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Microscopic elasticity of complex systems

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1 Introduction

Elasticity has the reputation of being a rather boring and un-physical subject. In fact, dealing with second (stress-strain) or fourth (elastic constants) rank tensor guarantees that the notations are in general rather heavy, and that the underlying physics is not easily captured¹. The elastic stress-strain behavior is, however, a very basic property of all solid materials, and one that is rather easy to obtain experimentally. Hence simulation methods for solid systems (hard or soft) should in general consider the obtention of these elastic properties. The determination of the response of a system to an imposed external stress is an important topic, which was first addressed in the simulation community through the pioneering work of Parrinello and Rahman [2, 3]. While the main issue addressed by the Parrinello-Ray-Rahman method was that of allotropic transformations in crystalline solids, the current interest in nanostructured materials opens a number of new questions. What are the appropriate measures of stress and strains at small scale? Can one scale down the constitutive laws of macroscopic elasticity, and if yes to what scale? Are the elastic constants of nanometric solids identical to those of the bulk? What about the elastic/plastic transition at small scales? Many of these questions are still unanswered, and the object of active studies. In the following, I will describe recent studies that investigate some of these questions. After briefly recalling the appropriate definitions, I will particularly concentrate on the case of amorphous systems, in which some surprises arise due to the non-affine character of deformations at small scales. In the last section, I will describe how the Parrinello-Rahman scheme can be extended to systems in which the particle representation has been replaced by a field representa-

¹ To appreciate the very nice physical content of elementary elasticity theory, the reader is referred to the "Feynman lectures on Physics" or in a more formal style to the first chapters of the Landau and Lifschitz textbook[1]

tion, as is common in polymer or amphiphilic systems that self organize at a mesoscopic scale.

2 Some definitions

A convenient way to study elasticity with a microscopic viewpoint is to think of systems contained in periodic cells with variable shape. This approach, which was initiated by Parrinello and Rahman, is useful from a practical, but also conceptual viewpoint. In a system with periodic boundary conditions, the simulation cell can be defined by three (in general nonorthogonal) independent vectors $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ forming the sides of the parallelepiped cell. The Cartesian coordinates of these vectors can be used to construct a 3×3 matrix \underline{h} defined by $\underline{h} = (\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3)$. The Cartesian coordinates of any point \mathbf{R} in the cell can be expressed as

$$\mathbf{R} = \underline{h}\mathbf{X} \quad (1)$$

where \mathbf{X} is a rescaled vector whose components lie in $[0, 1]$. Integrals on \mathbf{R} can be converted into integrals over \mathbf{X} by using a scaling factor $\det \underline{h}$, which represents the volume of the cell, V . In the case of a particle or monomer number density, for example, one can write

$$\rho(\mathbf{R}) = \rho(\mathbf{X})(\det \underline{h})^{-1} \quad (2)$$

The metric tensor \underline{G} is constructed from \underline{h} as

$$\underline{G} = \underline{h}^T \underline{h} \quad (3)$$

where \underline{h}^T is the transpose of \underline{h} . \underline{G} is used in transforming dot products from the original Cartesian to rescaled coordinates, according to

$$\mathbf{R} \cdot \mathbf{R}' = \mathbf{X} \cdot \underline{G} \cdot \mathbf{X}' = X_\alpha G_{\alpha\beta} X'_\beta \quad (4)$$

where here and in the following summation over repeated indexes is implicit.

Elasticity theory describes the deformation of any configuration from a reference configuration in terms of a strain tensor. This tensor is constructed by relating the vector connecting two points in the deformed configuration to the corresponding displacement of the same points in the reference configuration. If the reference configuration of the simulation box is denoted by \underline{h}_0 , the displacement is $\mathbf{u} = \mathbf{R} - \mathbf{R}_0 = (\underline{h}\underline{h}_0^{-1} - 1)\mathbf{R}_0$, and the strain is given by citeParrinello81, Ray84

$$\underline{\epsilon} = \frac{1}{2} \left[(\underline{h}^T \underline{h}_0)^{-1} \underline{h}^T \underline{h} (\underline{h}_0)^{-1} - \underline{\mathbb{1}} \right] = \frac{1}{2} \left[(\underline{h}^T \underline{h}_0)^{-1} \underline{G} (\underline{h}_0)^{-1} - \underline{\mathbb{1}} \right] \quad (5)$$

where $\underline{\mathbb{1}}$ denotes the unit tensor. It is important to note that this expression, usually known as the *Lagrangian strain tensor* is not limited to small deformations [1]. Usually, the reference configuration \underline{h}_0 will be defined as a state

of the system under zero applied external stress. If one starts with a cubic cell, \underline{h}_0 is the identity matrix and the relation between $\underline{\epsilon}$ and \underline{G} simplifies. The thermodynamic variable conjugate to this strain tensor, in the sense that the elementary work done on the system can be written in the form

$$\delta W = V_0 \text{Tr}(\underline{t} \delta \underline{\epsilon}), \quad (6)$$

is the thermodynamic *tension* tensor \underline{t} [4], also known as Piola-Kirchhoff second stress tensor. $V_0 \equiv \det \underline{h}_0$ denotes the volume of the system in the reference configuration. This thermodynamic tension tensor can be related to the more usual *Cauchy stress tensor* $\underline{\sigma}$ through

$$\underline{\sigma} = \frac{V_0}{V} \underline{h} (\underline{h}_0)^{-1} \underline{t} (\underline{h}_0^T)^{-1} \underline{h}^T \quad (7)$$

The tension is the derivative of the free energy with respect to the strain, which is calculated from the reference configuration. The Cauchy stress, on the other hand, is the derivative of the free energy with respect to an incremental strain taken with respect to the actual configuration. This Cauchy stress tensor is the one that enters momentum conservation and whose expression is given by the usual Irving-Kirkwood formula for pairwise additive potentials (see below). The difference between these two quantities can be understood, qualitatively, from the fact that the strain is not an additive quantity, as can be seen from the existence of the nonlinear term in equation 5. While the Cauchy stress has a mechanical meaning in terms of forces within the sample, the thermodynamic tension is a purely thermodynamic quantity, and does not in general have a simple mechanical interpretation.

Fortunately, in the limit of small deformations which I will concentrate on, the differences between these various expressions of stress tensors can be forgotten. This is not the case, however, for large deformations, where these differences result in a whole variety of stress/strain relations and associated elastic constants. This is especially important when dealing with solids under high pressure, where for example one has to be careful as to which of these elastic constants is used to compute e.g. sound velocities. I will refer the interested reader to the reference publication of Klein and Baron [5] for an in depth discussion of these subtleties.

3 Finite temperature elastic constants: Born and fluctuation terms

The elastic constants for a material made of particles interacting through a pair potential $\phi(r)$ (I'll keep this simplifying assumption in the following) can be determined from simulations using an approach presented by Hoover and coworkers [6]. These authors start from the explicit expression of the free energy in terms of a configuration integral

$$\exp(-\beta F) = V^N \int d\mathbf{X}_1 d\mathbf{X}_2 \dots d\mathbf{X}_N \exp(-\beta H(\{\underline{h}\mathbf{X}_i\})) \quad (8)$$

where $H(\{\mathbf{R}_i\}) = \sum_{ij} \phi(\mathbf{R}_i - \mathbf{R}_j)$ is the total interaction energy.

The derivative with respect to strain is taken using

$$dF = \text{Tr}\left(\frac{\partial F}{\partial \underline{G}} d\underline{G}\right) = 2\text{Tr}\left(\underline{h}_0 \frac{\partial F}{\partial \underline{G}} \underline{h}^T d\underline{\epsilon}\right) \quad (9)$$

which gives for the thermodynamic tension matrix

$$V_0 t_{\alpha\beta} = Nk_B T \underline{h}_{0,\alpha\gamma} \underline{G}_{\gamma\delta}^{-1} \underline{h}^T_{0,\delta\beta} + \underline{h}_{0,\alpha\gamma} \left\langle \sum_{ij} X_{ij,\gamma} X_{ij,\delta} \frac{\phi'(R_{ij})}{R_{ij}} \right\rangle \underline{h}_{0,\delta\beta} = Nk_B T \underline{h}_{0,\alpha\gamma} \underline{G}_{\gamma\delta}^{-1} \underline{h}^T_{0,\delta\beta} + \langle \hat{\underline{T}}_{\alpha\beta} \rangle \quad (10)$$

where $X_{ij} = X_i - X_j$, \sum_{ij} is the summation over all distinct pairs of particles, and the pair potential ϕ is assumed to depend only on the particle separation R_{ij} . The brackets $\langle \rangle$ denote a thermal average. This obviously reduces to the usual Kirkwood formula for small deformations ($\underline{h}_0 = \underline{h}$). Note that the first term arises here from the volume factor V^N in the configuration integral, but could also be obtained by introducing the momenta and the kinetic energy contribution in the partition function. The last term defines the potential energy contribution to the microscopic stress tensor, denoted by $\hat{\underline{T}}$. Carrying out one more derivation with respect to strain, one obtains the elastic constants in the limit of zero strain (more general expressions for arbitrary strain can be found in refs [7, 8]):

$$C_{\alpha\beta\gamma\delta} = \frac{\partial t_{\alpha\beta}}{\partial \epsilon_{\gamma\delta}} = 2Nk_B T (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) - \frac{V_0}{k_B T} \left[\langle \hat{\underline{T}}_{\alpha\beta} \hat{\underline{T}}_{\gamma\delta} \rangle - \langle \hat{\underline{T}}_{\alpha\beta} \rangle \langle \hat{\underline{T}}_{\gamma\delta} \rangle \right] + C_{\alpha\beta\gamma\delta}^{Born} \quad (11)$$

Where the last (Born) term is written in terms of potential energy functions

$$C_{\alpha\beta\gamma\delta}^{Born} = \frac{1}{V_0} \left\langle \sum_{ij} R_{ij,\alpha} R_{ij,\beta} R_{ij,\gamma} R_{ij,\delta} \left(\frac{\phi''(R_{ij})}{R_{ij}^2} - \frac{\phi'(R_{ij})}{R_{ij}^3} \right) \right\rangle \quad (12)$$

with $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$. The term in square brackets in 11 is called the fluctuation term, and is generally expected to be a correction to the main Born term at finite temperature. We will see below that this term, even in the low temperature limit, remains an essential contribution to the elastic properties of disordered systems. Formulae that generalize the equations above to local stresses and elastic constants can be found in references [9, 10].

Note that a different approach must be used for hard core potentials. In that case, one possibility is to study strain fluctuations either in a cell of variable cell [11], or to directly study the stress-strain relation in a deformed cell [12].

4 Amorphous systems at zero temperature: nonaffine deformation

The simulation of amorphous systems at low temperatures is interesting from the point of view of the physics of glasses, but also because these models can serve as very elementary examples of "athermal" systems such as granular piles or foams. The elastic/plastic response of such complex systems is not well understood, and is currently the subject of many experimental studies [13, 14, 15, 16].

A naive approach to the calculation of elastic properties in such systems would consist in taking the second derivative of the potential energy $H = \sum_{i<j} \phi(R_{ij})$ with respect to strain. Such an approach is easily shown to yield elastic constants that correspond to the Born expression, without the thermal average brackets. Although such an approach seems natural - the "fluctuation" term could be ignored at zero temperature -, it proves in fact completely incorrect for disordered systems, or even for crystals with a complex unit cell.

The essential point is that the derivatives have to be taken not at constant X , but rather keeping the force on each atom equal to zero in the deformed configuration. In other words, one has to allow for relaxation of the deformed configuration before computing the energy and stresses. It was shown by Lutsko [7] (see also the recent work by Lematre and Maloney, ref[8]) that this relaxation gives a contribution to elasticity which is identical to the zero temperature limit of the fluctuation term. The corresponding proof can be briefly summarized as follows.

The elastic constant is written as

$$C_{\alpha\beta\gamma\delta} = \left. \frac{\partial t_{\alpha\beta}}{\partial \epsilon_{\gamma\delta}} \right|_{\mathbf{F}_i=0} \quad (13)$$

$F_i = 0$ indicates the constraint that forces on the particles must remain zero during the deformation. The variables in the problem are the reduced coordinates, \mathbf{X}_i , and the strain $\underline{\epsilon}$. The force \mathbf{F}_i is a function of these variables, so that the constrained derivative above can be written as (for simplicity, we drop in this formula and the following the Greek indexes for Cartesian coordinates):

$$\underline{C} = \left. \frac{\partial t}{\partial \epsilon} \right|_{\mathbf{X}_i} - \frac{\partial t}{\partial \mathbf{X}_i} \left(\frac{\partial \mathbf{F}_j}{\partial \mathbf{X}_i} \right)^{-1} \frac{\partial \mathbf{F}_j}{\partial \epsilon} \quad (14)$$

where terms such as $\left(\frac{\partial \mathbf{F}_j}{\partial \mathbf{X}_i} \right)$ have to be understood in a matrix sense. In fact, $D_{ij} = \left(\frac{\partial \mathbf{F}_j}{\partial \mathbf{X}_i} \right)$ is nothing but the *dynamical matrix* of second derivatives of the potential energy with respect to atomic positions. Finally, using the definition of the force \mathbf{F}_j and of the tension \underline{t} as derivatives of the potential energy, equation 14 can be rewritten in the more symmetric form

$$\underline{C} = \underline{C}^{Born} - \frac{\partial t}{\partial X_i} \left(\frac{\partial F_j}{\partial X_i} \right)^{-1} \frac{\partial t}{\partial X_j} \quad (15)$$

The direct evaluation of the second term in this equation is not straightforward, hence the actual procedure to obtain the zero temperature elastic constants generally consists in carrying out explicitly an affine deformation of all coordinates, then letting the atomic positions relax (using e.g. conjugate gradient minimization)[27] to the nearest energy minimum. Equation 15 however can be used to show that the resulting elastic constants are identical to those obtain at a finite, low temperature using equation 11. The proof goes simply by expanding both the stress and energy in terms of the atomic displacements in the unstrained reference configuration

$$H = H_0 + \frac{1}{2} D_{ij} \delta X_i \delta X_j \quad ; \quad t = t_0 + \frac{\partial t}{\partial X_i} \delta X_i \quad (16)$$

Performing the resulting gaussian integrals, it is seen that the "fluctuation" term in 11 and the "relaxation" term in 15 are identical in the limit of zero temperature.

5 Numerical results

We now address the importance, qualitative and quantitative, of this "relaxation-fluctuation" contribution. Quantitatively, the importance of this contribution can be estimated from figure 1. In this figure, the Lamé coefficients of a three dimensional, amorphous, Lennard-Jones system (see ref. [17]) at zero temperature are computed using the Born approximation and the exact formula, equation 11. It is seen that the relaxation term can account for as much as 50% of the absolute value of elastic constants. Although this fraction may obviously be system dependent, the situation is very different compared to simple crystals (with one atom per unit cell, e.g. FCC in the Lennard-Jones system) in which the elastic constants are exactly given by the Born term (see e.g. [18] for a comparison between amorphous systems and simple crystal structures). The relaxation contribution tends to lower the shear modulus μ , and to increase the coefficient λ . Remarkably, the bulk modulus $K = \lambda + 2\mu/d \approx 57$ ($d = 3$ is the dimensionality of space) would be correctly predicted by the Born calculation.

As discussed above, the Born formulae would be exact at zero temperature if the global deformation was equivalent to an affine deformation of atomic coordinates at all scales, i.e. a mere rescaling of \underline{h} at fixed values of $\{X_i\}$. The failure of the Born calculation can therefore be traced back to the existence of a *non-affine deformation field*, which stores part of the elastic deformation energy. This field is defined by subtraction from the actual displacement of the atoms (after relaxation) the displacement that would be obtained in the affine hypothesis. The existence of this non-affine deformation field was pointed out in several recent publications [9, 19, 20, 21]. In [21, 22], it was in particular shown that this non-affine contribution is correlated over large distances, and is organized in vortex like structures (i.e. is mostly rotational

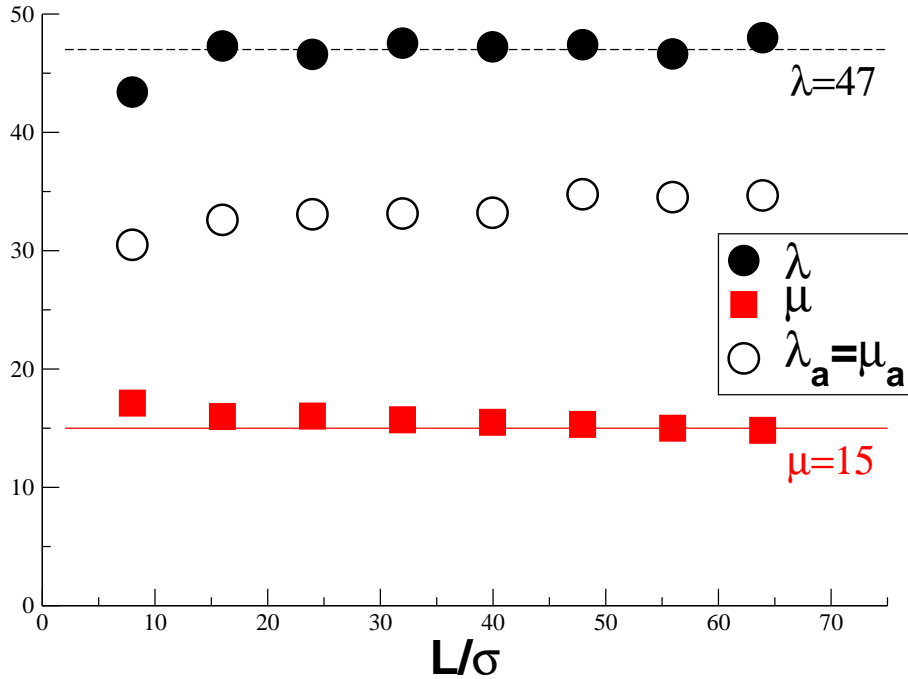


Fig. 1. Lamé coefficients λ (spheres) and μ (squares) *vs.* system size L , for a simple polydisperse Lennard-Jones "glass". Full symbols correspond to a direct measurement using Hooke's law with relaxation, open symbols correspond to the Born approximation). The effect of system size is weak. For large boxes we get $\mu \approx 15$ and $\lambda \approx 47$.

in nature). These properties are illustrated in figures 2 and 3, for a simple Lennard-Jones two dimensional system.

A slightly different, more local and general, definition of the nonaffine displacement field (or "displacement fluctuation") was proposed in ref. [9]. In this reference, the nonaffine field is defined by subtracting from the actual displacement a local displacement field built that is obtained using a coarse-graining procedure. This allows in principle to deal with situations in which the displacement field has a complex structure. In the case of simple shear considered here, our definition should be sufficient. Reference [9] also demonstrates that, even when the displacements are not locally affine, there exists a local linear relation between the stress and strain fields, at sufficiently large scales (resolution). These fields are evaluated at the same position with a chosen resolution. The derivation does assume that the displacement fluctuations are uncorrelated over sufficiently large scales, i.e. it will be valid at scales larger than the one discussed here.

A quick study of a simple one dimensional model is useful to understand the importance of the nonaffine displacement field. Let us consider a chain

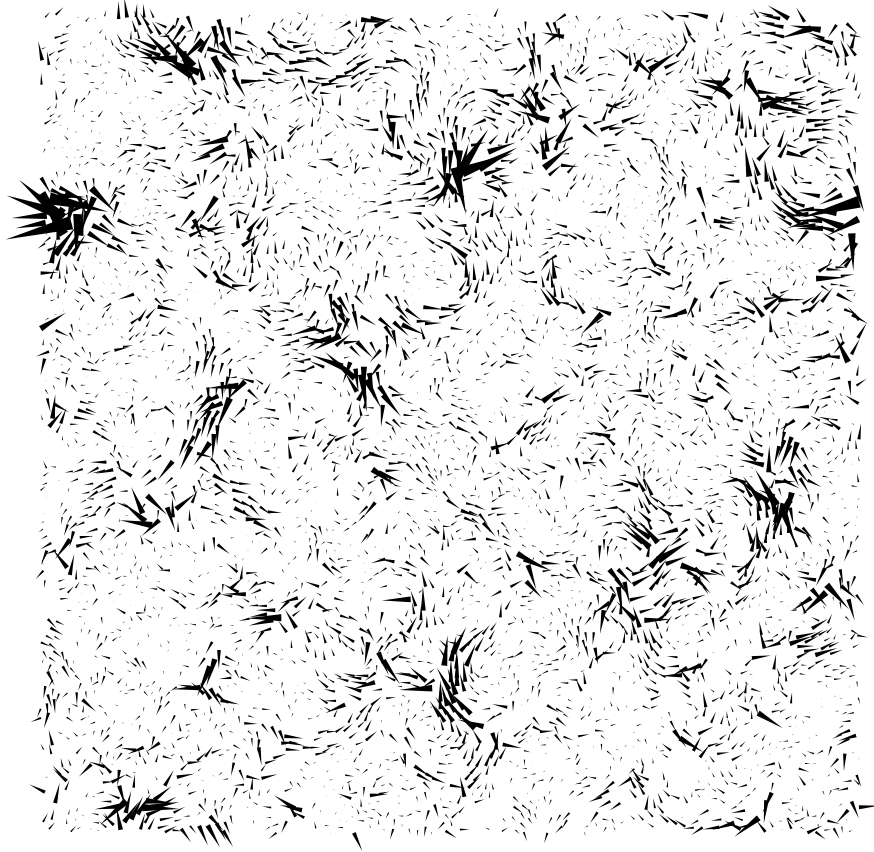


Fig. 2. Snapshot of the nonaffine displacement field in a 2d Lennard-Jones amorphous system undergoing uniaxial extension. Note the large scale, vortex like structures. The sample contains about 20 000 particles.

of N atoms, connected by springs k_i , submitted to a force F . The extension of spring i (linking site i to $i + 1$) is $\delta_i = F/k_i$. One can therefore write the displacement of atom p

$$u_p = F \times \sum_{i=1}^p k_i^{-1} \quad (17)$$

The affine displacement is just $u_p^{aff} = (p/N) \times F \times \sum_{i=1}^N k_i^{-1} = pF \langle k^{-1} \rangle$, where the $\langle \rangle$ refer to an average over the distribution of elastic constants and the large N limit has been taken to compute the affine displacement. As a result we have for the nonaffine displacement of atom p

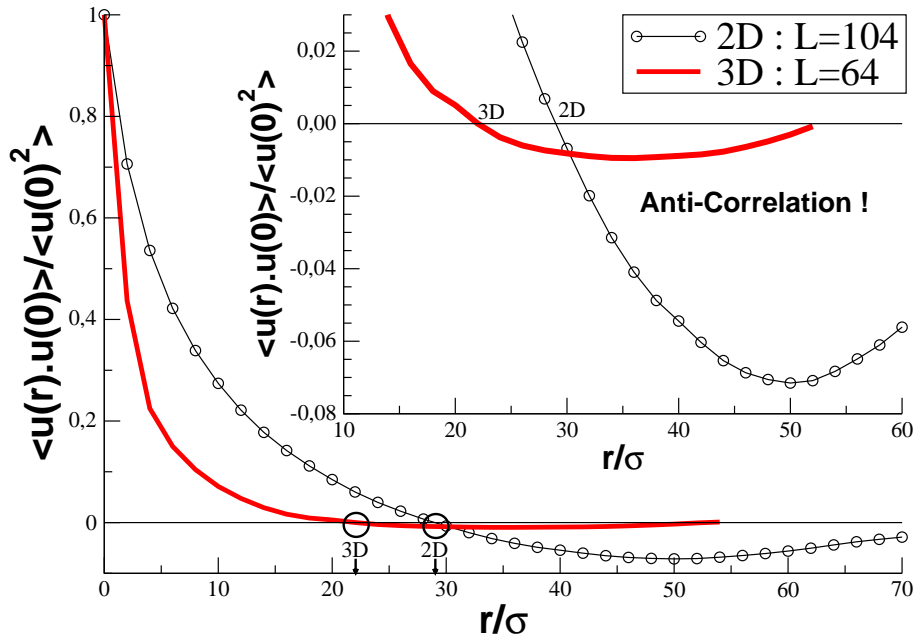


Fig. 3. Correlation function $C(r) = \langle \mathbf{u}^{NA}(\mathbf{r}) \cdot \mathbf{u}^{NA}(\mathbf{r}) \rangle$ of the nonaffine displacement field $\mathbf{u}^{NA}(\mathbf{r})$ in an amorphous sample undergoing a simple uniaxial extension. Both the 2d and 3d case show correlations that extend over scales of typically 20-30 particle sizes. A negative tail can be associated with "vortex like" structures that reflect the essentially rotational character of the non affine field.

$$u_p^{NA} = u_p - u_p^{aff} = F \times \sum_{i=1}^P (k_i^{-1} - \langle k^{-1} \rangle) \quad (18)$$

which shows that in this simple 1d situation the mean squared value $\langle (u_p^{NA})^2 \rangle \propto p \langle (\delta k^{-1})^2 \rangle$ is increasing linearly with p , and proportional to the variance of $1/k_i$ (see also the discussion by DiDonna and Lubensky, cond-mat/0506456).

The existence and nature of the length scale over which the non affine field is correlated is still a matter of debate². Clearly, the correlation length ξ is a lower limit for the applicability of continuous elasticity theory. This limit

² In a recent preprint (cond-mat/0506456, "Nonaffine correlations in Random Elastic Media"), DiDonna and Lubensky argued that the nonaffine field has logarithmic (in 2d) or $1/r$ (in 3d) correlations, and hence no characteristic length scale. That such singular behaviour is possible is already illustrated in the simple 1d example above. Such a behaviour, however, is not evident in our numerical results. Their calculation, based on the fact that elastic propagator have $1/k^2$ behaviour in Fourier space, is perturbative in the disorder strength, and it could be that we are investigating a "strong disorder" limit. In any case, further investigations are needed to assess the actual existence of such long range correlations

manifests itself in several different ways. If one considers the vibrations of a system of size L , these vibrations will be properly described by the classical elasticity theory only if the corresponding wavelength is larger than ξ . If one considers the response to a point force, this response will be correctly described by the continuum theory only beyond the length scale ξ . More precisely, it was found that the *average* response is described by continuum theory essentially down to atomic size, but that the *fluctuations* (from sample to sample) around this average are dominant below ξ [22].

Finally, it is very likely that the existence of this length scale is related to a prominent feature of many disordered systems, the so called 'boson peak'. This feature actually corresponds to an excess (as compared to the standard Debye prediction, $g(\omega) \propto \omega^{d-1}$ in d dimensions) in the vibrational density of states $g(\omega)$ of many amorphous systems. This excess shows up as a peak in a plot of $g(\omega)/\omega^{d-1}$ vs ω , that usually lies in the THz range. In terms of length scales, we found that this peak typically corresponds to wavelengths of the order of magnitude of ξ (see figure 4). A simple description [23] is therefore to assume that waves around this wavelength are scattered by inhomogeneities, and see their frequencies shifted to higher values. Pressure studies show that the boson peak is shifted to higher frequencies under pressure, consistent with a shift to smaller values for ξ obtained in simulations. Another very interesting evidence for the existence of mesoscale inhomogeneities was recently provided by Masciovecchio and coworkers [24], by studying Brillouin spectra in the ultraviolet range. The width of the Brillouin peak shows a marked change for wavelength between 50 and 80 nm, indicative of scattering by elastic inhomogeneities.

A very interesting question is whether this characteristic correlation length for elastic inhomogeneities, which can reach rather large values compared to atomic sizes, is somehow associated with a 'critical' phenomenon. An idea that was recently suggested by Nagel and co-workers [25] is that this correlation length should diverge at the so-called 'jamming' transition in purely athermal systems. The jamming density is defined, in a system with purely repulsive interactions at zero temperature, by the density at which the system will start to exhibit mechanical rigidity. Below the jamming density ϕ_c , an infinitesimal temperature results in diffusion, while systems above ϕ_c remain in a frozen state on macroscopic time scales. Based on general arguments concerning isostaticity of the packing at ϕ_c , Nagel and coworkers [25] suggested the existence of a correlation length associated with soft modes, that diverges at the transition. Although the arguments are in principle valid only for contact type interactions, it would be quite interesting to follow the evolution of ξ for a system *with attractive interactions, but under tension*, expecting perhaps a divergence close to the rupture threshold.

Finally, let us mention that a different way of studying local elastic properties was proposed by de Pablo and coworkers through the study of local elastic moduli, which can be defined by using the definition 11 to a small, finite box [10]. Depending on the scale at which they are measured, these

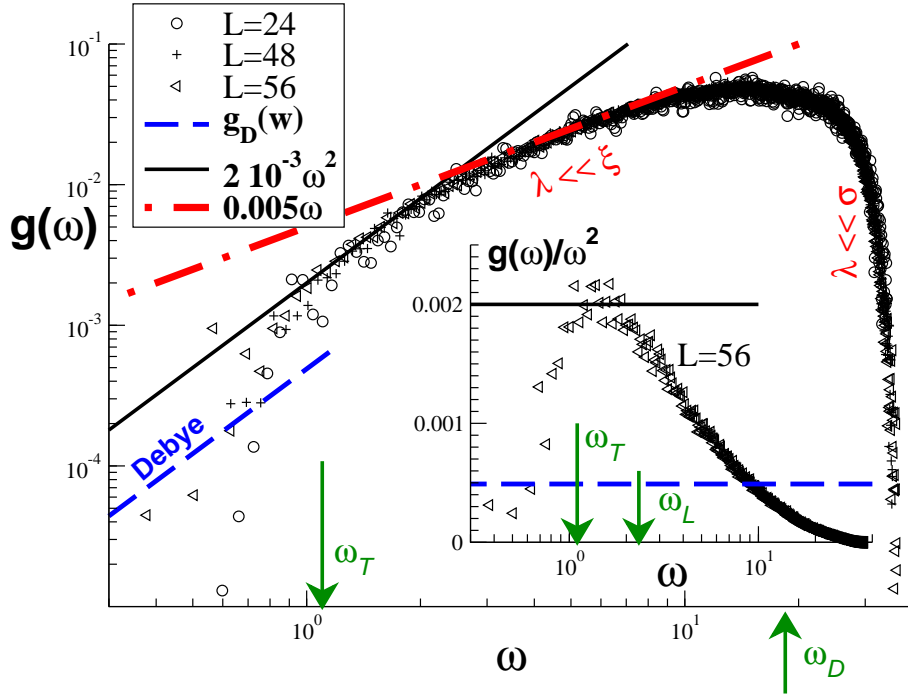


Fig. 4. Vibrational density of states in a 3d Lennard-Jones amorphous system. The "boson peak" is apparent as the deviations from the Debye prediction in the ratio $g(\omega)/\omega^2$. This peak is observed at frequencies of order $2\pi c/\xi$ where c is the speed of sound.

moduli can take negative values. Such regions would be unstable, if they were not immersed in a matrix of "normal" regions. The size over which local elastic constants are found to be negative is small (typically 3 particle sizes), and could probably be considered as a first coarse-graining scale for using classical methods for disordered systems [26].

6 Polymeric systems: stresses and self consistent field theory

Self consistent field theory is a powerful approach to the determination of phase equilibria in polymer systems with complex architectures. The theory directly deals with density fields rather than particles, and minimizes a mean field like free energy. The method is particularly suitable for polymers, in which interactions on length scales comparable to the chain size are effectively very soft. The method is well known and has been described in many publications (see e.g. [28, 29]) and I will only describe briefly the main steps and the way a constant stress method can be introduced in the simulation.

This option allows one to obtain relaxed configurations at zero imposed stress easily, or to study the effect of anisotropic tension on phase behavior.

As a representative example, I consider a model for an incompressible AB diblock copolymer melt [29]. The melt consists of n identical diblock copolymer chains composed of monomer species A and B and is contained in a volume V . Each of the chains has a total of N statistical segments; a fraction f of these segments are type A and constitute the A block of each macromolecule. For simplicity, the volume occupied by each segment, v_0 , and the statistical segment length, b , are assumed to be the same for the A and B type segments. The Hamiltonian for this system can be written

$$H = \sum_{i=1}^n \frac{k_B T}{4R_{g0}^2} \int_0^1 ds \left(\frac{d\mathbf{R}_i(s)}{ds} \right)^2 + v_0 \chi_{AB} k_B T \int d\mathbf{r} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r}) \quad (19)$$

where $\mathbf{R}_i(s)$ with $s \in [0, 1]$ is a space curve describing the conformation of the i th copolymer and $R_{g0}^2 = b^2 N/6$ is the radius of gyration of an ideal chain of N statistical segments. Interactions between dissimilar segments A and B are described by the Flory parameter χ_{AB} . The densities $\hat{\rho}_{A,B}(\mathbf{r})$ are microscopic segment density fields defined by

$$\hat{\rho}_A(\mathbf{r}) = N \sum_{i=1}^n \int_0^f ds \delta(\mathbf{r} - \mathbf{R}_i(s)) \quad (20)$$

and

$$\hat{\rho}_B(\mathbf{r}) = N \sum_{i=1}^n \int_f^1 ds \delta(\mathbf{r} - \mathbf{R}_i(s)) \quad (21)$$

A local incompressibility constraint $\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}) = \rho_0$ is imposed in this standard copolymer melt model for all points \mathbf{r} in the simulation domain. The total segment density ρ_0 can evidently be expressed as $\rho_0 = nN/V = 1/v_0$. Using the rescaled coordinates $\mathbf{X}(s)$ (taken in $[0, 1]^3$), the generalized partition function that has to be sampled *for a fixed value of the thermodynamic tension* \underline{t} reads

$$Z = \int d(\underline{h}) (\det \underline{h})^{nN} \delta(\det \underline{h} - V_0) \exp(-\beta V_0 \underline{t} : \underline{\epsilon}) \\ \times \prod_{i=1}^n \int \mathcal{D}\mathbf{X}_i(s) \exp(-\beta H) \prod_{\mathbf{x}} \delta(\hat{\rho}_A(\mathbf{x}) + \hat{\rho}_B(\mathbf{x}) - nN) \quad (22)$$

($\underline{t} : \underline{\epsilon}$ is the contraction $t_{\alpha\beta} \epsilon_{\alpha\beta}$). The final factor in the above expression imposes the constraint of local incompressibility. Moreover, incompressibility implies globally that the cell volume remains fixed at its initial value, i.e. $\det \underline{h} = V = V_0 = \det \underline{h}_0$. This is enforced by the delta function in the first line above. Hence all shape transformations should be volume preserving. The practical implementation of this constraint will be discussed below.

Hubbard-Stratonovich transformations are used to convert the particle-based partition function 22 into a field theory [28]. These can be carried out straightforwardly on the polymer partition function for a given cell shape \underline{h} , $Z(\underline{h})$, with the result

$$\begin{aligned} Z(\underline{h}) &\equiv \prod_{i=1}^n \int \mathcal{D}\mathbf{X}_i(s) \exp(-\beta H) \prod_{\mathbf{x}} \delta(\hat{\rho}_A(\mathbf{x}) + \hat{\rho}_B(\mathbf{x}) - nN) \\ &= \int \mathcal{D}w \exp(n \ln Q[w, \underline{h}] - E[w]) \end{aligned} \quad (23)$$

where $Q[w, \underline{h}]$ is the partition function of a single copolymer chain experiencing a chemical potential field $w(\mathbf{x}, s)$, $\int \mathcal{D}w$ denotes a functional integral over the field w , and $E[w]$ is a local quadratic functional of w that reflects the A-B monomer interactions and the local incompressibility constraint: [28]

$$E[w] = \frac{n}{2} \int d\mathbf{x} \left[\frac{1}{2\chi N} (w_B - w_A)^2 - (w_A + w_B) \right] \quad (24)$$

Here we have noted that for an AB diblock copolymer melt, the potential $w(\mathbf{x}, s)$ amounts to a two-component potential, i.e. $w(\mathbf{x}, s) = w_A(\mathbf{x})$ for $s \in [0, f]$ and $w(\mathbf{x}, s) = w_B(\mathbf{x})$ for $s \in [f, 1]$.

The object $Q[w, \underline{h}]$ is a normalized partition function for a single copolymer experiencing a potential field $w(\mathbf{x}, s)$. This partition function can be obtained from a single-chain propagator $q(\mathbf{x}, s)$ that is the solution of a modified diffusion equation

$$\frac{\partial q}{\partial s} = R_{g0}^2 (\underline{G}^{-1})_{\alpha\beta} \frac{\partial^2 q}{\partial x_\alpha \partial x_\beta} - w(\mathbf{x}, s) q(\mathbf{x}, s) \quad (25)$$

subject to $q(\mathbf{x}, 0) = 1$. The single chain partition function is given by $Q[w, \underline{h}] = \int d\mathbf{x} q(\mathbf{x}, 1)$.

Finally, the partition function for an incompressible diblock copolymer melt confined to a cell of variable shape can be expressed as a field theory in the variables \underline{h} and w :

$$Z = \int d(\underline{h}) (\det \underline{h})^{nN} \int \mathcal{D}w \delta(\det \underline{h} - V_0) \exp(-F[w, \underline{h}]) \quad (26)$$

where $F[w, \underline{h}]$ is an effective Hamiltonian given by

$$F[w, \underline{h}] = \beta V_0 \underline{t} : \underline{\epsilon} + E[w] - n \ln Q[w, \underline{h}] \quad (27)$$

In the mean-field approximation (SCFT), for a given shape \underline{h} of the simulation box, we approximate the functional integral over w in eq 26 by the saddle point method. For this purpose, the functional $Q[w, \underline{h}]$ can be evaluated for any w and \underline{h} by solving the modified diffusion equation (using e.g. a pseudo-spectral approach). The saddle point (mean-field) value of w , w^* , is obtained by applying a relaxation algorithm [28, 30] to solve

$$\left. \frac{\delta F[w, \underline{h}]}{\delta w(\mathbf{x}, s)} \right|_{w=w^*} = 0 \quad (28)$$

In the mean-field approximation, $F[w^*, \underline{h}]$ corresponds to the free energy of the copolymer melt (in units of $k_B T$).

In a simulation at constant tension, the relaxation equation for the fields must be supplemented by a corresponding evolution equation for the cell. This equation is chosen to be a simple relaxation

$$\frac{d\underline{h}}{dt} = -\lambda_0 \underline{h} \underline{D} \underline{h}^{-1} \frac{\partial F[w, \underline{h}]}{\partial \underline{h}} \quad (29)$$

where the tensor \underline{D} is a projection operator whose action on an arbitrary tensor \underline{M} is a traceless tensor, i.e. $\underline{D} \underline{M} \equiv \underline{M} - (1/3) \text{Tr}(\underline{M}) \underline{1}$. Equation 29 corresponds to a cell shape relaxation that (for $\lambda_0 > 0$) is down the gradient $\partial F / \partial \underline{h}$, approaching a local minimum of the mean-field free energy $F[w^*, \underline{h}]$. The ‘‘mobility’’ tensor $\underline{h} \underline{D} \underline{h}^{-1}$ is chosen so that the cell shape dynamics described by eq 29 conserves the cell volume.

Application of eq 29 requires an expression for the thermodynamic force $\partial F / \partial \underline{h}$. Explicit differentiation, noting the constraint of constant $\det \underline{h}$, leads to

$$\frac{\partial F[w, \underline{h}]}{\partial \underline{h}} = \beta V_0 \left(\frac{\partial}{\partial \underline{h}} \text{Tr}(\underline{\epsilon} \underline{t}) + \underline{h} \underline{\Sigma} \right) \quad (30)$$

where $\underline{\Sigma}$ is a symmetric tensor defined by

$$\begin{aligned} \Sigma_{\alpha\beta}[w, \underline{h}] &= -\frac{2k_B T n}{V} \frac{\partial \ln Q[w, \underline{h}]}{\partial G_{\alpha\beta}} \\ &= \frac{k_B T n}{2V R_{g0}^2} \left\langle \int_0^1 ds \frac{dX_\alpha(s)}{ds} \frac{dX_\beta(s)}{ds} \right\rangle \end{aligned} \quad (31)$$

The angular brackets in the second expression denote an average over all conformations $\mathbf{X}(s)$ of a single copolymer chain that is subject to a prescribed chemical potential field w and fixed cell shape \underline{h} .

The first term on the right hand side of eq 30 can be conveniently rewritten as

$$\frac{\partial}{\partial h_{\alpha\beta}} (\text{Tr}(\underline{\epsilon} \underline{t})) = \frac{\partial}{\partial h_{\alpha\beta}} (\text{Tr} \frac{1}{2} \underline{h}^T \underline{t} \underline{h} \underline{h}_0^{-1} \underline{t}) = (\underline{h} \underline{h}_0^{-1} \underline{t} \underline{h}^T \underline{t})_{\alpha\beta}. \quad (32)$$

Hence, eq 29 can be compactly expressed as

$$\frac{d\underline{h}}{dt} = -\lambda \underline{h} \underline{D} \left[(\underline{h}_0^{-1} \underline{t} \underline{h}^T \underline{t}) + \underline{\Sigma} \right] \quad (33)$$

where $\lambda > 0$ is a new relaxation parameter defined by $\lambda = \beta V_0 \lambda_0$.

Equation 33 will evolve the cell shape to a configuration of minimum free energy (in the mean-field approximation). This configuration can either be

metastable (local minimum) or stable (global minimum). Addition of a noise source to the equation provides a means for overcoming free energy barriers between metastable and stable states, i.e. a simple simulated annealing procedure.

An equilibrium solution of the cell shape equation 33 is evidently obtained when

$$(\underline{h}_0^{-1} \underline{t} \underline{h}_0^T)^{-1} + \underline{\Sigma} = 0 \quad (34)$$

Combining eqs 7, 31 and 34, it is seen that this equilibrium condition corresponds to a balance between the *externally* applied Cauchy stress, $\underline{\sigma}$, and the *internal* elastic stress, $\underline{\sigma}^{int}$, sustained by the polymer chains

$$\underline{\sigma} + \underline{\sigma}^{int} = 0 \quad (35)$$

where

$$\sigma_{\alpha\beta}^{int}[w, \underline{h}] \equiv (\underline{h} \underline{\Sigma} \underline{h}^T)_{\alpha\beta} = \frac{k_B T}{2V R_{g0}^2} \sum_{i=1}^n \left\langle \int_0^1 ds \frac{dR_{i\alpha}}{ds} \frac{dR_{i\beta}}{ds} \right\rangle. \quad (36)$$

This expression for the internal polymer stress is well-known in the polymer literature [31].

Equation 33 drives a change in the shape of the simulation cell (at constant cell volume) to approach the equilibrium condition 34 at which the internal elastic stress of the copolymers balances the imposed external stress.

The last step is to find an expression for the internal stress tensor $\underline{\sigma}^{int}$ (eq 36) or $\underline{\Sigma}$ (eq 31) in terms of the single chain propagator, which is the central object computed in a field-theoretic simulation [28]. The appropriate expression turns out to be

$$\frac{\sigma_{\alpha\beta}^{int}}{(n/V)k_B T} = -\frac{2R_{g0}^2}{Q} h_{\gamma\alpha}^{-1} \int d\mathbf{X} \int_0^1 ds \frac{\partial q(\mathbf{X}, s)}{\partial X_\gamma} \frac{\partial q(\mathbf{X}, 1-s)}{\partial X_\delta} h_{\delta\beta}^{-1} \quad (37)$$

we refer to the appendix and to [32] for the derivation of this expression.

From the above derivations, it is clear that the quantity that is externally imposed in the method is not the Cauchy stress, but rather the thermodynamic tension. The Cauchy stress, which is the experimentally accessible quantity, is a result of the simulation, as is the cell shape. This feature is general in any application of the Parrinello-Rahman method in which a partition function of the form refzpol is sampled using Monte-Carlo, Langevin or molecular dynamics. The Cauchy stress has therefore to be obtained independently, using equation 44 in the present case, or in the case of molecular system through the Irving-Kirkwood formula.

To illustrate the method, figure 5 shows the evolution of the simulation cell under zero tension in a simple case. In the system under study, the parameters have been chosen so that the equilibrium phase is ordered on a triangular lattice, under zero external stress. Starting with a square simulation cell, evolution to the correct rhombohedral shape is obtained after a few relaxation steps. Other examples of application may be found in [32].

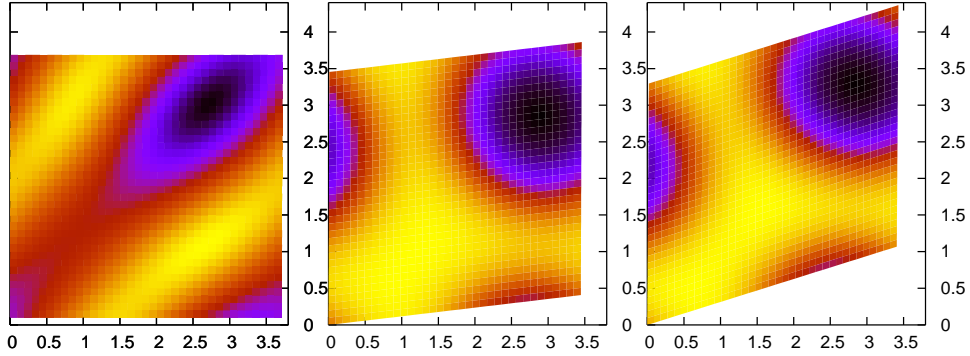


Fig. 5. Transformation of a square cell under zero external stress, when the melt is quenched into the stability region of the cylindrical phase ($\chi N = 15.9$, $f = 0.64$).

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A Expression for the stress tensor in SCFT

To obtain equation 37, we start with the definition of $\underline{\Sigma}$

$$\beta V \Sigma_{\alpha\beta} = -2n \frac{1}{Q} \frac{\partial Q[w, G]}{\partial G_{\alpha\beta}} \quad (38)$$

The derivative of the single chain partition function can be calculated by discretizing the paths with a small contour step Δ .

$$\begin{aligned}
 -\frac{2}{Q} \frac{\partial Q[w, G]}{\partial G_{\alpha\beta}} = & \frac{1}{2R_{g0}^2 Q} \int_0^1 ds \int d\mathbf{X} \int d\mathbf{X}' \\
 & \int \mathcal{D}\mathbf{X}(s) \delta(\mathbf{X} - \mathbf{X}(s)) \delta(\mathbf{X}' - \mathbf{X}(s + \Delta)) \left(\frac{X_\alpha - X'_\alpha}{\Delta} \right) \left(\frac{X_\beta - X'_\beta}{\Delta} \right) \\
 & \exp \left(-\frac{1}{4R_{g0}^2} \int_0^1 ds \frac{dX_\alpha(s)}{ds} G_{\alpha\beta} \frac{dX_\beta(s)}{ds} - \int_0^1 ds w(\mathbf{X}(s), s) \right) \quad (39)
 \end{aligned}$$

Except between the points \mathbf{X} , s and \mathbf{X}' , $s + \Delta$ one can replace the path integrals with propagators q , so that

$$\begin{aligned}
 -\frac{2}{Q} \frac{\partial Q[w, G]}{\partial G_{\alpha\beta}} = & \frac{1}{2R_{g0}^2 Q} \int_0^1 ds \int d\mathbf{X} \int d\mathbf{X}' q(\mathbf{X}, s) q(\mathbf{X}', 1 - s - \Delta) \\
 & \left(\frac{X_\alpha - X'_\alpha}{\Delta} \right) \left(\frac{X_\beta - X'_\beta}{\Delta} \right) \exp \left(-\frac{1}{4\Delta R_{g0}^2} G_{\alpha\beta} (X_\alpha - X'_\alpha) (X_\beta - X'_\beta) \right) \quad (40)
 \end{aligned}$$

One can then set $\mathbf{X}' = \mathbf{X} + \mathbf{u}$, and expand for small \mathbf{u} and Δ according to

$$q(\mathbf{X} + \mathbf{u}, 1 - s - \Delta) = q(\mathbf{X}, 1 - s) - \Delta \frac{\partial q}{\partial s} + u_\gamma \frac{\partial q}{\partial X_\gamma} + \frac{1}{2} u_\gamma u_\delta \frac{\partial^2 q}{\partial X_\gamma \partial X_\delta} \quad (41)$$

The derivative w.r.t. s can be eliminated by applying the modified diffusion eq 25. One also requires second and fourth moments of the Gaussian distribution of displacements \mathbf{u} ,

$$\overline{u_\alpha u_\beta} = G_{\alpha\beta}^{-1} (2R_{g0}^2 \Delta)$$

$$\overline{u_\alpha u_\beta u_\gamma u_\delta} = (2R_{g0}^2 \Delta)^2 (G_{\alpha\beta}^{-1} G_{\gamma\delta}^{-1} + G_{\alpha\gamma}^{-1} G_{\beta\delta}^{-1} + G_{\alpha\delta}^{-1} G_{\beta\gamma}^{-1})$$

By means of these results, we have

$$\begin{aligned}
 -\frac{2}{Q} \frac{\partial Q[w, G]}{\partial G_{\alpha\beta}} = & G_{\alpha\beta}^{-1} \frac{\int d\mathbf{X} \rho(\mathbf{X})}{\Delta} + G_{\alpha\beta}^{-1} \int d\mathbf{X} w(\mathbf{X}) \rho(\mathbf{X}) \\
 - & \frac{R_{g0}^2}{Q} G_{\alpha\beta}^{-1} G_{\gamma\delta}^{-1} \int d\mathbf{X} \int_0^1 ds q(\mathbf{X}, s) \frac{\partial^2 q}{\partial x_\gamma \partial x_\beta} \\
 + & \frac{R_{g0}^2}{Q} (G_{\alpha\beta}^{-1} G_{\gamma\delta}^{-1} + G_{\alpha\gamma}^{-1} G_{\beta\delta}^{-1} + G_{\alpha\delta}^{-1} G_{\beta\gamma}^{-1}) \int d\mathbf{X} \int_0^1 ds q(\mathbf{X}, s) \frac{\partial^2 q}{\partial x_\gamma \partial x_\delta} \quad (42)
 \end{aligned}$$

where $\rho(\mathbf{X}) = Q^{-1} \int_0^1 ds q(\mathbf{X}, s) q(\mathbf{X}, 1 - s)$ is the single-chain total monomer density operator. There is a partial cancellation in the last two terms so that

$$\begin{aligned}
 -\frac{2}{Q} \frac{\partial Q[w, G]}{\partial G_{\alpha\beta}} = & G_{\alpha\beta}^{-1} \frac{\int d\mathbf{X} \rho(\mathbf{X})}{\Delta} + i G_{\alpha\beta}^{-1} \int d\mathbf{X} w(\mathbf{X}) \rho(\mathbf{X}) \\
 + & \frac{2R_{g0}^2}{Q} G_{\alpha\gamma}^{-1} G_{\beta\delta}^{-1} \int d\mathbf{X} \int_0^1 ds q(\mathbf{X}, s) \frac{\partial^2 q}{\partial X_\gamma \partial X_\delta} \quad (43)
 \end{aligned}$$

The internal polymer stress is obtained after matrix multiplication by \underline{h} on the left and \underline{h}^T on the right. This implies that the first two terms become a simple isotropic stress contribution, and are therefore not relevant to

an incompressible system. The final formula for the internal stress tensor is therefore, apart from this diagonal contribution,

$$\sigma_{\alpha\beta}^{int} = \left(\frac{nk_B T}{V} \right) \frac{2R_{g0}^2}{Q} h_{\gamma\alpha}^{-1} \int d\mathbf{X} \int_0^1 ds q(\mathbf{X}, s) \frac{\partial^2 q(\mathbf{X}, 1-s)}{\partial X_\gamma \partial X_\delta} h_{\delta\beta}^{-1} \quad (44)$$

The tensor Σ appearing in equation 33 is given by an expression similar to 44, with \underline{G} replacing \underline{h} . The factor $k_B T n/V$ accounts for the total number of chains, and produces a stress with the correct dimensions. In practice, the stress will be made dimensionless by dividing by this factor, so that the dimensionless stress is given by

$$\frac{\sigma_{\alpha\beta}^{int}}{(n/V)k_B T} = \frac{2R_{g0}^2}{Q} h_{\gamma\alpha}^{-1} \int d\mathbf{X} \int_0^1 ds q(\mathbf{X}, s) \frac{\partial^2 q(\mathbf{X}, 1-s)}{\partial X_\gamma \partial X_\delta} h_{\delta\beta}^{-1} \quad (45)$$

Equation 37 is obtained after integrating by parts.

A local (rather than volume averaged) version of this connection between the stress tensor and the polymer propagator was derived previously in [33]. Numerically, $\sigma_{\alpha\beta}$ is evaluated from eq 45 using a pseudo-spectral scheme. The derivatives with respect to spatial coordinates are obtained by multiplying the propagator by the appropriate components of the wavevector in Fourier space, and transforming back into real space.

References

1. L.D. Landau and E.M. Lifshitz, *Theory of Elasticity* (Butterworth-Heinemann, London, 1995).
2. M. Parrinello, A. Rahman *J. Appl. Phys.* **52**, 7182 (1981)
3. J.R. Ray, A. Rahman, *J. Chem. Phys.* **80**, 4423 (1984)
4. D. Wallace *Thermodynamics of crystals* (Wiley, New-York 1973)
5. T.H.K Barron, M.L. Klein *Proc. Phys. Soc.* **65**, 523 (1965)
6. D.R. Squire, A.C. Holt, W.G. Hoover, *Physica*, 42, 388 (1968)
7. J.F. Lutsko, *J. Appl. Phys.* **65**, 2991 (1989)
8. A. Lematre, C. Maloney, *J. Stat. Phys.*, in press (2005)
9. I. Goldhirsch, C. Goldenberg, *Eur. Phys. J. E* **9**, 245 (2002).
10. K. Yoshimoto, T.S. Jain, K. van Workum, P.F. Nealey, J.J. de Pablo, *Phys. Rev. Lett.* **93**, 175501 (2004).
11. S. Sengupta, P. Nielaba, M. Rao, K. Binder *Phys. Rev. E* 61, 1072 (2000)
12. S. Pronk, D. Frenkel, *Phys. Rev. Lett.* 90, 255501 (2003)
13. J.Geng, G.Reydellet, E.Clement, R.P.Behringer *Physica D* **182**, 274 (2003)
14. E. Pratt, M. Dennin, *Phys. Rev. E* **67**, 051402 (2003)
15. A. Kabla, G. Debrégeas, *Phys. Rev. Lett.* **90**, 258303-1 (2003).
16. M. Aubouy, Y. Jiang, J. A. Glazier, F. Graner *Granular Matter*, **5**, 67-70 (2003).
17. F. Leonforte, R. Boissire, A. Tanguy, J. Wittmer, J-L. Barrat, *Phys. Rev B* 72, 224206 (2005)
18. J-L. Barrat, J-N. Roux, J-P. Hansen, M.L. Klein, *Europhysics Letters*, 7, 707 (1988)

19. M.L. Falk, J.S. Langer, *Phys. Rev. E* **57**, 7192 (1998)
20. S.A. Langer, A.J. Liu, *J. Phys. Chem. B* **101**, 8667 (1997).
21. J.P. Wittmer, A. Tanguy, J.-L. Barrat, and L. Lewis, *Europhys. Lett.* **57**, 423 (2002); A. Tanguy, J.P. Wittmer, F. Leonforte, and J.-L. Barrat, *Phys. Rev. B* **66**, 174205 (2002).
22. F. Leonforte, A. Tanguy, J. P. Wittmer, J.-L. Barrat *Phys. Rev. B* **70**, 014203 (2004)
23. E. Duval, A. Mermet, *Phys. Rev. B* **58**, 8159 (1998)
24. "Evidence for a new nano-scale stress correlation in silica glass", C. Masciovecchio, G. Baldi, S. Caponi, L. Comez, S. Di Fonzo, D. Fioretto, A. Fontana, A. Gessini, S. C. Santucci, F. Sette, G. Vilianni, G. Ruocco, preprint 2005
25. L.E. Silbert, A.J. Liu, S.R. Nagel, preprint condmat/0501616. M. Wyart, S.R. Nagel and T.A. Witten, preprint condmat/0409687.
26. E. Maurer, W. Schirmacher, *J. Low Temp. Phys.* **137**, 453 (2004)
27. W. H. Press, B. P. Flannery, S. A. Teukolsky, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986)
28. G.H. Fredrickson, V. Ganesan, F. Drolet *Macromolecules*, **35**, 16 (2002)
29. M.W. Matsen, M. Schick, *Phys. Rev. Lett.* **72**, 2660 (1994)
30. S.W. Sides, G.H. Fredrickson *Polymer*, **44**, 5859 (2003)
31. M. Doi, S.F. Edwards *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1988)
32. J.-L. Barrat, G.H. Fredrickson, S.W. Sides, *J. Phys. Chem.* **B109**, 6694 (2005)
33. G.H. Fredrickson *J. Chem. Phys.* **117**, 6810 (2002)