Dynamics of interfaces and rheology of immiscible liquid–liquid mixtures

Dynamique des interfaces et rhéologie des mélanges de deux liquides non miscibles

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Abstract

In a mixture of two immiscible liquids, interfacial tension is responsible for the visco-elastic behaviour of the blend. To model such a peculiar behaviour, we formulate a fine-grained description of the interface motions and, after averaging, we obtain a coarse-grained description in the spirit of the Doi and Ohta model. While the Doi–Ohta model was restricted to immiscible liquids with equal viscosity and equal volume fractions, we here develop a model for arbitrary viscosities and concentrations. *To cite this article: D. Lhuillier, C. R. Mecanique 331 (2003).*
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Résumé

Dans un mélange de deux liquides non miscibles, la tension superficielle est à l'origine de phénomènes qui confèrent au mélange des propriétés visco-élastiques. Pour rendre compte de ces phénomènes, il est d'abord nécessaire de suivre en détail le mouvement des interfaces puis, après moyenne, d'en donner une description macroscopique semblable à celle suggérée par Doi et Ohta il y a une dizaine d'années. Le modèle de Doi–Ohta supposait cependant l'égalité des viscosités et des concentrations volumiques des deux liquides. Ces hypothèses contraignantes sont ici supprimées. *Pour citer cet article : D. Lhuillier, C. R. Mecanique 331 (2003).*
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Le comportement visco-élastique d'un mélange de deux liquides non-miscibles (émulsion) est du à la tension superficielle et à la déformabilité des interfaces séparant les deux liquides. Si on sait comment les déformations interfaciales interviennent dans le tenseur des contraintes du mélange, et si on connaît également la façon dont ces déformations évoluent dans le temps, alors on peut en déduire le comportement du mélange en écoulement, c'est à dire sa rhéologie. Cette démarche est précisément celle du modèle proposé il y a une dizaine d'années par Doi et Ohta [6]. Ce modèle était cependant basé sur deux hypothèses contraignantes, l'égalité des viscosités et des concentrations des deux liquides. Dans cette Note nous nous affranchissons de ces contraintes.

Dans la première partie (Section 2) nous obtenons des résultats généraux concernant (a) l'évolution temporelle (5) du tenseur symétrique $\mathbf{Q} = \langle \mathbf{nn} \delta_I \rangle$ où δ_I est une fonction de Dirac qui localise les interfaces, $\mathbf{n}$ est le vecteur unitaire normal aux interfaces tandis que les crochets $\langle \cdot \rangle$ représentent une moyenne sur toutes les configurations possibles des interfaces, et (b) l'expression générale (6) du tenseur des contraintes du mélange en fonction du tenseur d'anisotropie des interfaces $\mathbf{q}$ défini en (2).

Ces deux résultats contiennent des termes entre crochets qu'il faut exprimer en fonction de $\mathbf{q}$ et du taux de déformation moyen $\mathbf{D}$ de l'émulsion. Dans la seconde partie (Section 3), nous obtenons les expressions recherchées en adoptant une approche phénoménologique basée sur des résultats exacts obtenus pour des émulsions où l'une des phases est dispersée dans l'autre. Nous aboutissons ainsi à l'expression (9) pour le tenseur des contraintes ainsi qu'à Éq. (14) pour l'évolution de la densité d'interfaces $Q = \mathrm{tr}(\mathbf{Q})$. L'évolution temporelle du tenseur d'anisotropie est plus difficile à obtenir, et nous nous contentons de donner pour $\mathbf{q}$ le résultat (19), valable pour des interfaces dont la distribution est faiblement anisotrope.

1. Introduction

An emulsion (a mixture of two non-miscible liquids) provides a rather simple example of a continuous medium with a visco-elastic behaviour. The early studies considered dilute emulsions and slightly deformed drops, with exact results [1,2]. The following studies were concerned with non-dilute dispersions of drops, using a phenomenological approach [3–5]. Then, Doi and Ohta [6] considered the case of an emulsion made of two liquids with the same viscosity and with almost equal volume fractions (the so-called inversion range in which bi-continuous interfaces are likely to appear). Subsequent studies have extended the Doi–Ohta model to compressible fluids [7], to polymeric liquids [8,9] and to liquids with different viscosities but zero surface tension [10]. Recent reviews [11, 12] attest to the vivacity of the subject. Our aim here is to extend the Doi–Ohta model for non-miscible liquids with arbitrary viscosities and arbitrary volume fractions. A certain number of general results are provided in Section 2, before we give them an explicit and manageable form in Section 3.

2. General results

2.1. The interfacial stress and the dynamics of interfaces

In a emulsion of two non-miscible liquids, the two phases are separated by interfaces of more or less complex geometry. Each element of interface is characterized by its unit normal $\mathbf{n}$. The surface tension Γ is responsible for interfacial forces which, per unit area, have a normal component $\mathbf{F}_N = -\Gamma(\nabla \cdot \mathbf{n})\mathbf{n}$ and a tangential component $\mathbf{F}_T = (\mathbf{I} - \mathbf{nn}) \cdot \nabla \Gamma$ where $\mathbf{I}$ is the unit tensor. The position of the interfaces is depicted by a Dirac-like function δ_I. The integral of δ_I over any fixed volume gives the amount of interfaces present in that volume and it is clear that its dimension is the inverse of a length. Per unit volume of the mixture, the interfacial forces are represented by $\delta_I(\mathbf{F}_N + \mathbf{F}_T)$. The momentum conservation of the whole mixture requires this interfacial force to appear as the divergence of some interfacial stress, and indeed one can check that $\delta_I(\mathbf{F}_N + \mathbf{F}_T) = \nabla \cdot [\Gamma(\mathbf{I} - \mathbf{nn})\delta_I]$. The interfacial

stress tensor is a quantity which, because of the complex motion of the interfaces, displays strong spatial variations and time fluctuations. The quantity which is likely to be measured in experiments is an average taken over all possible interface configurations. Noting this statistical average by brackets, the average interfacial stress appears as [13]

$$\boldsymbol{\sigma}_\Gamma = \langle \Gamma (\mathbf{I} - \mathbf{nn}) \delta_I \rangle \approx \Gamma(T) \langle (\mathbf{I} - \mathbf{nn}) \delta_I \rangle \tag{1}$$

where T is the average temperature of the mixture. It is now clear that quantities particularly relevant for the description of interfacial properties are the interfacial orientation tensor $\mathbf{Q}$, the average density of interfaces Q and the interfacial anisotropy tensor $\mathbf{q}$ respectively defined as

$$\mathbf{Q} = \langle \mathbf{nn}\delta_I \rangle, \quad Q = \langle \delta_I \rangle \quad \text{and} \quad \mathbf{q} = \langle (\mathbf{nn} - \mathbf{I}/3)\delta_I \rangle \tag{2}$$

To describe the time evolution of the interfaces, one must find the time evolution of these quantities, hence the time evolution of $\mathbf{n}$ and δ_I. To this end, we introduce the local velocity $\mathbf{v}$ of each little piece of interface. *This interface velocity is nothing but the common velocity the two liquids have on the two sides of any piece of interface.* The knowledge of $\mathbf{v}(\mathbf{x}, t)$ is enough to deduce the time evolution of $\mathbf{n}$ and δ_I in the form [14,15]

$$\frac{\partial \delta_I}{\partial t} + \mathbf{v} \cdot \boldsymbol{\nabla} \delta_I = -\delta_I \mathbf{nn} \cdot \boldsymbol{\nabla} \mathbf{v} \tag{3}$$

and

$$\frac{\partial n_i}{\partial t} + (\mathbf{v} \cdot \boldsymbol{\nabla}) n_i = -(\delta_{ij} - n_i n_j) n_k \frac{\partial v_k}{\partial x_j} \tag{4}$$

It is now easy to obtain the time evolution of the tensor $\mathbf{nn}\delta_I$, and then to take its statistical average which can be written:

$$\frac{\partial Q_{ij}}{\partial t} + \langle \mathbf{v} \cdot \boldsymbol{\nabla}(n_i n_j \delta_I) \rangle = \left\langle \delta_I (n_i n_j n_l n_k - n_i n_k \delta_{jl} - n_j n_k \delta_{il}) \frac{\partial v_k}{\partial x_l} \right\rangle \tag{5}$$

The time evolution of the interface density is obtained from the trace of Eq. (5) or more directly, from the average of Eq. (3). The evolution equation for the anisotropy tensor $\mathbf{q} = \mathbf{Q} - \frac{Q}{3}\mathbf{I}$ is then deduced without any difficulty. We insist that $\mathbf{v}$ is a "microscopic" quantity which can display large variations from one piece of interface to another. This fine-grained field depends not only on the macroscopic motion of the emulsion but also on the relaxation motions which persist when the macroscopic motion is suppressed. In fact, all kinds of dynamical processes involving interfaces (with the exception of nucleation and collapse) are present in Eq. (5).

2.2. The mixture stress

Each liquid of the mixture is supposed to behave like a non-compressible Newtonian fluid with respective viscosities η_1 and η_2. The total average stress of the emulsion is made from the contributions of the two phases and of the interfaces [13] $\boldsymbol{\sigma} = -\phi_1 \langle p_1 \rangle \mathbf{I} + 2\phi_1 \eta_1 \langle \mathbf{d}_1 \rangle - \phi_2 \langle p_2 \rangle \mathbf{I} + 2\phi_2 \eta_2 \langle \mathbf{d}_2 \rangle + \boldsymbol{\sigma}_\Gamma$ where $\langle p_k \rangle$ and $\langle \mathbf{d}_k \rangle$ are the average pressure and strain rate of phase k which occupies a volume fraction ϕ_k with $\phi_1 + \phi_2 = 1$. Defining the mixture strain rate as $\mathbf{D} = \phi_1 \langle \mathbf{d}_1 \rangle + \phi_2 \langle \mathbf{d}_2 \rangle$, the mixture pressure as $p = \phi_1 \langle p_1 \rangle + \phi_2 \langle p_2 \rangle - 2\Gamma Q/3$, and the interface stress tensor as in (1), the emulsion stress can be rewritten as

$$\boldsymbol{\sigma} = -p\mathbf{I} + 2(\phi_1 \eta_1 + \phi_2 \eta_2)\mathbf{D} + 2\phi_1 \phi_2 (\eta_1 - \eta_2)(\langle \mathbf{d}_1 \rangle - \langle \mathbf{d}_2 \rangle) - \Gamma \mathbf{q} \tag{6}$$

The rheology of a mixture of two non-miscible fluids is entirely determined by (5) and (6). The issue is to express all bracketed quantities in terms of such macroscopic variables as $\mathbf{D}$, Q and $\mathbf{q}$. The most direct way would be to use a probability distribution expressed in terms of these macroscopic quantities. Unfortunately, this probability distribution is extremely difficult to obtain, and we will proceed differently, using a more phenomenological approach.

3. Phenomenological results

3.1. The stress tensor

In a suspension of deformed drops (index d) dispersed in a continuous liquid (index c), the average strain rate inside the drops is given by [4]

$$\langle \mathbf{d}^{\mathrm{d}} \rangle - \mathbf{D} = \left[\eta_{\mathrm{c}} \mathbf{F} + \left(\eta_{\mathrm{d}} + \frac{3\eta_{\mathrm{c}}}{2} \right) \mathbf{I} \right]^{-1} : \left[\frac{\Gamma}{2\phi_{\mathrm{d}}} \mathbf{q} - (\eta_{\mathrm{d}} - \eta_{\mathrm{c}}) \mathbf{D} \right] \tag{7}$$

where $\mathbf{F}(\mathbf{q}/Q, \phi_{\mathrm{d}})$ is a completely symmetric and traceless fourth-order tensor, which vanishes for dilute suspensions of quasi-spherical drops, while the fourth-order unit tensor $\mathbf{I}$ is defined by $I_{ijkl} = (1/2)(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il} - 2/3\delta_{ij}\delta_{kl})$. From (7) one obtains the exact values of $\phi_1\phi_2(\langle \mathbf{d}_1 \rangle - \langle \mathbf{d}_2 \rangle)$ for $\phi_2 \ll 1$ and $\phi_1 \ll 1$. The simplest *extrapolated expression* between these two limits is without doubt

$$2\phi_1\phi_2\big(\langle \mathbf{d}_1 \rangle - \langle \mathbf{d}_2 \rangle\big) = \mathbf{G} : \big[(\phi_2 - \phi_1)\Gamma\mathbf{q} + 2\phi_1\phi_2(\eta_2 - \eta_1)\mathbf{D} \big] \tag{8}$$

Like $\mathbf{F}$, the fourth-order tensor $\mathbf{G}$ is symmetric and traceless with respect to its first two and last two indices. Taking (8) for granted, the overall emulsion stress tensor (6) becomes

$$\boldsymbol{\sigma} = -p\mathbf{I} + 2(\phi_1\eta_1 + \phi_2\eta_2)\mathbf{D} - 2\phi_1\phi_2(\eta_1 - \eta_2)^2\mathbf{G} : \mathbf{D} - \Gamma\mathbf{q} - \Gamma(\phi_1 - \phi_2)(\eta_1 - \eta_2)\mathbf{G} : \mathbf{q} \tag{9}$$

This expression simplifies considerably when $\eta_1 = \eta_2$ [6]. Note the special behaviour of the elastic part of the stress in the inversion region $\phi_1 \approx \phi_2$. For a quasi-isotropic distribution of interfaces, $\mathbf{G}$ no longer depends on $\mathbf{q}$ and is proportional to the fourth-order unit tensor $\mathbf{I}$. For that quasi-isotropic case, we propose to write

$$\mathbf{G} = G_0\mathbf{I} \quad \text{with } G_0 = \frac{\phi_1^2\eta_2 + \phi_2^2\eta_1}{3/2\eta_1\eta_2 + (\phi_1\eta_2 + \phi_2\eta_1)^2} \tag{10}$$

as the simplest possible interpolation suggested by (7) when $\mathbf{F} = 0$.

3.2. The evolution equation for the density of interfaces Q

The statistical average of Eq. (3), or the trace of Eq. (5), leads to $\partial Q/\partial t + \langle \mathbf{v} \cdot \nabla \delta_{\mathrm{I}} \rangle = -\langle \delta_{\mathrm{I}} \mathbf{nn} : \mathbf{d} \rangle$ where $d_{ij} = 1/2(\partial v_i/\partial x_j + \partial v_j/\partial x_i)$ is the fine-grained strain rate of the interfaces. How to express the bracketed quantities in terms of coarse-grained variables such as $\mathbf{D}$, Q and $\mathbf{q}$? Let us consider first a dispersed emulsion. On the average, the velocity $\mathbf{v}$ of the interfaces stays close to the translation velocity of the dispersed phase, which itself is close to the average velocity $\mathbf{V}$ of the emulsion when the two liquids have almost equal mass densities (as will be supposed henceforth). Concerning the strain rate $\mathbf{d}$ of the interfaces, it is close to the average strain rate $\langle \mathbf{d}^{\mathrm{d}} \rangle$ of the dispersed phase (in fact, $\mathbf{d}^{\mathrm{d}}$ is almost uniform all over the drop). Hence, for a dispersed emulsion, the evolution of the interfacial area density can be approximated by

$$\frac{\partial Q}{\partial t} + \mathbf{V} \cdot \nabla Q = -\mathbf{q} : \langle \mathbf{d}^{\mathrm{d}} \rangle \tag{11}$$

after taking into account the incompressibility of the two liquids. The relation between $\langle \mathbf{d}^{\mathrm{d}} \rangle$, $\mathbf{D}$ and $\mathbf{q}$ is expressed in (7) and this means we know the evolution equation for Q in the two limits $\phi_2 \ll 1$ and $\phi_1 \ll 1$. A simple interpolation, analogue to (8), is

$$\langle \mathbf{d}^{\mathrm{d}} \rangle - \mathbf{D} = \mathbf{G} : \left[\frac{\Gamma}{2\phi_1\phi_2} \mathbf{q} + (\phi_2 - \phi_1)(\eta_2 - \eta_1)\mathbf{D} \right] \tag{12}$$

which results in the evolution equation

$$\frac{\partial Q}{\partial t} + \mathbf{V} \cdot \nabla Q = -\mathbf{q} : \mathbf{D} - (\phi_1 - \phi_2)(\eta_1 - \eta_2)\mathbf{q} : \mathbf{G} : \mathbf{D} - \frac{\Gamma}{2\phi_1\phi_2}\mathbf{q} : \mathbf{G} : \mathbf{q} \tag{13}$$

This evolution equation has a noteworthy feature: the way the right-hand side depends on **D** is similar to the way the overall stress $\boldsymbol{\sigma}$ depends on **q** in (9). This is required by thermodynamics because the time-derivative of the interfacial energy ΓQ must include a term $\boldsymbol{\sigma}^{\mathrm{el}}(\mathbf{q}) : \mathbf{D}$ if $\boldsymbol{\sigma}^{\mathrm{el}}(\mathbf{q})$ is to represent the elastic part of the total stress, i.e., that part which depends on surface tension and which does not vanish when $\mathbf{D} = 0$. There is however a less satisfactory feature, in that the evolution of Q is stopped whenever **q** vanishes. This means that, as it stands, Eq. (13) is unable to mimic neither coalescence for dilute emulsions nor the evolution of an isotropic distribution of interfaces for non-dilute ones. This drawback can be corrected by *adding a relaxation term* $-\nu Q$ to its right-hand side. Since (a) the coalescence rate tends to zero for small volume fractions, and (b) all relaxation times are expected to have similar values in the inversion region, we propose $\nu = \Gamma \phi_1 \phi_2 G_0 Q$, so that (13) becomes

$$\frac{\partial Q}{\partial t} + \mathbf{V} \cdot \nabla Q = -\mathbf{q} : \mathbf{D} - (\phi_1 - \phi_2)(\eta_1 - \eta_2)\mathbf{q} : \mathbf{G} : \mathbf{D} - \frac{\Gamma}{2\phi_1\phi_2}\mathbf{q} : \mathbf{G} : \mathbf{q} - \Gamma \phi_1 \phi_2 G_0 Q^2 \tag{14}$$

where G_0 is defined in (10).

3.3. The evolution equation for the anisotropy tensor **q**

Like was done above for Q, let us consider first a dispersed emulsion. If we suppose that **v** is close to the average emulsion velocity **V** and that the velocity gradient of the interfaces $\nabla\mathbf{v}$ is almost equal to the average velocity gradient in the dispersed phase, we deduce from (5) and (11)

$$\frac{\partial q_{ij}}{\partial t} + \mathbf{V} \cdot \nabla q_{ij} + q_{ik}\langle \omega_{kj}^{\mathrm{d}} \rangle + q_{jk}\langle \omega_{ki}^{\mathrm{d}} \rangle$$
$$= \left\langle \delta_{\mathrm{I}}\left(n_i n_j - \frac{1}{3}\delta_{ij}\right)n_l n_k \right\rangle \langle d_{kl}^{\mathrm{d}} \rangle - q_{ik}\langle d_{kj}^{\mathrm{d}} \rangle - q_{jk}\langle d_{ki}^{\mathrm{d}} \rangle + \frac{2}{3}q_{kl}\langle d_{kl}^{\mathrm{d}} \rangle\delta_{ij} - \frac{2Q}{3}\langle d_{ij}^{\mathrm{d}} \rangle \tag{15}$$

where $\boldsymbol{\omega}^{\mathrm{d}}$ is the angular rotation rate of the dispersed phase. In the absence of external couples, and if we neglect rotary inertia, the couple exerted on the dispersed phase by the continuous phase must vanish and this results in a linear dependence of the relative rotation $\langle \boldsymbol{\omega}^{\mathrm{d}} \rangle - \boldsymbol{\Omega}$ on $\langle \mathbf{d}^{\mathrm{d}} \rangle - \mathbf{D}$ where $\boldsymbol{\Omega}$ is the anti-symmetric part of the emulsion velocity gradient $\nabla\mathbf{V} = \mathbf{D} + \boldsymbol{\Omega}$. This linear dependence results in

$$q_{ik}\langle \omega_{kj}^{\mathrm{d}} \rangle + q_{jk}\langle \omega_{ki}^{\mathrm{d}} \rangle = q_{ik}\Omega_{kj} + q_{jk}\Omega_{ki} + H_{ijkl}\left(\langle d_{kl}^{\mathrm{d}} \rangle - D_{kl}\right) \tag{16}$$

where **H** (like **G**) is a completely symmetric and traceless fourth-order tensor which depends quadratically on **q** and which (at variance with **G**) vanishes when **q** tends to zero. After inserting (12) and (16) into the above equation (15) for **q**, one obtains an equation which is not yet closed as it stands because it contains the fourth-order moment $\langle \delta_{\mathrm{I}} n_i n_j n_l n_k \rangle$. The issue is to express it in terms of **q** and Q. This closure problem has been considered at length by Edwards and Öttinger [16]. Among the possible solutions is the Doi–Ohta [6] closure. We propose below a complement of information by pointing out a necessary relation between the time-evolution of **q** and that of Q.

It is always possible to express the interfacial density in terms of the anisotropy tensor **q** and of the density Q_0 that would exist in the absence of anisotropy. Writing $Q = Q_0(1 + f(\mathbf{q}^*))$ where $\mathbf{q}^* = \mathbf{q}/Q_0$, and supposing that the evolution of Q_0 is due to coalescence processes only (hence $\partial Q_0/\partial t + \mathbf{V} \cdot \nabla Q_0 = -\nu Q_0$ with $\nu = \Gamma \phi_1 \phi_2 G_0 Q$), one deduces with the help of (11) the general relation that any evolution equation must satisfy

$$\frac{\partial f}{\partial \mathbf{q}^*} : \left(\frac{\mathrm{d}\mathbf{q}}{\mathrm{d}t} + \nu\mathbf{q}\right) = -\mathbf{q} : \langle \mathbf{d}^{\mathrm{d}} \rangle \tag{17}$$

where $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \mathbf{V} \cdot \nabla$ is the material time-derivative. The scalar function f must be a function of the invariants $q_2^* = q_{ij}^* q_{ji}^*$ and $q_3^* = q_{ij}^* q_{jk}^* q_{ki}^*$ of the traceless tensor $\mathbf{q}^*$, and consequently

$$\frac{\partial f}{\partial \mathbf{q}^*} = \frac{2\partial f}{\partial q_2^*}\mathbf{q}^* + \frac{3\partial f}{\partial q_3^*}\mathbf{q}^* \cdot \mathbf{q}^* = \alpha\mathbf{q} + \beta\mathbf{q} \cdot \mathbf{q} \tag{18}$$

The only case for which $f(\mathbf{q}^*)$ is known explicitly is the case of slight anisotropies for which $\mathbf{q}$ can be considered as a small parameter. After laborious calculations we obtained $\frac{\partial f}{\partial \mathbf{q}^*} = \frac{15}{8}\mathbf{q}^* - \frac{1125}{224}\mathbf{q}^* \cdot \mathbf{q}^* + \mathrm{O}(q^{*3})$. The special form of Eq. (15) that fulfils (17) and takes (16) into account, is then

$$\frac{\mathrm{d}q_{ij}}{\mathrm{d}t} + q_{ik}\Omega_{kj} + q_{jk}\Omega_{ki} = -\frac{8Q_0}{15}\langle d_{ij}^{\mathrm{d}}\rangle - \frac{5}{7}\left[q_{ik}\langle d_{kj}^{\mathrm{d}}\rangle + q_{jk}\langle d_{ki}^{\mathrm{d}}\rangle - \frac{2}{3}q_{kl}\langle d_{kl}^{\mathrm{d}}\rangle\delta_{ij}\right] - \nu q_{ij} + \mathrm{O}\big(q^2\langle d^{\mathrm{d}}\rangle\big) \qquad (19)$$

With the help of (12) and $\nu = \Gamma\phi_1\phi_2 G_0 Q$, a completely closed equation is obtained.

4. Summary and conclusions

We have obtained a plausible generalisation of the Doi–Ohta model in case of two liquids with different viscosities and arbitrary volume fractions. The main results are expression (9) for the stress tensor and Eq. (14) for the time evolution of the interfacial density. The evolution equation for the anisotropy tensor is more difficult to obtain in its full generality, and we contented ourselves with its special form (19) which holds for slight anisotropies.

One can notice a certain similarity between the interfacial dynamics and the turbulence dynamics. To the interfacial energy ΓQ corresponds the fluctuational kinetic energy $\rho\langle v'^2\rangle/2$ and the evolution of Q is connected to the evolution of q_{ij}, much like the evolution of $\langle v'^2\rangle$ is connected to the evolution of the Reynolds tensor $R_{ij} = \langle v_i'v_j' - (v'^2/3)\delta_{ij}\rangle$. The Doi–Ohta model, and its present generalisation, is thus for interfaces the analogue of the so-called $R_{ij} - \varepsilon$ model for turbulence.

Acknowledgements

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