left(\frac{\partial \rho}{\partial t}\right) + \left(\frac{\partial g(z,r)}{\partial T}\right)_z \left(\frac{\partial T}{\partial t}\right)$$

obtained from molecular level

These values can either be generated before hand (linked multiscale modeling) or on an as-needed basis (closely coupled multiscale modeling).

Pair Correlation Function as Messenger

This formulation can overcome the problems with local equilibrium approximation by incorporating dependence of the pair correlation function on the density and/or temperature gradients.

$$\frac{\partial g(z,r)}{\partial t} = \left(\frac{\partial g(z,r)}{\partial \rho}\right)_z \left(\frac{\partial \rho}{\partial t}\right) + \left(\frac{\partial g(z,r)}{\partial T}\right)_z \left(\frac{\partial T}{\partial t}\right)$$

$$+ \left(\frac{\partial g(z,r)}{\partial \nabla\rho}\right)_z \left(\frac{\partial \nabla\rho}{\partial t}\right) + \left(\frac{\partial g(z,r)}{\partial \nabla T}\right)_z \left(\frac{\partial \nabla T}{\partial t}\right)$$

Conclusions

The PCF is an intrinsically multiscale function that has great potential use as a messenger in transferring information between scales.

Continuum equations require many thermodynamic and transport parameters to be evaluated. For novel and/or nanostructured materials, these functions are not commonly available.

The local equilibrium approximation, which allows the use of bulk equations of state, may be invalid in nanostructured materials.

These thermodynamic and transport properties can be obtained from the collision integrals and PCF.

Solving a macroscopic evolution of the PCF simultaneously with the mass, momentum and energy balances allows one to generate all necessary thermodynamic and transport properties during the macroscopic simulation, so long as the dependence of the PCF on these variables is known.