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Rheological modeling with Hookean bead-spring cubes (SC, BCC and FCC)

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Abstract. In this study a general bead-spring model is used for predicting some rheological properties of a cubic bead-spring structure of arbitrary size immersed in a Newtonian solvent. The topology of this bead-spring structure is based upon the well-known cubic crystals (SC, BCC or FCC) and it consists of equal Hookean springs and beads with equal friction coefficients, while hydrodynamic interaction is not included. An appropriate combination of the equations of motion, the expression for the stress tensor and the equation of continuity leads to an explicit constitutive equation with three sets of relaxation times belonging to the three types of bead-spring cubes (SC, BCC or FCC). For small-amplitude oscillatory shear flow it is found that the three relaxation spectra, which are significantly different, result in dynamic moduli which differ mainly in one aspect: the characteristic SC, BCC and FCC time scales are different. The BCC and FCC time scales can be obtained by multiplication of the SC time scale by the ratios $M^{\mathrm{sc}}/M^{\mathrm{bcc}}$ and $M^{\mathrm{sc}}/M^{\mathrm{fcc}}$ respectively, where M^{sc}, M^{bcc} and M^{fcc} denote the number of springs in the three types of cubic bead-spring structures.

Keywords: rheology, bead-spring cubes, relaxation spectra, dynamic moduli.

1. Introduction

During the past forty years several bead-spring models have been developed to predict the rheological properties of a dilute solution of flexible polymer molecules in a Newtonian solvent. In our previous paper [1] we generalized the existing bead-spring models in such a way that the following four features were incorporated simultaneously:

(i) the linear (Hookean) springs may have different spring moduli,
(ii) the friction coefficients belonging to the beads may be different,
(iii) pre-averaged hydrodynamic interaction may be included and
(iv) the geometry of the bead-spring structure may contain cycles.

In this paper we consider bead-spring structures of arbitrary size with a topology based upon the well-known cubic crystals, *i.e.* the simple cubic (SC) lattice, the body-centered cubic (BCC) lattice and the face-centered cubic (FCC) lattice. Throughout this paper we restrict ourselves to cubic bead-spring structures, which consist of equal Hookean springs and beads with equal friction coefficients, while hydrodynamic interaction is not included.

In subsequent publications we will modify the bead-spring formalism considered in this paper by replacing the Hookean springs by nonlinear ones with nonzero equilibrium lengths and we will use this new formalism for the modeling of a colloidal crystal, *i.e.* the beads will represent the charged colloidal particles and the nonlinear springs the inter-particle forces.

The outline of this paper is as follows. In Section 2 we present some general aspects about the topology of the three types of bead-spring cubes (SC, BCC and FCC). In Section 3 we discuss a bead-spring model which is valid for all kinds of Hookean bead-spring structures and we use this model for calculating the spectrum of relaxation times belonging to a bead-spring cube (SC, BCC and FCC) immersed in a Newtonian fluid. These three relaxation spectra appear to be significantly different and the rheological consequences of these differences are investigated in Section 4. In Section 5 we give some concluding remarks about the results obtained in this paper.

2. The topology of a bead-spring structure

2.1. The $\mathbf{r}$-, $\tilde{\mathbf{r}}$- and $\hat{\mathbf{r}}$-representation

To describe the topology of a bead-spring structure consisting of N beads and $M \geqslant N-1$ springs we first introduce, according to the basic terminology of graph theory [2, 3], the following two concepts: the *spanning tree* and the *fundamental cycles*. A spanning tree is a substructure of the entire bead-spring structure which includes all the N beads and has a tree geometry, *i.e.* we have to leave out $M-(N-1)$ springs in such a way that all beads still keep attached to each other. The fundamental cycles are strongly related to the spanning tree and the $M-(N-1)$ omitted springs. Namely, if we add an omitted spring to the chosen spanning tree, then the obtained cycle is defined as a fundamental cycle. Consequently there are $M-(N-1)$ fundamental cycles associated with a chosen spanning tree.

We may describe the configuration of a bead-spring structure by using one of the following vector representations:

(i) the $\mathbf{r}$-representation: a set of N bead position vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ with respect to some fixed origin in space,

(ii) the $\tilde{\mathbf{r}}$-representation: a linearly dependent set of M connector vectors $\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \ldots, \tilde{\mathbf{r}}_M$ belonging to all the springs of the entire bead-spring structure and

(iii) the $\hat{\mathbf{r}}$-representation: a linearly independent set of $N-1$ connector vectors $\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \ldots, \hat{\mathbf{r}}_{N-1}$ belonging to the springs of a chosen spanning tree of the entire bead-spring structure.

The $\tilde{\mathbf{r}}$-representation coincides with the $\hat{\mathbf{r}}$-representation for a bead-spring structure with a tree geometry, *i.e.* no cycles in its geometry. The interrelations between the bead position representation $\mathbf{r}_i$ and the two connector vector representations $\tilde{\mathbf{r}}_a$ and $\hat{\mathbf{r}}_b$ are given by

$$\tilde{\mathbf{r}}_a = \sum_{i=1}^{N} \widetilde{G}_{ai}\, \mathbf{r}_i, \qquad \hat{\mathbf{r}}_b = \sum_{i=1}^{N} \widehat{G}_{bi}\, \mathbf{r}_i, \qquad \tilde{\mathbf{r}}_a = \sum_{b=1}^{N-1} D_{ab}\, \hat{\mathbf{r}}_b. \tag{1}$$

We obtain the matrix elements of $\widetilde{G}$ and $\widehat{G}$ by noting that each connector vector is equal to the difference of the position vectors of two directly connected beads, *i.e.* each row of $\widetilde{G}$ and $\widehat{G}$ consists of $N-2$ row elements of value 0, one row element of value 1 and one row element of value -1, while the M rows of $\widetilde{G}$ and the $N-1$ rows of $\widehat{G}$ are related to the M springs of the entire bead-spring structure and the $N-1$ springs of the chosen spanning tree, respectively.

The matrix elements of $N-1$ rows of D are obtained when we realize that the $N-1$ independent vectors $\hat{\mathbf{r}}_b$ elonging to the spanning tree are, by definition, identical to the $N-1$ corresponding connector vectors $\tilde{\mathbf{r}}_a$ (one-to-one coupling) and we obtain the matrix elements

Table 1. The primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ belonging to a SC, BCC and FCC lattice. The vectors $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ form an orthonormal basis in space and the parameter a refers to the repeated cube of volume a^3.

	SC	BCC	FCC
$\mathbf{a}_1$	$a\,\mathbf{e}_x$	$\frac{1}{2}a\left(-\mathbf{e}_x+\mathbf{e}_y+\mathbf{e}_z\right)$	$\frac{1}{2}a\left(\mathbf{e}_y+\mathbf{e}_z\right)$
$\mathbf{a}_2$	$a\,\mathbf{e}_y$	$\frac{1}{2}a\left(\mathbf{e}_x-\mathbf{e}_y+\mathbf{e}_z\right)$	$\frac{1}{2}a\left(\mathbf{e}_x+\mathbf{e}_z\right)$
$\mathbf{a}_3$	$a\,\mathbf{e}_z$	$\frac{1}{2}a\left(\mathbf{e}_x+\mathbf{e}_y-\mathbf{e}_z\right)$	$\frac{1}{2}a\left(\mathbf{e}_x+\mathbf{e}_y\right)$

of the other $M-(N-1)$ rows of D by noting that each of the $M-(N-1)$ fundamental cycles relates, by definition, one connector vector $\tilde{\mathbf{r}}_a$ with two or more independent connector vectors $\hat{\mathbf{r}}_b$.

The particular values of all the matrix elements of $\widetilde{G}$, $\widehat{G}$ and D depend upon the chosen directions of the connector vectors $\tilde{\mathbf{r}}_a$ and $\hat{\mathbf{r}}_b$, the chosen spanning tree and the schemes used to number the vectors $\mathbf{r}_i$, $\tilde{\mathbf{r}}_a$ and $\hat{\mathbf{r}}_b$.

2.2. Cubic crystals (SC, BCC and FCC)

In this paper we are interested in the prediction of some rheological properties of a crystal-like bead-spring structure immersed in a Newtonian fluid. Here, the topology of such a structure is based upon the periodic structure of a real crystal, *i.e.*

(i) we first place each bead at a lattice point of a real crystal,
(ii) we then connect each bead with its nearest neighbor beads by springs and
(iii) after a systematic numbering of the beads and the springs we allow them to move.

Due to the motion of the beads, the configuration of the bead-spring structure does not have to resemble the periodic ordering of a real crystal, *i.e.* a crystal-like topology does not imply a crystal-like configuration.

We now restrict ourselves to crystal-like bead-spring structures with a topology based upon the cubic crystals, *i.e.* the simple cubic (SC) lattice, the body-centered cubic (BCC) lattice and the face-centered cubic (FCC) lattice. Each lattice point of a cubic crystal can be described by a lattice vector $\mathbf{s}_{xyz}$ defined as

$$\mathbf{s}_{xyz} = x\,\mathbf{a}_1 + y\,\mathbf{a}_2 + z\,\mathbf{a}_3, \tag{2}$$

where x, y and z are arbitrary integers and the three primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ belonging to a SC, BCC and FCC lattice are given in Table 1. The lattice vector of an arbitrary lattice point subtracted by the lattice vector of its nearest neighbor is denoted by vector $\Delta\mathbf{s}$ and it appears that this vector can take the following values

SC (6 near. neighbors): $\Delta\mathbf{s} \in \{\pm\mathbf{a}_1,\ \pm\mathbf{a}_2,\ \pm\mathbf{a}_3\}$,
BCC (8 near. neighbors): $\Delta\mathbf{s} \in \{\pm\mathbf{a}_1,\ \pm\mathbf{a}_2,\ \pm\mathbf{a}_3,\ \pm(\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3)\}$,
FCC (12 near. neighbors): $\Delta\mathbf{s} \in \{\pm\mathbf{a}_1,\ \pm\mathbf{a}_2,\ \pm\mathbf{a}_3,\ \pm(\mathbf{a}_2-\mathbf{a}_1),\ \pm(\mathbf{a}_3-\mathbf{a}_2),\ \pm(\mathbf{a}_1-\mathbf{a}_3)\}$.

Instead of considering an infinitely large cubic bead-spring structure, we consider a structure consisting of $N = K^3$ beads, *i.e.* a $K \times K \times K$ cubic bead-spring structure where the indices of the lattice vectors $\mathbf{s}_{xyz}$ are bounded as: $x, y, z \in \{0, 1, \ldots, (K-1)\}$. For numbering purposes we place the K^3 beads at the lattice points of a cubic crystal (SC, BCC and FCC) and we choose the following interrelation between the index of bead position vector $\mathbf{r}_i$ and the indices of lattice vector $\mathbf{s}_{xyz}$

$$\mathbf{r}_i = \mathbf{s}_{xyz} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3 \quad \text{with} \quad i = K^2x + Ky + z + 1. \tag{3}$$

Each connector vector $\tilde{\mathbf{r}}_a$ is related to a spring connecting a bead with one of its nearest neighbor beads, *i.e.* we have $3K^2(K-1)$ connector vectors $\tilde{\mathbf{r}}_a$ related to springs in the $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$-direction (SC, BCC and FCC), $(K-1)^3$ connector vectors $\tilde{\mathbf{r}}_a$ related to springs in the $(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$-direction (BCC) and $3K(K-1)^2$ connector vectors $\tilde{\mathbf{r}}_a$ related to springs in the $(\mathbf{a}_2 - \mathbf{a}_1)$, $(\mathbf{a}_3 - \mathbf{a}_2)$ and $(\mathbf{a}_1 - \mathbf{a}_3)$-direction (FCC). Thus, a $K \times K \times K$ cubic bead-spring structure consists of K^3 beads and a certain number of springs denoted by the parameters M^{sc}, M^{bcc} and M^{fcc}, *i.e.*

$$M^{\mathrm{sc}} = 3K^2(K-1), \qquad M^{\mathrm{bcc}} = M^{\mathrm{sc}} + (K-1)^3,$$

$$M^{\mathrm{fcc}} = M^{\mathrm{sc}} + 3K(K-1)^2. \tag{4}$$

In Table 2 we give our chosen interrelation between the index of connector vector $\tilde{\mathbf{r}}_a$ and the indices of two different lattice vectors (*e.g.* $\mathbf{s}_{xyz}$ and $\mathbf{s}_{(x+1)yz}$). For example, for a $2 \times 2 \times 2$ cubic bead-spring structure with a topology based upon a SC lattice, the resulting structure is given in Figure 1a. If we add one spring (*i.e.* $\tilde{\mathbf{r}}_{13} = \mathbf{s}_{111} - \mathbf{s}_{000}$) to the depicted structure in Figure 1a, we obtain a structure which corresponds to a $2 \times 2 \times 2$ cubic structure with a topology based upon a BCC lattice and, similarly, if we add six springs (*i.e.* $\tilde{\mathbf{r}}_{13} = \mathbf{s}_{010} - \mathbf{s}_{100}, \ldots, \tilde{\mathbf{r}}_{18} = \mathbf{s}_{110} - \mathbf{s}_{011}$) we obtain a structure which corresponds to a $2 \times 2 \times 2$ cubic structure with a topology based upon a FCC lattice.

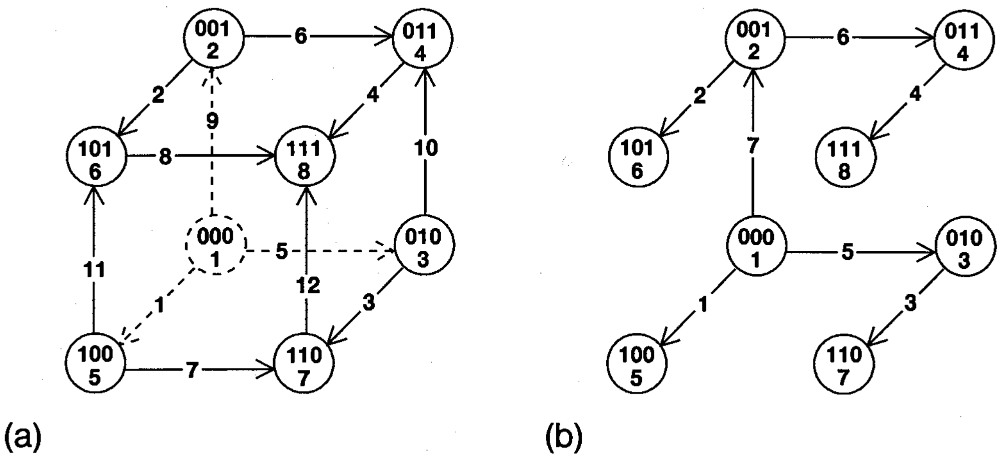

Figure 1. A $2 \times 2 \times 2$ cubic bead-spring structure with a topology based upon a SC lattice (a) and its chosen spanning tree (b). In both figures: the lower number inside each bead refers to index i of bead position vector $\mathbf{r}_i$ and the upper three numbers inside each bead refer to indices x, y and z of lattice vector $\mathbf{s}_{xyz}$. The numbering of the linearly dependent set of connector vectors $\tilde{\mathbf{r}}_a$ and the linearly independent set of connector vectors $\hat{\mathbf{r}}_b$ is given in (a) and (b), respectively. We note that the chosen spanning tree of a $2 \times 2 \times 2$ cubic structure with a topology based upon a BCC or FCC lattice is identical to the one based upon a SC lattice, which is shown in (b).

Table 2. The chosen numbering of the connector vectors $\tilde{\mathbf{r}}_a$ and $\hat{\mathbf{r}}_b$ in relation to the indices of two different lattice vectors. We note that the six indices of these lattice vectors are always non-negative and that they may never exceed the value $K-1$.

$3K^2(K-1)$ springs in $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$-direction (SC, BCC and FCC)	
$\tilde{\mathbf{r}}_a = \mathbf{s}_{(x+1)yz} - \mathbf{s}_{xyz}$	with $a = K^2x + Ky + z + 1$
$\tilde{\mathbf{r}}_a = \mathbf{s}_{x(y+1)z} - \mathbf{s}_{xyz}$	with $a = K(K-1)x + Ky + z + 1 + K^2(K-1)$
$\tilde{\mathbf{r}}_a = \mathbf{s}_{xy(z+1)} - \mathbf{s}_{xyz}$	with $a = K(K-1)x + (K-1)y + z + 1 + 2K^2(K-1)$
$(K-1)^3$ springs in $(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$-direction (BCC)	
$\tilde{\mathbf{r}}_a = \mathbf{s}_{(x+1)(y+1)(z+1)} - \mathbf{s}_{xyz}$	with $a = (K-1)^2x + (K-1)y + z + 1 + 3K^2(K-1)$
$3K(K-1)^2$ springs in $(\mathbf{a}_2 - \mathbf{a}_1)$, $(\mathbf{a}_3 - \mathbf{a}_2)$ and $(\mathbf{a}_1 - \mathbf{a}_3)$-direction (FCC)	
$\tilde{\mathbf{r}}_a = \mathbf{s}_{x(y+1)z} - \mathbf{s}_{(x+1)yz}$	with $a = K(K-1)x + Ky + z + 1 + 3K^2(K-1)$
$\tilde{\mathbf{r}}_a = \mathbf{s}_{xy(z+1)} - \mathbf{s}_{x(y+1)z}$	with $a = (K-1)^2x + (K-1)y + z + 1 + K(K-1)(4K-1)$
$\tilde{\mathbf{r}}_a = \mathbf{s}_{(x+1)yz} - \mathbf{s}_{xy(z+1)}$	with $a = K(K-1)x + (K-1)y + z + 1 + K(K-1)(5K-2)$
(K^3-1) springs of the spanning tree in $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$-direction (SC, BCC and FCC)	
$\hat{\mathbf{r}}_b = \mathbf{s}_{(x+1)yz} - \mathbf{s}_{xyz}$	with $b = K^2x + Ky + z + 1$
$\hat{\mathbf{r}}_b = \mathbf{s}_{0(y+1)z} - \mathbf{s}_{0yz}$	with $b = Ky + z + 1 + K^2(K-1)$
$\hat{\mathbf{r}}_b = \mathbf{s}_{00(z+1)} - \mathbf{s}_{00z}$	with $b = z + 1 + K(K^2-1)$

The connector vectors $\hat{\mathbf{r}}_b$ belonging to the springs of a chosen spanning tree are numbered in the same manner as the vectors $\tilde{\mathbf{r}}_a$ (see Table 2) and, for example, for a $2\times2\times2$ bead-spring cube with a topology based upon a SC, BCC or FCC lattice, the chosen spanning tree is given in Figure 1b. Indeed, these three spanning trees (SC, BCC and FCC) are chosen to be identical to each other.

2.3. The matrices $\widetilde{G}$, $\widehat{G}$ and D belonging to a cubic bead-spring structure

In the previous section we presented a systematic numbering of the beads and the springs. Our way of numbering leads to the following expressions for the matrix $\widetilde{G}$ defined by (1) belonging to a $K \times K \times K$ bead-spring cube with a topology based upon a SC, BCC or FCC lattice

$$\widetilde{G}^{\mathrm{sc}} = \begin{pmatrix} G \otimes \delta_K \otimes \delta_K \\ \delta_K \otimes G \otimes \delta_K \\ \delta_K \otimes \delta_K \otimes G \end{pmatrix}, \qquad \widetilde{G}^{\mathrm{bcc}} = \begin{pmatrix} \widetilde{G}^{\mathrm{sc}} \\ H^{\mathrm{bcc}} \end{pmatrix}, \qquad \widetilde{G}^{\mathrm{fcc}} = \begin{pmatrix} \widetilde{G}^{\mathrm{sc}} \\ H^{\mathrm{fcc}} \end{pmatrix}, \tag{5}$$

where the matrices H^{bcc} and H^{fcc} are given by

$$H^{\mathrm{bcc}} = E \otimes E \otimes E + F \otimes F \otimes F,$$

$$H^{\text{fcc}} = \begin{pmatrix} E \otimes F \otimes \delta_K - F \otimes E \otimes \delta_K \\ \delta_K \otimes E \otimes F - \delta_K \otimes F \otimes E \\ F \otimes \delta_K \otimes E - E \otimes \delta_K \otimes F \end{pmatrix}. \tag{6}$$

The symbol $\otimes$ used in (5) and (6) denotes the so called Kronecker product (also known as direct product or tensor product, see *e.g.* Horn and Johnson [4] and Davis [5] for its basic properties). This product is defined for an arbitrary $Q \times P$ matrix X and an arbitrary $R \times S$ matrix Y as

$$X \otimes Y \equiv \begin{pmatrix} X_{11}Y & \dots & X_{1P}Y \\ \vdots & \ddots & \vdots \\ X_{Q1}Y & \dots & X_{QP}Y \end{pmatrix}, \tag{7}$$

in which $X \otimes Y$ is a $QR \times PS$ matrix. The matrix δ_P in (5) and (6) is a $P \times P$ identity matrix and the $(K-1) \times K$ matrices E, F and G in (5) and (6) are defined as

$$E = \begin{pmatrix} O_{(K-1)\times 1} & \delta_{K-1} \end{pmatrix}, \qquad F = \begin{pmatrix} -\delta_{K-1} & O_{(K-1)\times 1} \end{pmatrix}, \qquad G = E + F, \tag{8}$$

where matrix $O_{Q\times R}$ is a $Q \times R$ zero matrix, *i.e.* all its matrix elements are zero. We note that matrix G is identical to the matrices $\widetilde{G}$ and $\widehat{G}$ belonging to a linear Rouse chain consisting of K beads and $K-1$ springs [6].

As mentioned in Section 2.2 the three spanning trees belonging to a $K \times K \times K$ bead-spring cube based upon a SC, BCC and FCC lattice are chosen to be identical to each other and, consequently, we obtain the following expression for the matrix $\widehat{G}$ defined by (1)

$$\widehat{G}^{\text{sc}} = \widehat{G}^{\text{bcc}} = \widehat{G}^{\text{fcc}} = \begin{pmatrix} G \otimes \delta_K \otimes \delta_K \\ G \otimes \delta_K \quad O_{K(K-1)\times K^2(K-1)} \\ G \quad O_{(K-1)\times K(K^2-1)} \end{pmatrix}. \tag{9}$$

The expressions for the matrix D defined by (1) belonging to a $K \times K \times K$ bead-spring cube based upon a SC, BCC and FCC lattice are somewhat more complex than the expressions for the matrices $\widetilde{G}^{\text{sc}}$, $\widetilde{G}^{\text{bcc}}$, $\widetilde{G}^{\text{fcc}}$, $\widehat{G}^{\text{sc}}$, $\widehat{G}^{\text{bcc}}$ and $\widehat{G}^{\text{fcc}}$, *i.e.*

$$D^{\text{sc}} = \begin{pmatrix} \delta_{K-1} \otimes \delta_K \otimes \delta_K & O_{K^2(K-1)\times K(K-1)} & O_{K^2(K-1)\times(K-1)} \\ S \otimes G \otimes \delta_K & V_K \otimes \delta_{K-1} \otimes \delta_K & O_{K^2(K-1)\times(K-1)} \\ S \otimes \delta_K \otimes G & V_K \otimes S \otimes G & V_K \otimes V_K \otimes \delta_{K-1} \end{pmatrix}, \tag{10}$$

$$D^{\text{bcc}} = \begin{pmatrix} D^{\text{sc}} \\ I_1^{\text{bcc}} + I_2^{\text{bcc}} \end{pmatrix}, \qquad D^{\text{fcc}} = \begin{pmatrix} D^{\text{sc}} \\ I_1^{\text{fcc}} + I_2^{\text{fcc}} \end{pmatrix}, \tag{11}$$

where the matrices $I_1^{\rm bcc}$, $I_2^{\rm bcc}$, $I_1^{\rm fcc}$ and $I_2^{\rm fcc}$ are given by

$$I_1^{\rm bcc} = \left(S^{\rm E} \otimes E \otimes E \quad V_{K-1} \otimes S^{\rm E} \otimes E \quad V_{K-1} \otimes V_{K-1} \otimes \delta_{K-1} \right), \tag{12}$$

$$I_2^{\rm bcc} = \left(S^{\rm F} \otimes F \otimes F \quad -V_{K-1} \otimes S^{\rm F} \otimes F \quad O_{(K-1)^3 \times (K-1)} \right), \tag{13}$$

$$I_1^{\rm fcc} = \begin{pmatrix} S^{\rm E} \otimes F \otimes \delta_K & V_{K-1} \otimes \delta_{K-1} \otimes \delta_K & O_{K(K-1)^2 \times (K-1)} \\ S \otimes E \otimes F & V_K \otimes S^{\rm E} \otimes F & V_K \otimes V_{K-1} \otimes \delta_{K-1} \\ S^{\rm F} \otimes \delta_K \otimes E & -V_{K-1} \otimes S \otimes E & -V_{K-1} \otimes V_K \otimes \delta_{K-1} \end{pmatrix}, \tag{14}$$

$$I_2^{\rm fcc} = \begin{pmatrix} -S^{\rm F} \otimes E \otimes \delta_K & O_{K(K-1)^2 \times K(K-1)} & O_{K(K-1)^2 \times (K-1)} \\ -S \otimes F \otimes E & -V_K \otimes S^{\rm F} \otimes E & O_{K(K-1)^2 \times (K-1)} \\ -S^{\rm E} \otimes \delta_K \otimes F & -V_{K-1} \otimes S \otimes F & O_{K(K-1)^2 \times (K-1)} \end{pmatrix}. \tag{15}$$

Here, the column vector V_P is a $P \times 1$ vector with all its elements equal to one and the matrix $S^{\rm E}$ is a $(K-1) \times (K-1)$ step matrix defined as

$$S_{ij}^{\rm E} = \begin{cases} 0 \ \text{if} \ i < j \\ 1 \ \text{if} \ i \geqslant j \end{cases} \quad \text{with} \quad \begin{cases} i = 1 \dots (K-1) \\ j = 1 \dots (K-1) \end{cases}, \tag{16}$$

i.e. matrix $S^{\rm E}$ is a lower triangular matrix with all its nonzero elements equal to one. The $(K-1) \times (K-1)$ step matrix $S^{\rm F}$ and $K \times (K-1)$ step matrix S are related to matrix $S^{\rm E}$ as

$$S^{\rm F} = \delta_{K-1} - S^{\rm E}, \qquad S = \begin{pmatrix} O_{1 \times (K-1)} \\ S^{\rm E} \end{pmatrix}, \tag{17}$$

As an example we give in appendix A the nonzero matrix elements of the matrices $\widetilde{G}^{\rm sc}$, $\widehat{G}^{\rm sc}$ and $D^{\rm sc}$ belonging to a $3 \times 3 \times 3$ cubic bead-spring structure.

We note that each row of $\widetilde{G}^{\rm sc}$ (or $D^{\rm sc}$) is related to one of the $M^{\rm sc}$ springs of a cubic structure with a topology based upon a SC lattice and, in the same way, each row of $H^{\rm bcc}$ (or $I_1^{\rm bcc} + I_2^{\rm bcc}$) and $H^{\rm fcc}$ (or $I_1^{\rm fcc} + I_2^{\rm fcc}$) is related to one of the $M^{\rm bcc} - M^{\rm sc}$ and $M^{\rm fcc} - M^{\rm sc}$ springs, respectively, which we must add to the cubic structure based upon a SC lattice for creating a cubic structure based upon a BCC and FCC lattice, respectively.

3. Bead-spring model for Hookean structures

3.1. Bead-spring structure with an arbitrary topology

Up to now we have obtained expressions for the topology matrices $\widetilde{G}$, $\widehat{G}$ and D belonging to the three types of bead-spring cubes (SC, BCC or FCC), but we have not mentioned anything about

the forces acting on each bead,
the equations of motion for the beads and

the expression for the stress tensor.

Here, we will repeat briefly a bead-spring formalism presented in a previous paper [1], which is valid for Hookean bead-spring structures with an arbitrary topology immersed in a Newtonian fluid.

Omitting external forces, such as gravitational and electrical forces, we observe that a bead i experiences, in principle, three kinds of forces: the bead interaction force $\mathbf{f}_i^{\Phi}$, the Brownian force $\mathbf{f}_i^{\mathrm{b}}$ and the hydrodynamic drag force $\mathbf{f}_i^{\mathrm{h}}$. The expressions for these three forces are given by

$$\mathbf{f}_i^{\Phi} = -\sum_{a=1}^{M} \widetilde{G}_{ai} \tilde{\mathbf{f}}_a, \qquad \mathbf{f}_i^{\mathrm{b}} = -kT \frac{\partial \log \psi(\mathbf{r}^N, t)}{\partial \mathbf{r}_i}, \qquad \mathbf{f}_i^{\mathrm{h}} = -\zeta\,(\dot{\mathbf{r}}_i - \mathbf{L}\cdot\mathbf{r}_i)\,, \tag{18}$$

where $\tilde{\mathbf{f}}_a$ is the spring force parallel to connector vector $\tilde{\mathbf{r}}_a$, k the Boltzmann constant, T the absolute temperature, $\psi(\mathbf{r}^N, t)$ the distribution function in configuration space of the set of N beads, ζ a friction coefficient, $\mathbf{L}\cdot\mathbf{r}_i$ the ambient velocity of the solvent at bead i (the velocity gradient tensor $\mathbf{L}$ is the same at all points in the flow field, but it may be dependent on time t) and $\dot{\mathbf{r}}_i$ the flux velocity of bead i appearing in the equation of continuity for $\psi(\mathbf{r}^N, t)$ given by

$$\frac{\partial \psi}{\partial t} = -\sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{r}_i} \cdot (\dot{\mathbf{r}}_i \psi)\,. \tag{19}$$

Neglecting inertial effects we obtain the force balance $\mathbf{f}_i^{\Phi} + \mathbf{f}_i^{\mathrm{h}} + \mathbf{f}_i^{\mathrm{b}} = \mathbf{0}$ and by combining this force balance with (18) we obtain the following equation of motion

$$\dot{\mathbf{r}}_i = \mathbf{L}\cdot\mathbf{r}_i - \frac{1}{\zeta}\left(kT\frac{\partial \log \psi}{\partial \mathbf{r}_i} + \sum_{a=1}^{M} \widetilde{G}_{ai}\tilde{\mathbf{f}}_a\right). \tag{20}$$

Throughout this paper we are only considering bead-spring structures consisting of equal Hookean springs with spring forces $\tilde{\mathbf{f}}_a$ given by

$$\tilde{\mathbf{f}}_a = \kappa\,\tilde{\mathbf{r}}_a, \tag{21}$$

where κ is the spring modulus belonging to each spring. By substituting (21) in (20) and by using the transformations as given in (1), we transform (20) into the following equations of motion

$$\dot{\mathbf{r}}_i = \mathbf{L}\cdot\mathbf{r}_i - \frac{1}{\zeta}\left(kT\frac{\partial \log \psi}{\partial \mathbf{r}_i} + \kappa\sum_{a=1}^{M} A_{ia}\mathbf{r}_a\right), \tag{22}$$

$$\dot{\tilde{\mathbf{r}}}_a = \mathbf{L}\cdot\tilde{\mathbf{r}}_a - \frac{1}{\zeta}\sum_{j=1}^{M} \widetilde{A}_{aj}\left(kT\frac{\partial \log \widetilde{\psi}}{\partial \tilde{\mathbf{r}}_j} + \kappa\tilde{\mathbf{r}}_j\right), \tag{23}$$

$$\dot{\hat{\mathbf{r}}}_b = \mathbf{L}\cdot\hat{\mathbf{r}}_b - \frac{1}{\zeta}\sum_{j=1}^{N-1} \widehat{A}_{bj}\left(kT\frac{\partial \log \widehat{\psi}}{\partial \hat{\mathbf{r}}_j} + \kappa\sum_{k=1}^{M} M_{jk}\hat{\mathbf{r}}_k\right), \tag{24}$$

where the symmetric matrices $A = \widetilde{G}^T \widetilde{G}$, $\widetilde{A} = \widetilde{G}\widetilde{G}^T$ and $\widehat{A} = \widehat{G}\widehat{G}^T$ are generalizations of the matrix used by Rouse [7, 6] and we note that these three matrices are positive (semi)definite, *i.e.* the nonzero eigenvalues of these matrices are always positive. The symmetric matrix M in (24) is defined by the relation $M = D^T D$ and the distribution functions $\widetilde{\psi}$ and $\widehat{\psi}$ in (23) and (24) are defined as

$$\psi(\mathbf{r}^N, t) \equiv \widetilde{\psi}(\tilde{\mathbf{r}}^M, t) \equiv \widehat{\psi}(\hat{\mathbf{r}}^{N-1}, t), \tag{25}$$

in which it is understood that the sets of vectors $\mathbf{r}^N$, $\tilde{\mathbf{r}}^M$ and $\hat{\mathbf{r}}^{N-1}$ are interrelated according to (1). In our previous paper [1] we showed that these equations of motion in the $\mathbf{r}$-, $\tilde{\mathbf{r}}$ and $\hat{\mathbf{r}}$-representation can be transformed into an equation of motion in a normal modes representation, *i.e.* the $\boldsymbol{\xi}$-representation:

$$\dot{\boldsymbol{\xi}}_i = \mathbf{L} \cdot \boldsymbol{\xi}_i - \frac{a_i}{\zeta}\left(kT \frac{\partial \log \bar{\psi}}{\partial \boldsymbol{\xi}_i} + \kappa \boldsymbol{\xi}_i\right), \tag{26}$$

where the vectors $\boldsymbol{\xi}_1, \boldsymbol{\xi}_2, \ldots, \boldsymbol{\xi}_{N-1}$ represent a set of normal coordinate vectors. The positive parameters a_i in (26) are the nonzero eigenvalues of the matrix A, $\widetilde{A}$ or $M\widehat{A}$ * and the $\boldsymbol{\xi}$-dependent configuration distribution function $\bar{\psi}$ in (26) is defined as

$$\bar{\psi}(\boldsymbol{\xi}^{N-1}, t) \equiv \psi(\mathbf{r}^N, t) \equiv \widetilde{\psi}(\tilde{\mathbf{r}}^M, t) \equiv \widehat{\psi}(\hat{\mathbf{r}}^{N-1}, t). \tag{27}$$

For an incompressible fluid the general expression for the stress tensor $\mathbf{T}$ is

$$\mathbf{T} = -p\mathbf{1} + \mathbf{T}^{\mathrm{E}}, \tag{28}$$

where $\mathbf{1}$ is a unit tensor, p the undetermined pressure and the extra stress tensor $\mathbf{T}^{\mathrm{E}}$ the part of the stress tensor $\mathbf{T}$ that, for a given fluid, is determined by its flow history. An expression for $\mathbf{T}^{\mathrm{E}}$ in terms of microscopic quantities is the so called 'Kramers form' [8, 6], *i.e*

$$\mathbf{T}^{\mathrm{E}} = 2\eta_{\mathrm{s}}\mathbf{D} - (N-1)nkT\mathbf{1} + n\sum_{a=1}^{M}\langle \tilde{\mathbf{r}}_a \tilde{\mathbf{f}}_a \rangle, \tag{29}$$

where η_{s} is the viscosity of the Newtonian solvent, n the number of bead-spring structures in a unit volume, $\mathbf{D} = \frac{1}{2}(\mathbf{L} + \mathbf{L}^T)$ the rate-of-strain tensor and $\langle \cdots \rangle$ denotes an average with respect to the distribution function in configuration space. Throughout this paper we are only considering the case that $n = 1/V_{\mathrm{s}}$, *i.e.* one bead-spring structure in a volume V_{s}. In the $\boldsymbol{\xi}$-representation the extra stress tensor $\mathbf{T}^{\mathrm{E}}$ in (29) is given by

$$\mathbf{T}^{\mathrm{E}} = 2\eta_{\mathrm{s}}\mathbf{D} + \sum_{i=1}^{N-1}\mathbf{T}_i^{\mathrm{P}} \tag{30}$$

with the particle contribution to the stress tensor given by [1]

$$\mathbf{T}_i^{\mathrm{P}} = \frac{\kappa}{V_{\mathrm{s}}}\langle \boldsymbol{\xi}_i \boldsymbol{\xi}_i \rangle - \frac{kT}{V_{\mathrm{s}}}\mathbf{1}. \tag{31}$$

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* Indeed, the three sets of nonzero eigenvalues belonging to A, $\widetilde{A}$ and $M\widehat{A}$ are identical [1].

By transforming the equation of continuity for $\psi(\mathbf{r}^N, t)$ given by (19) into an equation of continuity for $\bar{\psi}(\boldsymbol{\xi}^{N-1}, t)$, by multiplying both sides of the resulting equation by the dyadic $\boldsymbol{\xi}_i\boldsymbol{\xi}_i$ and by integrating it over the entire $\boldsymbol{\xi}$-space we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\boldsymbol{\xi}_i\boldsymbol{\xi}_i\rangle = \langle\dot{\boldsymbol{\xi}}_i\boldsymbol{\xi}_i\rangle + \langle\boldsymbol{\xi}_i\dot{\boldsymbol{\xi}}_i\rangle. \tag{32}$$

By combining (26), (31) and (32) we obtain a constitutive equation of the upper convected Maxwell type

$$\mathbf{T}_i^{\mathrm{p}} + \lambda_i \frac{\delta \mathbf{T}_i^{\mathrm{p}}}{\delta t} = \frac{2kT\lambda_i}{V_{\mathrm{s}}}\mathbf{D}, \tag{33}$$

where the relaxation times λ_i are equal to $\zeta/(2\kappa a_i)$ and is $\delta/\delta t$ the upper convective derivative defined as

$$\frac{\delta \mathbf{T}_i^{\mathrm{p}}}{\delta t} = \frac{\mathrm{d}\mathbf{T}_i^{\mathrm{p}}}{\mathrm{d}t} - \mathbf{L}\cdot\mathbf{T}_i^{\mathrm{p}} - \mathbf{T}_i^{\mathrm{p}}\cdot\mathbf{L}^T. \tag{34}$$

3.2. Relaxation times belonging to a cubic bead-spring structure

To calculate the relaxation times λ_i belonging to a cubic bead-spring structure consisting of equal Hookean springs immersed in a Newtonian fluid, we must determine the nonzero eigenvalues of the matrix A, $\widetilde{A}$ or $M\widehat{A}$ belonging to a $K\times K\times K$ bead-spring cube (SC, BCC or FCC) and substitute these eigenvalues a_i in the relation $\lambda_i = \zeta/(2\kappa a_i)$. In this section we are only considering the eigenvalues of matrix A.

By using (5) we obtain the following expressions for the symmetric matrix $A = \widetilde{G}^T\widetilde{G}$

$$A^{\mathrm{sc}} = G^TG\otimes\delta_K\otimes\delta_K + \delta_K\otimes G^TG\otimes\delta_K + \delta_K\otimes\delta_K\otimes G^TG, \tag{35}$$

$$A^{\mathrm{bcc}} = A^{\mathrm{sc}} + H^{\mathrm{bcc}\,T}H^{\mathrm{bcc}}, \tag{36}$$

$$A^{\mathrm{fcc}} = A^{\mathrm{sc}} + H^{\mathrm{fcc}\,T}H^{\mathrm{fcc}}. \tag{37}$$

For the determination of the nonzero eigenvalues a_i^{sc} of matrix A^{sc} we make use of Theorem 4.4.5 in Horn and Johnson [4], *i.e.*

THEOREM 1. *If the eigenvalues of an arbitrary $P\times P$ matrix X and an arbitrary $Q\times Q$ matrix Y are given by $x_1, x_2, \ldots, x_P$ and $y_1, y_2, \ldots, y_Q$ respectively, then the eigenvalues of the so called Kronecker sum $(\delta_Q\otimes X)+(Y\otimes\delta_P)$ are given by x_i+y_j with $i=1\ldots P$ and $j=1\ldots Q$.*

and we use the fact that the $K\times K$ matrix G^TG appearing in (35) is identical to the Rouse matrix belonging to a linear chain consisting of K beads and $K-1$ springs and that the K eigenvalues of G^TG are given by [6]

$$4\sin^2\left(\frac{i\pi}{2K}\right) \quad \text{with} \quad i=0\ldots(K-1).$$

From Theorem 1, the known eigenvalues of matrix $G^T G$ and the expression for matrix $A^{\rm sc}$ given by (35) we obtain an expression for the $K^3 - 1$ nonzero eigenvalues $a_i^{\rm sc}$ and by substituting this result in the relation for the relaxation times $\lambda_i^{\rm sc} = \zeta/(2\kappa a_i^{\rm sc})$, we obtain

$$\lambda_i^{\rm sc} \equiv \lambda_{klm}^{\rm sc} = \frac{\zeta}{8\kappa\left(\sin^2\left(\frac{k\pi}{2K}\right) + \sin^2\left(\frac{l\pi}{2K}\right) + \sin^2\left(\frac{m\pi}{2K}\right)\right)}$$

$$\text{with} \quad \begin{cases} i = K^2 k + Kl + m \\ k = 0 \ldots (K-1) \\ l = 0 \ldots (K-1) \\ m = 0 \ldots (K-1), \end{cases} \tag{38}$$

where we have to exclude the case that $k = 0$, $l = 0$ and $m = 0$. We note that all these relaxation times are larger than the minimum relaxation time $\lambda_{\rm min}^{\rm sc}$ defined by

$$\lambda_{\rm min}^{\rm sc} = \frac{\zeta}{24\kappa}. \tag{39}$$

The expression for the $K^3 - 1$ relaxation times $\lambda_i^{\rm sc}$ given by (38) was also obtained by Van der Vorst *et al.* [9] and they managed to find this expression without explicitly determining eigenvalues of matrix $A^{\rm sc}$ or some other matrix. However, their straightforward method is not easily extended to the case of cubic bead-spring structures with a topology based upon a BCC or FCC lattice instead of a SC lattice.

Although it was rather easy to find an analytical expression for the nonzero eigenvalues $a_i^{\rm sc}$ of matrix $A^{\rm sc}$, we did not succeed in finding analytical expressions for the nonzero eigenvalues $a_i^{\rm bcc}$ and $a_i^{\rm fcc}$ of the matrices $A^{\rm bcc}$ and $A^{\rm fcc}$, respectively. Therefore, we calculated eigenvalues $a_i^{\rm bcc}$ and $a_i^{\rm fcc}$ numerically by using the software packages *Octave 1.1.1* and *Scilab-2.2*. We note that no significant differences are observed between the numerical results obtained by these two software packages. Furthermore, there is no significant difference between the analytical expression for $a_i^{\rm sc}$ and the numerically-determined eigenvalues $a_i^{\rm sc}$.

We note that the $K^3 \times K^3$ matrices $A^{\rm bcc}$ and $A^{\rm fcc}$ given by (36) and (37) are very large for a relatively small value of K (*i.e.* for $K = 20$ both matrices consist of 64 million ($= K^6$) matrix elements) and our limited computing power appears to be sufficient for calculating the 1727 nonzero eigenvalues $a_i^{\rm bcc}$ and $a_i^{\rm fcc}$ of the 1728×1728 matrices $A^{\rm bcc}$ and $A^{\rm fcc}$, respectively, belonging to a $12 \times 12 \times 12$ cubic bead-spring structure, but not for larger cubic bead-spring structures (*i.e.* $K > 12$).

To compare the three sets of relaxation times $\lambda_i^{\rm sc}$, $\lambda_i^{\rm bcc}$ and $\lambda_i^{\rm fcc}$, it is convenient to introduce the function $H(\lambda,\ \Delta\log_{10}\lambda)$ which is defined as the number of relaxation times λ_i satisfying $\log_{10}\lambda - \Delta\log_{10}\lambda < \log_{10}\lambda_i \leqslant \log_{10}\lambda + \Delta\log_{10}\lambda$. This relaxation spectrum $H(\lambda,\ \Delta\log_{10}\lambda)$ is calculated for a $K \times K \times K$ cubic bead-spring structure from the expression for $\lambda_i^{\rm sc}$ given by (38) and, for relatively small structures (*i.e.* $K \leqslant 12$), from the numerically calculated relaxation times $\lambda_i^{\rm bcc} = \zeta/(2\kappa a_i^{\rm bcc})$ and $\lambda_i^{\rm fcc} = \zeta/(2\kappa a_i^{\rm fcc})$. In Figure 2 we depict the reduced relaxation spectrum $H(\lambda,\ 0{\cdot}0022)/(K^3 - 1)$ as a function of the reduced time $\lambda/\lambda_{\rm min}^{\rm sc}$ for four different cases: *i.e.* two corresponding with a SC lattice ($K = 1000$ and $K = 12$), one with a BCC lattice ($K = 12$) and one with a FCC lattice ($K = 12$).

The four relaxation spectra in Figure 2 differ significantly from each other and we note that each spectrum in Figure 2 consists of 614 vertical lines (including the lines with zero lengths, *i.e.* the ones where $H(\lambda,\ 0{\cdot}0022)=0$), which correspond to the 614 nonoverlapping regions bounded by $\log_{10}\lambda - 0{\cdot}0022$ and $\log_{10}\lambda + 0{\cdot}0022$ with $(\lambda/\lambda^{\mathrm{sc}}_{\mathrm{min}}) \in \{0{\cdot}6,\ 0{\cdot}6\times 10^{0{\cdot}0044}, \ldots, 0{\cdot}6\times 10^{2{\cdot}6972}\}$.

The difference between Figure 2a (SC lattice and $K = 1000$) and Figure 2b (SC lattice and $K = 12$) is not surprising due to the fact that in Figure 2a we have nearly 10^9 relaxation times λ_i^{sc} to be distributed over 614 regions, while in Figure 2b we only have 1727 relaxation times λ_i^{sc}. In fact, if K increases, then the reduced relaxation spectrum $H(\lambda,\ 0{\cdot}0022)/(K^3-1)$ for $K = 12$ converges to the one for $K = 1000$ and it does not really change anymore for larger K. Furthermore, we observe that almost all relaxation times λ_i^{sc} are in the region $\lambda^{\mathrm{sc}}_{\mathrm{min}} \leqslant \lambda_i^{\mathrm{sc}} < 10\lambda^{\mathrm{sc}}_{\mathrm{min}}$ and by using (38) we find that, for large K, the maximum relaxation time $\lambda^{\mathrm{sc}}_{\mathrm{max}}$ is given by

$$\lambda^{\mathrm{sc}}_{\mathrm{max}} = \frac{12\lambda^{\mathrm{sc}}_{\mathrm{min}} K^2}{\pi^2} = \frac{\zeta K^2}{2\pi^2\kappa}. \tag{40}$$

The relaxation spectra $H(\lambda,\ 0{\cdot}0022)$ in Figures 2b (SC), 2c (BCC) and 2d (FCC) correspond to $K\times K\times K$ cubic bead-spring structures of the same size ($K = 12$). As mentioned in Section 2.2, we construct the last two cubic structures (BCC and FCC) by simply adding some springs ($M^{\mathrm{bcc}} - M^{\mathrm{sc}} = 1331$ and $M^{\mathrm{fcc}} - M^{\mathrm{sc}} = 4356$) to the first cubic structure (SC and $M^{\mathrm{sc}} = 4752$). As a result of this adding of springs the relaxation times λ_i^{bcc} and λ_i^{fcc} are on average smaller than the times λ_i^{sc}, as can be observed in Figure 2. In particular, the minimum relaxation times $\lambda^{\mathrm{bcc}}_{\mathrm{min}}$ and $\lambda^{\mathrm{fcc}}_{\mathrm{min}}$ are given by

$$\lambda^{\mathrm{bcc}}_{\mathrm{min}} = \lambda^{\mathrm{fcc}}_{\mathrm{min}} = \frac{3}{4}\lambda^{\mathrm{sc}}_{\mathrm{min}} = \frac{\zeta}{32\kappa} \tag{41}$$

and the maximum relaxation times belonging to a $12\times 12\times 12$ cubic bead-spring structure are given by $\lambda^{\mathrm{sc}}_{\mathrm{max}} = 176\lambda^{\mathrm{sc}}_{\mathrm{min}}$, $\lambda^{\mathrm{bcc}}_{\mathrm{max}} = 168\lambda^{\mathrm{sc}}_{\mathrm{min}}$ and $\lambda^{\mathrm{fcc}}_{\mathrm{max}} = 163\lambda^{\mathrm{sc}}_{\mathrm{min}}$. By extrapolating the results for $K \leqslant 12$ to large K we obtain

$$\lambda^{\mathrm{bcc}}_{\mathrm{max}} \approx \lambda^{\mathrm{fcc}}_{\mathrm{max}} \approx 1{\cdot}1\lambda^{\mathrm{sc}}_{\mathrm{min}} K^2. \tag{42}$$

We note that there are always three times λ_i^{sc} with value $\lambda^{\mathrm{sc}}_{\mathrm{max}}$, two times λ_i^{bcc} with value $\lambda^{\mathrm{bcc}}_{\mathrm{max}}$ and one time λ_i^{fcc} with value $\lambda^{\mathrm{fcc}}_{\mathrm{max}}$.

4. Storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$

In the previous section we observed that the relaxation spectra belonging to the three types of cubic bead-spring structures differ significantly from each other. In this section we are interested in the rheological consequences of these differences for the case that a $K\times K\times K$ cubic bead-spring structure is immersed in a Newtonian fluid of volume V_s on which a small-

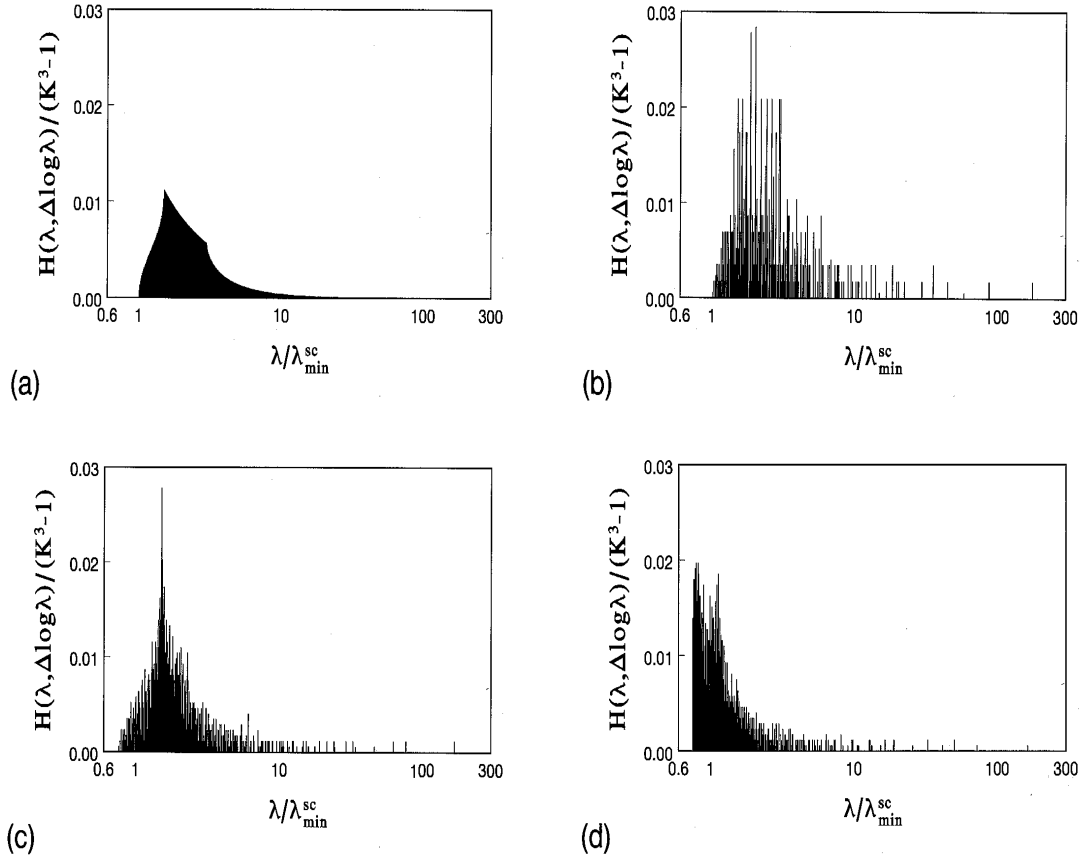

Figure 2. The relaxation spectrum $H(\lambda, \Delta \log_{10} \lambda = 0{\cdot}0022)$ for a $K \times K \times K$ cubic bead-spring structure: (a) $K = 1000$ and a topology based upon a SC lattice, (b) $K = 12$ and a topology based upon a SC lattice, (c) $K = 12$ and a topology based upon a BCC lattice and (d) $K = 12$ and a topology based upon a FCC lattice.

amplitude oscillatory shear flow with angular frequency ω is applied. The measurable rheological quantities are then the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ [6].

Instead of considering a $K \times K \times K$ cubic bead-spring structure (immersed in a Newtonian fluid), we first consider the more general case of a structure with an arbitrary topology, which consists of N beads and M equal Hookean springs (see Section 3.1). For this case we obtained the constitutive equation given by (33) and it can be shown that the moduli $G'(\omega)$ and $G''(\omega)$ are related to the relaxation times λ_i in (33) as follows [6]

$$G'(\omega) = \frac{kT}{V_s} \sum_{i=1}^{N-1} \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2}, \tag{43}$$

$$G''(\omega) = \eta_s \omega + \frac{kT}{V_s} \sum_{i=1}^{N-1} \frac{\omega\lambda_i}{1 + (\omega\lambda_i)^2}. \tag{44}$$

By substituting $\lambda_i = \zeta/(2\kappa a_i)$ in (43) and (44) we obtain for low frequencies ($\omega \to 0$)

$$G'(\omega) \;=\; \frac{kT\zeta^2\omega^2}{4\kappa^2 V_s} \sum_{i=1}^{N-1} \left(\frac{1}{a_i}\right)^2 \;=\; \frac{kT\zeta^2\omega^2}{4\kappa^2 V_s}\,\mathrm{tr}\Big(\big[M\widehat{A}\,\big]^{-2}\Big)\,, \tag{45}$$

$$G''(\omega) - \eta_s\omega \;=\; \frac{kT\zeta\omega}{2\kappa V_s} \sum_{i=1}^{N-1} \frac{1}{a_i} \;=\; \frac{kT\zeta\omega}{2\kappa V_s}\,\mathrm{tr}\Big(\big[M\widehat{A}\,\big]^{-1}\Big) \tag{46}$$

and in the same way we obtain for high frequencies ($\omega \to \infty$)

$$G'(\omega) = \frac{kT}{V_s}\,(N-1)\,, \tag{47}$$

$$G''(\omega) - \eta_s\omega \;=\; \frac{2kT\kappa}{V_s\zeta\omega} \sum_{i=1}^{N-1} a_i \;=\; \frac{2kT\kappa}{V_s\zeta\omega}\,\mathrm{tr}\big(M\widehat{A}\,\big) \;=\; \frac{4kT\kappa}{V_s\zeta\omega}\,M. \tag{48}$$

In (45) and (46) we used the matrix $M\widehat{A} = D^T D\widehat{G}\widehat{G}^T$ instead of the equivalent matrices $A = \widetilde{G}^T\widetilde{G}$ and $\widetilde{A} = \widetilde{G}\widetilde{G}^T$ for the reason that the first one is nonsingular (its inverse exists), while the latter two are singular (their inverses do not exist). In (48) we used the following relation for the trace of matrix $M\widehat{A}$ *

$$\mathrm{tr}(M\widehat{A}\,) = \mathrm{tr}(A\,) = \mathrm{tr}(\widetilde{A}\,) = 2M. \tag{49}$$

We emphasize that (49) is valid for any bead-spring structure consisting of N beads and M springs, *i.e.* the validity of this relation does not depend upon the specific topology of the bead-spring structure. Thus, for high frequencies the storage modulus $G'(\omega)$ is proportional to the number of springs in the spanning tree (*i.e.* $N-1$) and the loss modulus $G''(\omega)-\eta_s\omega$ is proportional to the number of springs in the entire bead-spring structure (*i.e.* M).

4.1. Cubic bead-spring structure with topology based upon SC lattice

The relaxation times λ_i^{sc} belonging to a $K\times K\times K$ cubic bead-spring structure with a topology based upon a SC lattice are given by (38) and by substituting these relaxation times in (43) and (44) we can calculate the moduli $G'(\omega)$ and $G''(\omega)$ for different values of K. These calculations will indicate that three different frequency regions can be distinguished, *i.e.* a low, an intermediate and a high frequency region. The two boundaries of these three regions depend on the values of the minimum and maximum relaxation times $\lambda_{\mathrm{min}}^{\mathrm{sc}}$ and $\lambda_{\mathrm{max}}^{\mathrm{sc}}$ as defined by (39) and (40), respectively. For each region we have obtained asymptotic expressions for the moduli $G'(\omega)$ and $G''(\omega)$, which are consistent with equivalent asymptotic expressions obtained by Van der Vorst *et al* [9].

In the low frequency region and for large K, *i.e.* $\omega\lambda_{\mathrm{min}}^{\mathrm{sc}} \ll \omega\lambda_{\mathrm{max}}^{\mathrm{sc}} \ll 1$, the expressions for $G'(\omega)$ and $G''(\omega)$ given by (45) and (46), respectively, are given by

$$G'(\omega) \;=\; \frac{kT}{V_s}(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}})^2 \sum_{i=1}^{K^3-1} \left(\frac{12}{a_i^{\mathrm{sc}}}\right)^2 \;\approx\; 7{\cdot}596\,\frac{kT}{V_s}(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}})^2 K^4, \tag{50}$$

* The first M in (48) and (49) refers to the matrix $M = D^T D$, while the second M refers to the number of springs in the entire bead-spring structure.

$$G''(\omega) - \eta_s\omega \;=\; \frac{kT}{V_s}(\omega\lambda_{\min}^{sc}) \sum_{i=1}^{K^3-1} \frac{12}{a_i^{sc}} \;\approx\; 3{\cdot}034\,\frac{kT}{V_s}(\omega\lambda_{\min}^{sc})K^3, \tag{51}$$

where $a_i^{sc} = \zeta/(2\kappa\lambda_i^{sc})$ with λ_i^{sc} as defined by (38).

In the intermediate frequency region and for large K, *i.e.* $\omega\lambda_{\min}^{sc} \ll 1 \ll \omega\lambda_{\max}^{sc}$, it is useful to introduce a function c_{klm} as follows

$$\lambda_i^{sc} \equiv \lambda_{klm}^{sc} = \frac{c_{klm}\,\lambda_{\max}^{sc}}{k^2+l^2+m^2}, \tag{52}$$

where the function c_{klm} is dependent upon the indices k, l and m in such a way that the relaxation times λ_i^{sc} given by (52) are identical to the relaxation times λ_i^{sc} given by (38). By noting that the values of the relaxation times λ_{klm}^{sc} given by (38) are bounded as

$$\frac{\lambda_{\max}^{sc}}{k^2+l^2+m^2} < \lambda_{klm}^{sc} < \frac{\pi^2}{4}\left(\frac{\lambda_{\max}^{sc}}{k^2+l^2+m^2}\right), \tag{53}$$

we obtain that the values of the function c_{klm} are bounded as $1 < c_{klm} < 2{\cdot}47$. By assuming that the function c_{klm} may be approximated by a constant, *i.e.* $c_{klm} = c$, by substituting (52) in (43) and (44), by replacing the summations by integrations and by using the transformation $\rho^2 = k^2+l^2+m^2$, we obtain

$$G'(\omega) \approx \frac{\pi}{2}\frac{kT}{V_s}\int_1^{\sqrt{3}K} \frac{\rho^2\left(c\omega\lambda_{\max}^{sc}\right)^2}{\rho^4+\left(c\omega\lambda_{\max}^{sc}\right)^2}\,d\rho \;\approx\; \frac{3\sqrt{6}}{\pi}\frac{kT}{V_s}\left(c\omega\lambda_{\min}^{sc}\right)^{3/2}K^3, \tag{54}$$

$$G''(\omega) - \eta_s\omega \approx \frac{\pi}{2}\frac{kT}{V_s}\int_1^{\sqrt{3}K} \frac{\rho^4\left(c\omega\lambda_{\max}^{sc}\right)}{\rho^4+\left(c\omega\lambda_{\max}^{sc}\right)^2}\,d\rho \;\approx\; \frac{6\sqrt{3}}{\pi}\frac{kT}{V_s}\left(c\omega\lambda_{\min}^{sc}\right)K^3. \tag{55}$$

The deviations between these approximations and the exact calculation of the moduli $G'(\omega)$ and $G''(\omega)$ appear to be minimized (for large K) if we substitute the constants $c = 1{\cdot}1$ and $c = 0{\cdot}9$* in (54) and (55), respectively, *i.e.*

$$G'(\omega) \approx 2{\cdot}7\,\frac{kT}{V_s}\left(\omega\lambda_{\min}^{sc}\right)^{3/2}K^3, \tag{56}$$

$$G''(\omega) - \eta_s\omega \approx 3{\cdot}0\,\frac{kT}{V_s}\left(\omega\lambda_{\min}^{sc}\right)K^3. \tag{57}$$

We note that (51) and (57) are identical, *i.e.* the frequency dependency of the loss modulus $G''(\omega)$ is in the low frequency region and in the intermediate region the same.

In the high frequency region and for all K, *i.e.* $1 \ll \omega\lambda_{\min}^{sc} < \omega\lambda_{\max}^{sc}$, the expressions for $G'(\omega)$ and $G''(\omega)$ given by (47) and (48), respectively, are given by

$$G'(\omega) \;=\; \frac{kT}{V_s}(K^3-1), \tag{58}$$

* The constant $c = 0{\cdot}9$ does not satisfy the condition $1 < c < 2{\cdot}47$ as a result of the replacement of the summations in (43) and (44) by integrations.

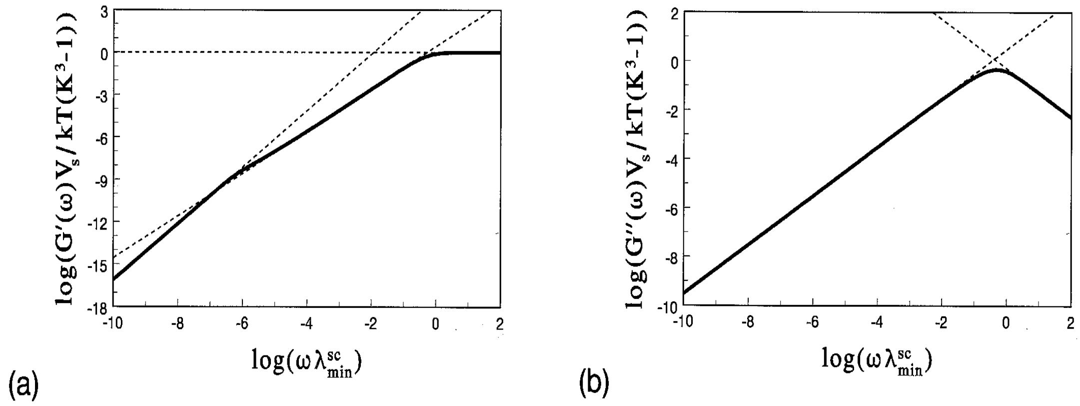

Figure 3. The moduli $G'(\omega)$ and $G''(\omega)$ belonging to a $1000 \times 1000 \times 1000$ cubic bead-spring structure with a topology based upon a SC lattice immersed in a Newtonian fluid with $\eta_s = 0$, *i.e.* (a) the reduced storage modulus $\log_{10} G'(\omega)V_s/kT(K^3-1)$ as a function of reduced frequency $\log_{10} \omega\lambda^{sc}_{min}$ (the dashed lines are the asymptotic expressions given by (50), (56) and (58) and the thick line is its exact calculation) and (b) the reduced loss modulus $\log_{10} G''(\omega)V_s/kT(K^3-1)$ as a function of reduced frequency $\log_{10} \omega\lambda^{sc}_{min}$ (the dashed lines are asymptotic expressions given by (51), (57) and (59) and the thick line is its exact calculation).

$$G''(\omega) - \eta_s\omega = \frac{1}{6}\frac{kT}{V_s}(\omega\lambda^{sc}_{min})^{-1}M^{sc} = \frac{1}{2}\frac{kT}{V_s}(\omega\lambda^{sc}_{min})^{-1}K^2(K-1), \tag{59}$$

where $M^{sc} = 3K^2(K-1)$ is the number of springs in a $K \times K \times K$ cubic bead-spring structure with a topology based upon a SC lattice.

As an example we consider a $1000 \times 1000 \times 1000$ cubic bead-spring structure consisting of equal Hookean springs and with a topology based upon a SC lattice, which is immersed in a Newtonian fluid with viscosity $\eta_s = 0$. By substituting the $10^9 - 1$ relaxation times λ_i^{sc} given by (38) in (43) and (44) and by evaluating the summations numerically, we obtain an exact calculation of the moduli $G'(\omega)$ and $G''(\omega)$. In Figure 3a we compare the exact calculation of $G'(\omega)$ with the three approximations for the storage modulus given by (50), (56) and (58) and in Figure 3b we compare the exact calculation of $G''(\omega)$ with the three approximations for the loss modulus given by (51), (57) and (59). In both figures the two boundaries of the three different frequency regions are given by $\log_{10}(\omega\lambda^{sc}_{min}) = 0$ and $\log_{10}(\omega\lambda^{sc}_{min}) = -6 \cdot 1$ (*i.e.* $\log_{10}(\omega\lambda^{sc}_{max}) = 0$) and we observe that the approximations for the three frequency regions do approximate the exact calculation of the moduli very well.

4.2. The three types of bead-spring cubes (SC, BCC and FCC)

The moduli $G'(\omega)$ and $G''(\omega)$ belonging to the three types of bead-spring cubes (SC, BCC and FCC) are obtained by substituting the relaxation times λ_i^{sc}, λ_i^{bcc} and λ_i^{fcc} in (43) and (44), respectively. Here, the relaxation times λ_i^{sc} are given by (38) and, as mentioned in Section 3.2, the relaxation times λ_i^{bcc} and λ_i^{fcc} have to be calculated numerically, which was only possible, due to our limited computing power, for $K \times K \times K$ cubic bead-spring structures with $K \leqslant 12$ and not for larger structures.

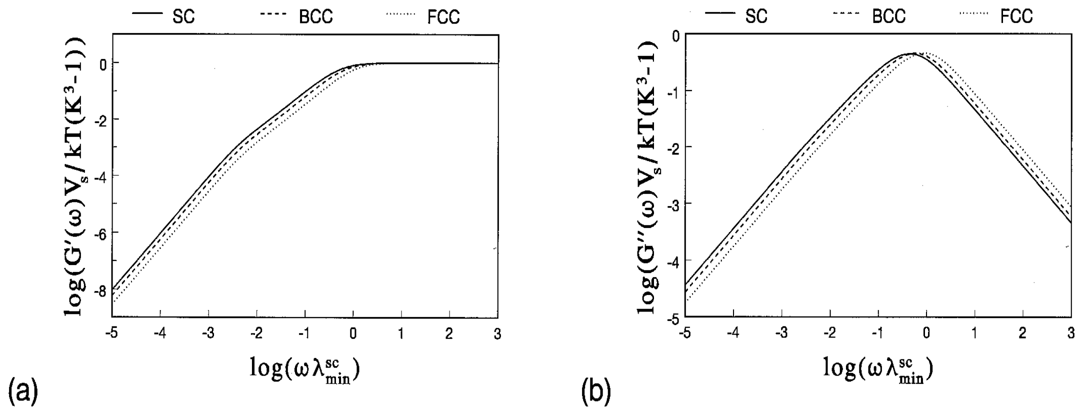

Figure 4. The moduli $G'(\omega)$ and $G''(\omega)$ belonging to a $12 \times 12 \times 12$ bead-spring cube (SC, BCC and FCC) immersed in a Newtonian fluid with $\eta_s = 0$, *i.e.* (a) the reduced storage modulus $\log_{10} G'(\omega)V_s/kT(K^3-1)$ as a function of reduced frequency $\log_{10} \omega\lambda_{i\,\mathrm{min}}^{\mathrm{sc}}$ and (b) the reduced loss modulus $\log_{10} G''(\omega)V_s/kT(K^3-1)$ as a function of reduced frequency $\log_{10} \omega\lambda_{\mathrm{min}}^{\mathrm{sc}}$.

In Figure 4 we give the moduli $G'(\omega)$ and $G''(\omega)$ belonging to a $12\times12\times12$ bead-spring cube (SC, BCC and FCC) consisting of equal Hookean springs immersed in a Newtonian fluid with viscosity $\eta_s = 0$. We observe that the three different relaxation spectra given in Figures 2b, 2c and 2d lead to moduli $G'(\omega)$ and $G''(\omega)$ which differ mainly from each other in one aspect: shifting the SC moduli a distance $d^{\mathrm{bcc}} \approx 0{\cdot}1$ and $d^{\mathrm{fcc}} \approx 0{\cdot}3$ to the right along the reduced frequency axis, we will obtain, approximately, the BCC and FCC moduli, respectively. In fact, in every frequency region (low, intermediate and high) the frequency dependency (*i.e.* the slope) of the moduli $G'(\omega)$ and $G''(\omega)$ can be considered to be independent of the specific topology (SC, BCC and FCC) of the cubic bead-spring structure.

In the previous section we obtained asymptotic expressions for the moduli $G'(\omega)$ and $G''(\omega)$ belonging to a $K \times K \times K$ cubic bead-spring structure with a topology based upon a SC lattice. The same kind of asymptotic expression appears to be valid for the case that the topology of a cubic bead-spring structure is based upon a BCC or FCC lattice, instead of a SC lattice. For low frequencies and for large K we obtain expressions which are reminiscent of (50) and (51)

$$\text{BCC:}\quad G'(\omega) \approx 4{\cdot}3\,\frac{kT}{V_s}(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}})^2K^4, \qquad G''(\omega) - \eta_s\omega \approx 2{\cdot}2\,\frac{kT}{V_s}(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}})K^3, \tag{60}$$

$$\text{FCC:}\quad G'(\omega) \approx 2{\cdot}1\,\frac{kT}{V_s}(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}})^2K^4, \qquad G''(\omega) - \eta_s\omega \approx 1{\cdot}4\,\frac{kT}{V_s}(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}})K^3. \tag{61}$$

For intermediate frequencies and for large K we obtain expressions which are reminiscent of (56) and (57)

$$\text{BCC:}\quad G'(\omega) \approx 1{\cdot}6\,\frac{kT}{V_s}\left(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}}\right)^{3/2}K^3, \qquad G''(\omega) - \eta_s\omega \approx 2{\cdot}2\,\frac{kT}{V_s}\left(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}}\right)K^3, \tag{62}$$

$$\text{FCC:}\quad G'(\omega) \approx 0{\cdot}8\,\frac{kT}{V_s}\left(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}}\right)^{3/2}K^3, \qquad G''(\omega) - \eta_s\omega \approx 1{\cdot}4\,\frac{kT}{V_s}\left(\omega\lambda_{\mathrm{min}}^{\mathrm{sc}}\right)K^3. \tag{63}$$

For high frequencies and for all K we obtain expressions which are reminiscent of (58) and (59)

$$\text{BCC:}\quad G'(\omega) = \frac{kT}{V_\mathrm{s}}(K^3-1), \qquad G''(\omega) - \eta_\mathrm{s}\omega = \frac{1}{6}\frac{kT}{V_\mathrm{s}}\,(\omega\lambda^{\mathrm{sc}}_{\min})^{-1}M^{\mathrm{bcc}}, \tag{64}$$

$$\text{FCC:}\quad G'(\omega) = \frac{kT}{V_\mathrm{s}}(K^3-1), \qquad G''(\omega) - \eta_\mathrm{s}\omega = \frac{1}{6}\frac{kT}{V_\mathrm{s}}\,(\omega\lambda^{\mathrm{sc}}_{\min})^{-1}M^{\mathrm{fcc}}. \tag{65}$$

At the beginning of this section we introduced the distances d^{bcc} and d^{fcc}. By combining the expressions for the high frequency loss modulus $G''(\omega)$ given by (59), (64) and (65) we obtain that $d^{\mathrm{bcc}} = \log_{10}(M^{\mathrm{bcc}}/M^{\mathrm{sc}})$ and $d^{\mathrm{fcc}} = \log_{10}(M^{\mathrm{fcc}}/M^{\mathrm{sc}})$, where M^{sc}, M^{bcc} and M^{fcc} are defined in (4) and are equal to the number of springs in a $K\times K\times K$ bead-spring cube (SC, BCC and FCC).

The rheological consequences of these expressions for d^{bcc} and d^{fcc} are interesting: if we depict in a figure the reduced SC moduli $\log_{10} G'(\omega)V_\mathrm{s}/kT(K^3-1)$ and $\log_{10} G''(\omega)V_\mathrm{s}/kT(K^3-1)$ as a function of the reduced frequency $\log_{10}\omega\lambda^{\mathrm{sc}}_{\min}$, then we observe that the same figure is also valid, approximately, for the reduced BCC and FCC moduli, which are now depicted as functions of the reduced frequencies $\log_{10}(\omega\lambda^{\mathrm{sc}}_{\min}M^{\mathrm{sc}}/M^{\mathrm{bcc}})$ and $\log_{10}(\omega\lambda^{\mathrm{sc}}_{\min}M^{\mathrm{sc}}/M^{\mathrm{fcc}})$, respectively. Thus, the characteristic SC time scale has to be multiplied by the ratios $M^{\mathrm{sc}}/M^{\mathrm{bcc}}$ and $M^{\mathrm{sc}}/M^{\mathrm{fcc}}$ to obtain the characteristic BCC and FCC time scale, respectively.

5. Concluding remarks

So far we have given a bead-spring formalism about some rheological properties of a $K\times K\times K$ Hookean bead-spring cube (SC, BCC and FCC) immersed in a Newtonian fluid. In subsequent papers we will modify this formalism by replacing the Hookean springs by nonlinear ones with nonzero equilibrium lengths and we will use this new formalism for the modeling of a colloidal crystal.

The bead-spring formalism in this paper contains many results which will be useful for our future work, *e.g.* the expressions for the topology matrices $\widetilde{G}$, $\widehat{G}$ and D belonging to a bead-spring cube (SC, BCC and FCC) given in Section 2.3 will not change if only the characteristics of the springs are changed. Furthermore, at the end of Section 4.2 we mentioned that the characteristic BCC and FCC time scales were obtained by simply multiplying the characteristic SC time scale by the ratios $M^{\mathrm{sc}}/M^{\mathrm{bcc}}$ and $M^{\mathrm{sc}}/M^{\mathrm{fcc}}$, respectively, and it is interesting to investigate if this relation between time scales is not only valid for linear springs, but also valid for nonlinear ones.

Another way of modifying the bead-spring formalism in this paper is that where one does not restrict oneself to bead-spring structures with a topology based upon a cubic lattice. In this case we only have to find appropriate expressions for the topology matrices $\widetilde{G}$, $\widehat{G}$ and D belonging to some chosen bead-spring structure (*e.g.* a structure with a topology based upon a hexagonal lattice). An important piece of work concerning different kinds of Hookean bead-spring structures was presented by Sammler *et al.* [10, 11, 12]. Their work includes ring-shaped structures, combs, cyclic combs, stars and H-shaped structures, but excludes crystal-like structures as presented in this paper.

Appendix

Nonzero matrix elements of $\widetilde{G}^{\mathrm{sc}}$, $\widehat{G}^{\mathrm{sc}}$ and D^{sc}

For a 3×3×3 bead-spring cube with a topology based upon a SC lattice, the nonzero matrix elements of $\widetilde{G}^{\mathrm{sc}}$ and $\widehat{G}^{\mathrm{sc}}$, as defined by (5) and (9), are given by

$$
\widetilde{G}^{\mathrm{sc}} = \begin{pmatrix} G \otimes \delta_3 \otimes \delta_3 \\ \delta_3 \otimes G \otimes \delta_3 \\ \delta_3 \otimes \delta_3 \otimes G \end{pmatrix} = \begin{array}{*{27}{c}}
-1&&&&&&&&&1 \\
&-1&&&&&&&&&1 \\
&&-1&&&&&&&&&1 \\
&&&-1&&&&&&&&&1 \\
&&&&-1&&&&&&&&&1 \\
&&&&&-1&&&&&&&&&1 \\
&&&&&&-1&&&&&&&&&1 \\
&&&&&&&-1&&&&&&&&&1 \\
&&&&&&&&-1&&&&&&&&&1 \\
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&&&&&&&&&&&&&&&&&&&-1&1 \\
&&&&&&&&&&&&&&&&&&&&&-1&1 \\
&&&&&&&&&&&&&&&&&&&&&&-1&1 \\
&&&&&&&&&&&&&&&&&&&&&&&&-1&1 \\
&&&&&&&&&&&&&&&&&&&&&&&&&-1&1
\end{array}
$$

$$
\widehat{G}^{\mathrm{sc}} = \begin{pmatrix} G \otimes \delta_3 \otimes \delta_3 \\ G \otimes \delta_3 \quad O_{6\times 18} \\ G \quad O_{2\times 24} \end{pmatrix} = \begin{array}{*{27}{c}}
-1&&&&&&&&&1 \\
&-1&&&&&&&&&1 \\
&&-1&&&&&&&&&1 \\
&&&-1&&&&&&&&&1 \\
&&&&-1&&&&&&&&&1 \\
&&&&&-1&&&&&&&&&1 \\
&&&&&&-1&&&&&&&&&1 \\
&&&&&&&-1&&&&&&&&&1 \\
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&&&&&&&&&&&&&&&&&-1&&&&&&&&&1 \\
-1&&&1 \\
&-1&&&1 \\
&&-1&&&1 \\
&&&-1&&&1 \\
&&&&-1&&&1 \\
&&&&&-1&&&1 \\
-1&1 \\
&-1&1
\end{array}
$$

in which we easily recognize the identity matrices δ_3 and $\delta_9 = \delta_3 \otimes \delta_3$, the zero matrices $O_{6\times 18}$ and $O_{2\times 24}$ and the matrix G given by

$$
G = \begin{pmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \end{pmatrix}.
$$

For a 3×3×3 bead-spring cube with a topology based upon a SC lattice, the nonzero matrix elements of D^{sc}, as defined by (10), are given by

$$D^{\mathrm{sc}} = \begin{pmatrix} \delta_3 \otimes \delta_3 \otimes \delta_2 & O_{18\times 6} & O_{18\times 2} \\ S \otimes G \otimes \delta_3 & V_3 \otimes \delta_3 \otimes \delta_2 & O_{18\times 2} \\ S \otimes \delta_3 \otimes G & V_3 \otimes S \otimes G & V_3 \otimes V_3 \otimes \delta_2 \end{pmatrix},$$

$$= \left|\begin{array}{*{18}{c}|*{6}{c}|cc}
1 &&&&& &&&&& &&&&& &&&&& &&&&& \\
& 1 &&&&& &&&&& &&&&& &&&&& &&&& \\
&& 1 &&&&& &&&&& &&&&& &&&&& &&& \\
&&& 1 &&&&& &&&&& &&&&& &&&&& && \\
&&&& 1 &&&&& &&&&& &&&&& &&&&& & \\
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&&&&& &&&&& &&&&& &&&&& && 1 &&& \\
&&&&& &&&&& &&&&& &&&&& &&& 1 && \\
-1 &&& 1 &&&&& &&&&& &&&&& 1 &&&&& && \\
& -1 &&& 1 &&&&& &&&&& &&&&& 1 &&&&& & \\
&& -1 &&& 1 &&&&& &&&&& &&&&& 1 &&&&& \\
&&& -1 &&& 1 &&&&& &&&&& &&&&& 1 &&&& \\
&&&& -1 &&& 1 &&&&& &&&&& &&&&& 1 &&& \\
&&&&& -1 &&& 1 &&&&& &&&&& &&&&& 1 && \\
-1 &&& 1 &&&&& & -1 &&& 1 &&&&& & 1 &&&&& && \\
& -1 &&& 1 &&&&& & -1 &&& 1 &&&&& & 1 &&&&& & \\
&& -1 &&& 1 &&&&& & -1 &&& 1 &&&&& & 1 &&&&& \\
&&& -1 &&& 1 &&&&& & -1 &&& 1 &&&&& & 1 &&&& \\
&&&& -1 &&& 1 &&&&& & -1 &&& 1 &&&&& & 1 &&& \\
&&&&& -1 &&& 1 &&&&& & -1 &&& 1 &&&&& & 1 && \\ \hline
&&&&& &&&&& &&&&& &&&&& &&&& 1 & \\
&&&&& &&&&& &&&&& &&&&& &&&&& 1 \\
&&&&& &&&&& &&&&& &&& -1 & 1 &&&&& 1 & \\
&&&&& &&&&& &&&&& &&&& -1 & 1 &&&&& 1 \\
&&&&& &&&&& &&&&& &&& -1 & 1 && -1 & 1 && 1 & \\
&&&&& &&&&& &&&&& &&&& -1 & 1 && -1 & 1 && 1 \\
-1 & 1 &&&&& &&&&& &&&&& &&&&& &&& 1 & \\
& -1 & 1 &&&&& &&&&& &&&&& &&&&& &&& 1 \\
&&& -1 & 1 &&&&& &&&&& &&&& -1 & 1 &&&&& 1 & \\
&&&& -1 & 1 &&&&& &&&&& &&&& -1 & 1 &&&&& 1 \\
&&&&& & -1 & 1 &&&&& &&&&& & -1 & 1 && -1 & 1 && 1 & \\
&&&&& && -1 & 1 &&&&& &&&&& & -1 & 1 && -1 & 1 && 1 \\
-1 & 1 &&&&& &&& -1 & 1 &&&&& &&&&& &&&& 1 & \\
& -1 & 1 &&&&& &&& -1 & 1 &&&&& &&&&& &&&& 1 \\
&&& -1 & 1 &&&&& &&& -1 & 1 &&&&& -1 & 1 &&&&& 1 & \\
&&&& -1 & 1 &&&&& &&& -1 & 1 &&&&& -1 & 1 &&&&& 1 \\
&&&&& & -1 & 1 &&&&& &&& -1 & 1 && -1 & 1 && -1 & 1 && 1 & \\
&&&&& && -1 & 1 &&&&& &&& -1 & 1 && -1 & 1 && -1 & 1 && 1
\end{array}\right|$$

in which we easily recognize the identity matrices δ_2, δ_3, $\delta_6 = \delta_3 \otimes \delta_2$, $\delta_{18} = \delta_3 \otimes \delta_3 \otimes \delta_2$, the zero matrices $O_{18\times 6}$ and $O_{18\times 2}$, and the matrix G, the step matrix S and the column vector V_3 given by

$$G = \begin{pmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \end{pmatrix}, \qquad S = \begin{pmatrix} 0 & 0 \\ 1 & 0 \\ 1 & 1 \end{pmatrix}, \qquad V_3 = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}.$$

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