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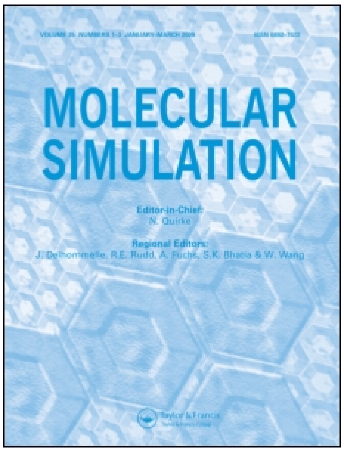

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Dissipative particle dynamics of non-spherical particles using a Gaussian density model

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The Gaussian density molecular model has been adapted for dissipative particle dynamics. The model, when combined with a soft potential, is shown to be a very flexible mesoscale model exhibiting a wide range of phase behaviour. The soft potential allows relatively large time steps to be used and hence a more rapid equilibration. In addition, the model can be used to study both uniaxial and biaxial systems. We have undertaken a number of pilot studies and have demonstrated that the Gaussian model is able to identify nematic–isotropic phase transitions in liquid crystals and the formation of ordered discotic phases.

Keywords: dissipative particle dynamics; Gaussian density model; liquid crystal

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1. Introduction

The organisation and transformation of matter over extended length and timescales is a key challenge in the design of functional materials (e.g. controlled crystallisation and supramolecular assembly) [1] and colloidal suspensions with a wide variety of industrial applications (e.g. lubricants, cosmetics and soaps). Consequently, these materials have received a detailed investigation both experimentally and theoretically.

Despite the rapid increase in computer power, the calculation of the self-assembly or the physical properties of large, complex molecules on the atomic scale is still not feasible due to the number of atoms required in the simulation cell and the long equilibration times required [2]. To overcome the problems arising from the number of particles in the simulation cell, a number of coarse-grained models have been developed and benefited from a simplified description of the interaction of particles. These models include the merger of two or more atoms to form a bead [3,4] and the Gay–Berne particles [5]. Both models have been used successfully to study a range of molecules (e.g. lipids and liquid crystals) using molecular dynamics (MD) and Monte Carlo simulations. The Gay–Berne model has been used extensively to study liquid crystals or discotic systems since it is possible to construct non-spherical beads [6,7].

Access to longer timescales can be achieved through employing dissipative particle dynamics (DPD) [8,9]. The advantage of DPD over conventional MD is that a much softer potential function is used to describe the particle–particle interactions, which enables fast structural relaxation, even at high densities, and therefore the simulation explores the accessible phase space rapidly and also quickly reaches equilibration. A number of researchers have developed DPD models to study mesogens using rigid bodies of many beads to mimic non-spherical particles [4,10]. However, the number of beads/particles still influences the size of the calculation and it is desirable to develop a model similar to that of Gay–Berne in MD for DPD. With this in mind, a number of soft-core spherocylinder potentials have been investigated using MD [11], where the soft-core potential function depends on the distance between two line segments representing two spherocylindrical mesogens.

In this paper, we develop a model for DPD that is based on non-spherical particles represented by Gaussian density functions. This resembles the Gaussian overlap model devised by Berne and colleagues [12,13], but is significantly different in the details. The Gaussian density model was first devised by Smith and Singer [14] and subsequently by Ayton and Patey [15]. The model used in this study is identical to that of Smith and Singer [14], which had its origins in Gaussian wavepacket [16] studies. The method appears to be as versatile as the Berne–Pechukas model and represents an alternative that is particularly suitable for adaptation to DPD, on account of its soft interaction potential. The basis of the method is outlined below following a brief description of DPD.

2. Methods

DPD was first proposed by Hoogerbrugge and Koelman [8] to study the properties of macromolecular systems. However, popular use of the method owes much to the

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derivation of Españ̆ol and Warren [17] which we apply here. The method combines soft, conservative interactions between particles with random and dissipative interactions, such that the total force acting on particle i by particle j is given by

$$\underline{F}_{ij} = \underline{F}_{ij}^{(\mathrm{C})} + \underline{F}_{ij}^{(\mathrm{R})} + \underline{F}_{ij}^{(\mathrm{D})}, \tag{1}$$

where $\underline{F}^{(\mathrm{C})}$, $\underline{F}^{(\mathrm{R})}$ and $\underline{F}^{(\mathrm{D})}$ are the conservative, random and dissipative forces, respectively, where the latter forces are calculated using

$$\underline{F}_{ij}^{(\mathrm{D})} = -\gamma\omega^2(r_{ij})(\hat{r}_{ij}\cdot\underline{v}_{ij})\hat{r}_{ij}, \tag{2}$$

$$F_{ij}^{(\mathrm{R})} = \sigma\omega(r_{ij})\theta_{ij}\hat{r}_{ij}, \tag{3}$$

in which $\underline{r}_{ij} = \underline{r}_i - \underline{r}_j$, $\hat{r}_{ij} = \underline{r}_{ij}/r_{ij}$ and $\underline{v}_{ij} = \underline{v}_i - \underline{v}_j$, θ_{ij} is a Gaussian random number with the properties: $\theta_{ij} = \theta_{ji}$; $\langle\theta_{ij}(t)\rangle = 0$ and $\langle\theta_{ij}(t)\theta_{\ell m}(t')\rangle = (\delta_{i\ell}\delta_{jm} + \delta_{im}\delta_{j\ell})\delta(t - t')$. σ is the thermal noise and γ is the friction coefficient. The combined effect of the dissipative and random forces gives rise to a thermostatted system in which $\sigma^2 = 2\gamma k_{\mathrm{B}}T$ and, most importantly, system hydrodynamic effects are preserved through the property of Galilean invariance. The weight function $\omega(r_{ij})$ is defined to be $1 - r/r_{\mathrm{c}}$, where r_{c} is a truncation radius so that $\omega(r) = 0$ if $r > r_{\mathrm{c}}$. As we indicated earlier, the success of the DPD method relies on the adoption of soft-core potentials that allow fast structural relaxation. The translational equations of motion are integrated using the velocity Verlet scheme adapted for DPD [17]. The equations of motion for the Gaussians, expressed in terms of quaternions, are evaluated using the method of Matubayasi and Nakahara [18].

The Gaussian density model in this paper assumes that each particle can be represented by a Gaussian distribution of interaction sites. For a single Gaussian site, this can be written in the form

$$G_i = N_i \exp(\underline{x}'_i \underline{\underline{A}}_i\ \underline{x}_i), \tag{4}$$

where $\underline{x}_i = \underline{r}_i - \underline{R}_i$, G_i represents the Gaussian density function and $\underline{R}_i$ locates the centre of the ith Gaussian. N_i is a normalising factor, which ensures that the total density is unity. $\underline{\underline{A}}_i$ is a 3×3 matrix defining the shape, orientation and size of the Gaussian function. (In applications to systems of one molecular species, the size and shape of the Gaussians will be the same throughout, so that $N_i = N$ and $\mathrm{Tr}(\underline{\underline{A}}_i) = \mathrm{Tr}(\underline{\underline{A}})$ for all i.) The relative magnitudes of the diagonal elements determine the shape of the particle.

The potential energy is evaluated from the sum of n primitive Gaussian functions that describe the interaction between infinitesimal volumes within neighbouring Gaussian particles [14]:

$$u_{ij}(r_{ij}) = \sum_n c_n \exp(-d_n r_{ij}^2). \tag{5}$$

The primitive Gaussian parameters, c_n and d_n, can be determined using standard parameter fitting techniques and the parameters c_n evidently determine the 'softness' of the interactions and in particular, for all reasonable values of c_n and d_n, the potential remains finite at $r_{ij} = 0$. Both attractive and repulsive potentials can be established in this model.

The interaction between infinitesimal volumes in neighbouring Gaussian distributions in a typical arrangement is shown in Figure 1. A volume element $\mathrm{d}\underline{x}_i$ of the Gaussian G_i interacts with a volume element $\mathrm{d}\underline{x}_j$ of the Gaussian G_j via the potential function $u_{ij}(r_{ij})$. The contribution of this interaction to the potential energy of the pair of molecules is

$$\begin{aligned} &N_iN_j \exp(-\underline{x}_i\underline{\underline{A}}_i\ \underline{x}_i) \\ &\quad \times \exp(-\underline{x}_j\underline{\underline{A}}_j\ \underline{x}_j)\sum_n c_n \exp(-d_n|\underline{R}_{ij} + \underline{x}_i - \underline{x}_j|^2)\,\mathrm{d}\underline{x}_i\,\mathrm{d}\underline{x}_j. \end{aligned} \tag{6}$$

This interaction may readily be integrated separately over volume elements $\mathrm{d}\underline{x}_j$ and $\mathrm{d}\underline{x}_i$ to give the potential energy of the molecule pair as[14]

$$V_{ij}(R_{ij}) = \sum_n V_{ijn}(R_{ij}), \tag{7a}$$

where

$$V_{ijn}(R_{ij}) = c_n\sqrt{E_{ijn}}\exp(-d_n\underline{R}_{ij}\cdot\underline{\underline{E}}_{ijn}\ \cdot\underline{R}_{ij}) \tag{7b}$$

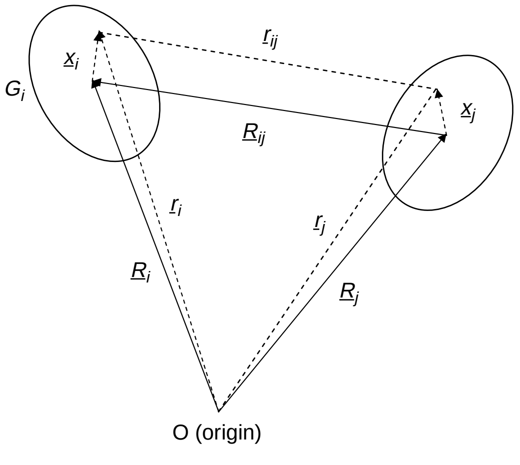

Figure 1. Schematic diagram for the calculation of energies and forces of two overlapping Gaussians (see text for further discussion).

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and

$$\underline{\underline{E}}_{ijn} = \left(\underline{\underline{I}} + d_n[\underline{\underline{A}}_i^{-1} + \underline{\underline{A}}_j^{-1}]\right)^{-1}. \tag{7c}$$

It can be seen from these formulae that the potential energy is angularly dependent via the matrices $\underline{\underline{A}}_i$ and $\underline{\underline{A}}_j$. It is also apparent that the matrix $\underline{\underline{E}}_{ijn}$ is symmetric.

The force acting on the Gaussian G_i is given simply by the usual differentiation:

$$\underline{F}_i = -\frac{\partial}{\partial \underline{R}_i} V(R_{ij}) \tag{8}$$

from which the force expression is easily obtained:

$$\underline{F}_i = \sum_n 2 d_n V_{ijn}(R_{ij}) \underline{\underline{E}}_{ijn} \cdot \underline{R}_{ij}. \tag{9}$$

The force acting on the Gaussian G_j is the negative of (9).

The torque acting on the Gaussian G_i is more difficult to obtain. In principle, it can be calculated from the infinitesimal torque arising from the force of the volume element $d\underline{x}_j$ of Gaussian G_j acting on the volume element $d\underline{x}_i$ of Gaussian G_i and integrating over both $d\underline{x}_j$ and $d\underline{x}_i$. This was the procedure followed by Smith and Singer [14]. However, a more elegant method was later described by Allen and Germano [19], which leads to the following results for the torques on particles i and j,

$$\underline{\tau}_i = \sum_n d_n V_{ijn}(R_{ij}) \times \left(\boldsymbol{\varepsilon} : [\underline{\underline{E}}_{ijn} \cdot \underline{\underline{A}}_i^{-1}] - 2d_n[\underline{\underline{A}}_i^{-1} \cdot \underline{\underline{E}}_{ijn} \cdot \underline{R}_{ij}] \times [\underline{\underline{E}}_{ijn} \cdot \underline{R}_{ij}]\right), \tag{10a}$$

$$\underline{\tau}_j = \sum_n d_n V_{ijn}(R_{ij}) \times \left(\boldsymbol{\varepsilon} : [\underline{\underline{E}}_{ijn} \cdot \underline{\underline{A}}_j^{-1}] - 2d_n[\underline{\underline{A}}_j^{-1} \cdot \underline{\underline{E}}_{ijn} \cdot \underline{R}_{ij}] \times [\underline{\underline{E}}_{ijn} \cdot \underline{R}_{ij}]\right), \tag{10b}$$

where $\boldsymbol{\varepsilon}$ is the Levi-Civita tensor, ':' is a double-contraction operator and ' × ' is a vector product.

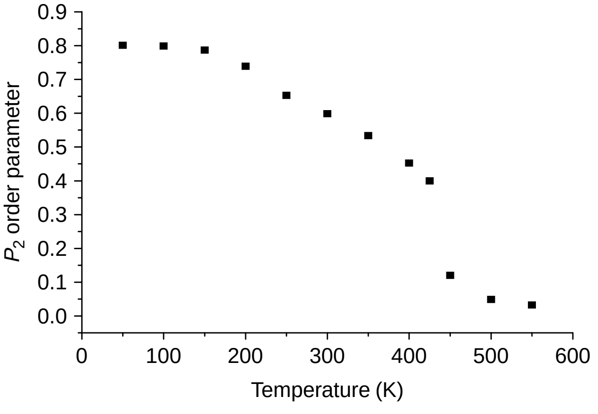

Figure 2. The P_2 order parameter for uniaxial nematic liquid crystal with length:width ratio 4:1:1.

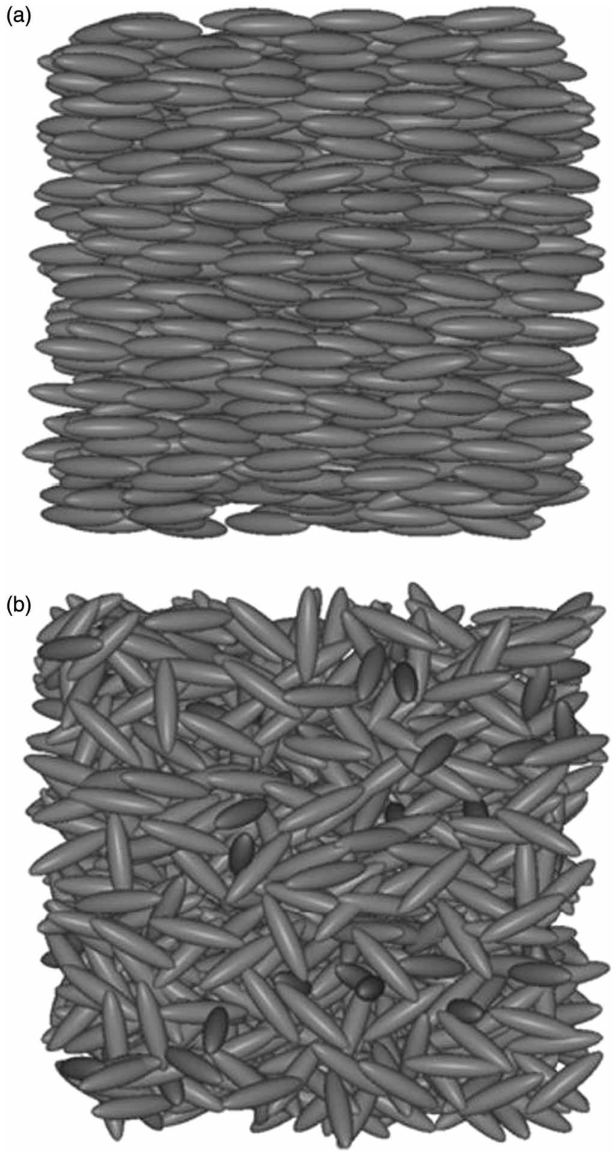

Figure 3. Snapshot of the uniaxial nematic fluid (a) below (250 K) and (b) above (500 K) the transition temperature.

3. Results

The previous section introduced the two sets of parameters that must be defined within the scope of this model; namely the matrix $\mathbf{A}_i$ (Equation (4)) and the Gaussian potential parameters (Equation (5)). The diagonal components of the matrix $\mathbf{A}_i$ can be chosen to represent the desired shape of a molecule or particle in four different combinations:

$$A_{xx} = A_{yy} = A_{zz} \rightarrow \text{sphere},$$

$$A_{xx} = A_{yy} < A_{zz} \rightarrow \text{disc (uniaxial) Gaussian},$$

$$A_{xx} = A_{yy} > A_{zz} \rightarrow \text{cigar (uniaxial) Gaussian and}$$

$$A_{xx} \neq A_{yy} \neq A_{zz} \rightarrow \text{lozenge (biaxial) Gaussian}.$$

The potential parameters (d_n and c_n) allow for complex models to be established, and this is a major difference between this model and others. The number of potential terms, n, will depend on the system of interest. For example, a single term is required for a purely repulsive model while using multiple potentials can be employed to design an attractive potential. It has been shown [7] that a number of common potentials can be accurately represented by a sum of Gaussian functions, which in most cases require two or three terms only to obtain a good fit. In this paper, we have restricted our calculations to models containing two parameters (one repulsive and one attractive) and where the matrix $\mathbf{A}_i$ has the following form $A_{xx} = A_{yy} \neq A_{zz}$. This is to allow for comparison with previous calculations, for example, those using Gay–Berne potentials. All the simulations were undertaken using 824 particles and each simulation was run for 100,000 steps. The first 50,000 steps were employed for equilibration and 50,000 steps for the collection of statistical data. A time step equivalent to 20 fs was used for all the simulations. γ was set to a value between 2 and 6 for all the simulations.

In our first example, we consider a system in which $A_{xx} = A_{yy} > A_{zz}$ and is similar to the Gay–Berne models used to study liquid crystals. The length:width ratio is 4:1 (determined from the FWHM) and the two Gaussian potential parameters adjusted by hand so that liquid crystal-like behaviour is observed. The values for c_n were 0.5 and $-0.09\,\text{kJ mol}^{-1}$ and for d_n 0.5 and $0.255\,\text{Å}^{-2}$. In MD, the existence of liquid phases is, in part, determined by calculating order parameters. The P_2 order parameter takes on values between 0 for a disordered phase and 1 for an ordered phase. The value of P_2 was evaluated from the second-rank order tensor following the method of Allen [20]:

$$Q_{\alpha\beta} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{3}{2}\hat{u}_i^{\alpha}\hat{u}_i^{\beta} - \frac{1}{2}\delta_{\alpha\beta}\right), \tag{11}$$

where unit vectors $\underline{\hat{u}}_i$ represent the long axes of the molecule, N is the number of molecules and $\delta_{\alpha\beta}$ is the Kronecker delta. In Figure 2, we present the P_2 order parameter for the 4:1 system, which demonstrates that it is possible to determine nematic to isotropic phase transitions using the DPD–Gaussian overlap model. Figure 3 presents snapshots of configurations below and above the transition temperature. The model is not restricted to studying liquid crystal phases and, for example, by increasing the cell volume and the attractive part of the short-range Gaussian potential it is possible to create ‘clumps’ of rod-shaped particles (Figure 4), i.e. micellisation occurs.

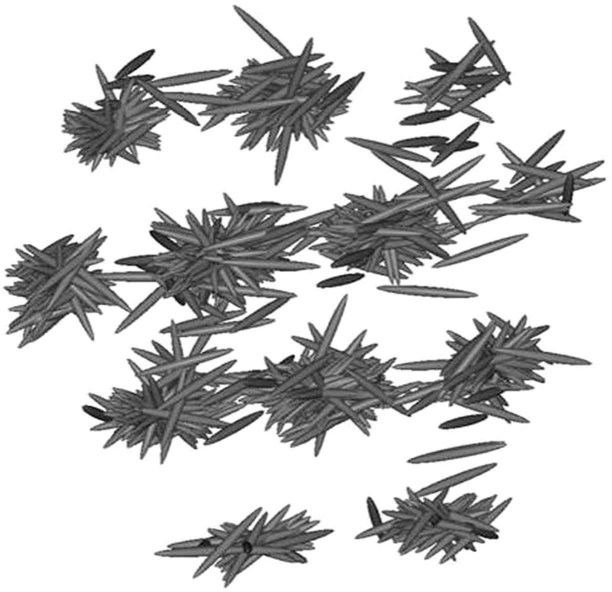

Figure 4. Snapshot of needle-like Gaussian particles (length:breadth is 10:1) forming a micelle-like structure. The values for c_n were 0.5 and $-0.14\,\text{kJ mol}^{-1}$ and for d_n 1.0 and $1.4\,\text{Å}^{-2}$.

Many studies have established that certain disc-shaped molecules may form stable thermotropic liquid crystalline phases, which are referred to as discotic liquid crystals. These liquid crystal phases may be categorised into two broad types: columnar and discotic nematic. For our second test case, we have investigated phases with a length:width ratio of 0.1:1 (although this is also a uniaxial model, we stress that it is possible to construct flat lozenge-shaped molecules). The Gaussian overlap model combined with DPD has been used to generate both columnar phases (not shown), isotropic and more exotic structures. In Figure 5, we exhibit an ordered cubic phase containing groups of discs.

4. Conclusions

We have presented a Gaussian density model that can be employed with DPD and have demonstrated its application to a range of systems. In order to demonstrate

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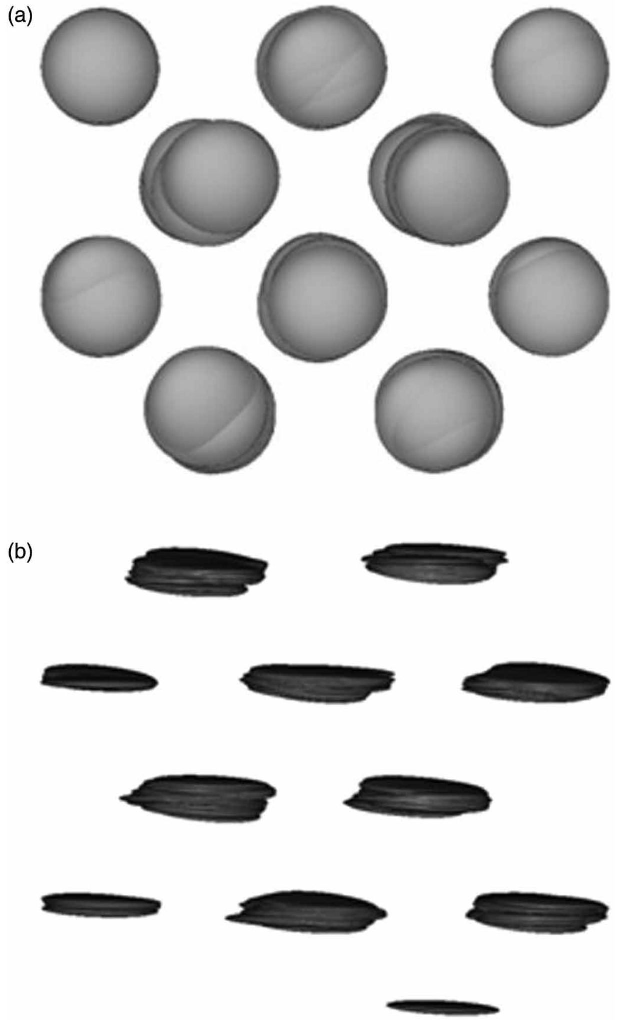

Figure 5. Discotic liquid crystal of length:width ratio 0.1:1, (a) plan view and (b) side view. The values for c_n were 0.4 and $-0.08\,\mathrm{kJ\,mol^{-1}}$ and for d_n 0.5 and $0.3\,\mathrm{\AA^{-2}}$.

the flexibility of the model, we have undertaken a number of pilot studies. We have demonstrated that it is possible to obtain nematic to isotropic phase transitions. These include nematic liquid crystals and discotic phases.

Moreover, our pilot studies have been restricted to uniaxial species for comparison with previous calculations, yet are suitable for studying biaxial liquid crystals [21]. In addition, bonded interactions could be included to construct larger molecules that contain both attractive and repulsive groups or molecules such as those described by Hughes et al. [22]. Future work will include further comparison with Gay–Berne potential models and the application of the technique to multicomponent systems will be investigated.

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