Entropy production in thermal phase separation: a kinetic-theory approach

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Entropy production during the process of thermal phase-separation of multiphase flows is investigated by means of a discrete Boltzmann kinetic model. The entropy production rate is found to increase during the spinodal decomposition stage and to decrease during the domain growth stage, attaining its maximum at the crossover between the two. Such behaviour provides a natural criterion to identify and discriminate between the two regimes. Furthermore, the effects heat conductivity, viscosity and surface tension on the entropy production rate is investigated by systematically probing the interplay between non-equilibrium energy and momentum fluxes. It is found that the entropy production rate due to energy fluxes is an increasing function of the Prandtl number, while the momentum fluxes exhibit an opposite trend. On the other hand, both contributions show an increasing trend with surface tension. The present analysis inscribes within the general framework of non-equilibrium thermodynamics and consequently it is expected to be relevant to a broad class of soft-flowing systems far from mechanical and thermal equilibrium.

1 Introduction

Multiphase flows with phase separation are ubiquitous and crucial in complex fluids such as polymers, colloids, surfactants, biological materials, etc.\textsuperscript{11} Understanding characteristics of the phase separation so as to control the morphological evolution is very important to design various materials with novel mechanical, optical, and electrical properties. For this reason significant efforts have been made to investigate the phase separation process by means of experimental, theoretical, and numerical methods.\textsuperscript{3–5}

Besides their wide range of applications, multiphase flows still raise a major challenge to fundamental science, notably non-equilibrium thermodynamics, mostly on account of the major complexity of their interfacial dynamics. Non-equilibrium thermodynamics is a notoriously difficult subject, especially far from the linear regime where fluxes no longer scale in linear proportion with the gradients that drive them. Under such circumstances, analytical solutions are precisely rare and resort to numerical methods becomes imperative.

Many numerical methods have been developed in the past to address these problems, including a list of major methods, phase-field, Lagrangian and Eulerian versions of non-ideal Navier-Stokes and so on.\textsuperscript{6,7} Despite their broad variety, most of these methods are based on the discretisation of the macroscopic equations of non-ideal thermo-hydrodynamics with suitable interface boundary conditions. Such methods have achieved major progress but they still face with a number of problems whenever interfacial dynamics presents large, localised gradients across complex topologies. In this respect, kinetic theory, being capable, at least in principle, of handling arbitrarily large gradients (large Knudsen numbers), is expected to offer a broader angle attack. Unfortunately, the cornerstone of kinetic theory, namely the Boltzmann equation, besides being computationally very demanding, does not easily extend to the dense fluid regime relevant to most multiphase flows.\textsuperscript{8,9–24}

However, in the last decade, suitable model Boltzmann equations, living in discrete phase-space, have proven capable of incorporating the basic features which control the physics of multiphase flows, namely a non-ideal equation of state, surface tension and disjoining pressure.\textsuperscript{24–29} Some of the models or the im-
proved versions have been successfully used in the simulation of complex fluids such as polymers, soft glassy materials, liquid crystals, and porous materials. With the help of those LB multiphase models, a wide variety of multiphase problems including wetting, droplet dynamic and evaporation, phase transition, hydrodynamic instability, etc., have been well simulated and investigated. This has opened up a new computational route to the exploration of multiphase flows, which is precisely the framework this paper inscribes to. More specifically, owing to the detailed information on the equilibrium and non-equilibrium kinetic moments of the discrete Boltzmann distribution, we provide a detailed analysis of the entropy evolution during the process of phase-separation process, as a function of the main transport coefficients, namely momentum and heat diffusivity, as well as surface tension. It is hoped an expected that this kind of analysis may prove useful to gain further insights into the physics of multiphase flows, as well as of other soft flowing systems, such as gels, foams and emulsions.

As a general study, we are not focusing on a specific fluid so all the parameters in this work are dimensionless. However, it is easy for the readers to recover the real situation according to the similarity principle. The remainder of this paper is organized as follows. Section 2 introduces the DBM for multiphase flows, presents the nondimensionalization, and derives the expression of entropy production rate. The liquid-vapor coexistence curves and Laplace law are verified to test the new model. Section 3 demonstrates the characteristics of entropy production for isothermal and thermal phase separations and the effects of heat conduction, viscous, and surface tension on entropy production. Section 4 concludes the present paper.

2 Methods and validation

2.1 Discrete Boltzmann model for nonideal fluid

For the multiphase flow DBM, the choice of the equation of state (EOS) is also important. There are many kinds of different EOS for nonideal fluids, such as the van der Waals (vdW) [31], Meshalkin-Kapln (M-K) [32], Peng-Robinson (P-R) [33], Redlich-Kwong (R-K) [34], and Carnahan-Starling (C-S) EOS [35]. Among which, the vdW EOS is the simplest EOS applied so far to polymer solutions. In fact, the vdW EOS is able to represent almost all basic types of binary phase diagrams for mixtures only if the size difference between the components is not too large. In this work, as a preliminary study, the vdW theory will be used to describe the EOS of nonideal fluid.

To describe the nonideal EOS and the surface tension effect, the collision term on the right side could be corrected by adding a extra term [12], then the discrete Boltzmann equation reads

$$\frac{df_{ki}}{dt} + \nabla \cdot f_{ki} = -\frac{1}{\tau} (f_{ki} - f_{eq}^{ki}) + l_{ki},$$

where $f_{ki}$ is distribution function of the discrete velocity $v_{ki}$ and the subscript $ki$ denotes the index of discrete velocity. $f_{eq}^{ki}$ is the discrete local equilibrium distribution function. The extra term $l_{ki}$ is used to describe the interparticle forces which is similar to the one introduced by Klimontovich for nonideal gases [13] and reads

$$l_{ki} = -\left[A + B \cdot c_{ki} + (C + C_{q}) \epsilon_{ki}^2\right] f_{eq}^{ki},$$

where $A$, $B$, $C$ and $C_{q}$ are four parameters depended on macroscopic quantities and their gradients, $c_{ki} = v_{ki} - u$ and $u$ is macroscopic velocity. The discretization of particle velocity space and calculations of $f_{eq}^{ki}$ and parameters used in Eq. (2) are referred to previous publications [36,37,38].

The model is consistent with the Onuki model for van der Waals fluid [39,40],

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0,$$

$$\frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho uu + \rho I) + \nabla \cdot (\mathbf{A} - \Pi) = 0,$$

$$\frac{\partial E}{\partial t} + \nabla \cdot (E u + P u) + \nabla \cdot [(\mathbf{A} - \Pi) \cdot u - j_{\mathbf{q}}] = 0,$$

in the hydrodynamic limit, where $P = \frac{\rho^T}{\rho_T^P} - a \rho^2$ is the van der Waals pressure, $\mathbf{I}$ is the unit tensor, $A = -\left[M \rho \nabla^2 \rho + \frac{M}{2} \nabla \rho^2 + \rho T V \rho \nabla \cdot \nabla (M/T)\right]$ + $M \rho \nabla \rho$ is the contribution of surface tension to the pressure tensor, and $M = K + C T$ with $K$ and $C$ are two constants. $\Pi$ and $j_{\mathbf{q}}$ are viscous stress and heat flux, respectively, $E = \rho e - a \rho^2 + \frac{5}{2} \nabla \rho^2 + \frac{1}{2} \nabla u^2$, and $e = D T / 2$ is internal energy density without contribution of density gradient.

2.2 Nondimensionalization and dimension recovery

In this work, all the parameters used in the simulation are dimensionless. Now we present how to recover the actual physical quantities from the numerical results. The reference variables are chose as $\rho_c$, $T_c$, and $L_c$, where $\rho_c$ and $T_c$ are the critical density and temperature, respectively. The relationship between the parameters in DBM and those of reality are

$$\hat{\rho} = \frac{\rho}{\rho_c}, \quad \hat{T} = \frac{T}{T_c}, \quad \hat{r}_\alpha = \frac{r_\alpha}{L_c},$$

$$\langle \hat{r}, \hat{T} \rangle = \left(\frac{r}{L_c}, \frac{T}{RT_c}\right), \quad \hat{u} = \frac{u}{RT_c}, \quad \hat{\rho} = \frac{\rho}{\rho_c},$$

$$\hat{\mu} = \frac{\mu}{\rho_c L_c \sqrt{RT_c}}, \quad \hat{\kappa} = \frac{\kappa}{\rho_c L_c \sqrt{RT_c}}, \quad \hat{\sigma} = \frac{\sigma}{\rho_c \kappa L_c},$$

where $r_\alpha$ indicates the space coordination in the $\alpha$ direction, $c_p$ is the specific heat at constant pressure, $\mu$ and $\kappa$ are coefficient of viscosity and heat conductivity, respectively, $\sigma$ is the surface tension which is calculated by $\sigma = K \int_{\alpha = 0}^{\pi/2} \frac{\partial r_\alpha}{\partial \alpha} d\alpha$, the variables with “^" sign on the left indicate the dimensionless and those without “^" sign possess real physical units.

The Prandtl number Pr and capillary number Ca is identical in both the simulations and reality, so that the simulation can be used to analogous to reality,

$$\text{Pr} = \frac{c_p \mu}{\kappa} = \frac{\hat{c}_p \hat{\mu}}{\hat{\kappa}},$$

$$\text{Ca} = \frac{\mu \nu}{\sigma} = \frac{\hat{\mu} \hat{\nu}}{\hat{\sigma}}.$$
The parameters in EOS and coefficient of surface tension can be determined by the properties of the fluids. In this work, all variables in the simulation are dimensionless and the sign “∧” will be dropped for simplicity.

### 2.3 Thermodynamic non-equilibrium measurement and entropy production

It has been known that the DBM is widely used in various complex flows with significant non-equilibrium characteristics. It presents two sets of measures for the TNE. One set is the differences of kinetic moments of two sets of measures for the TNE. One set is the differences of measures for the TNE. The other set includes the viscous stress and heat flux. In fact, it can be seen that there are two source terms that directly contribute to the entropy production. The first term is NOEF (or heat flux) and the second term is NOMF (or viscous stress). The two terms of entropy production rate are denoted by \( \dot{S}_{\text{NOEF}} \) and \( \dot{S}_{\text{NOMF}} \), respectively, which read

\[
\dot{S}_{\text{NOEF}} = \int \left( \frac{1}{T} \nabla \cdot \frac{1}{\rho} \right) dr,
\]

\[
\dot{S}_{\text{NOMF}} = \int \frac{1}{T} \Delta_{31} : \nabla \mathbf{u} dr.
\]

The total entropy production rate is denoted by \( \dot{S}_{\text{sum}} \) and it has

\[
\dot{S}_{\text{sum}} = \dot{S}_{\text{NOEF}} + \dot{S}_{\text{NOMF}}.
\]

The contribution of the surface tension vanish in the expression of entropy production because the work done by the surface tension is reversible.

Then the quantities of entropy production caused by NOEF and NOMF are denoted by \( \Delta S_{\text{NOEF}} \) and \( \Delta S_{\text{NOMF}} \), respectively, which are written as

\[
\Delta S_{\text{NOEF}} = \int \dot{S}_{\text{NOEF}} dt,
\]

\[
\Delta S_{\text{NOMF}} = \int \dot{S}_{\text{NOMF}} dt.
\]

The total entropy production is denoted by \( \Delta S_{\text{sum}} \) and it has

\[
\Delta S_{\text{sum}} = \Delta S_{\text{NOEF}} + \Delta S_{\text{NOMF}}.
\]

### 2.4 Numerical verification

In order to validate the DBM for nonideal fluid, we first evaluate that if the new model provides an accurate the vdW EOS. As the first test, the liquid-vapor coexistence curves at various temperatures are simulated. The computational grids are \( N_x \times N_y = 200 \times 4 \) with space step \( \Delta x = \Delta y = 0.01 \). Time step is \( \Delta t = 0.0001 \) and relaxation time \( \tau = 0.02 \). Periodic boundary conditions are adopted in both horizontal and vertical directions. The first and second order spatial derivatives are all calculated by the nine-point stencil (NPS) scheme which possesses a higher isotropy and is
able to reduce spurious velocities significantly. The coefficient of surface tension is \( K = 5 \times 10^{-5} \) when calculate the force term. The parameters \( a \) and \( b \) in the EOS are chosen as \( a = \frac{9}{8} \) and \( b = \frac{1}{3} \) so it has a critical point at \( \rho_c = T_c = 1 \).

The initial conditions are

\[
\begin{aligned}
(p, T, u_x, u_y)_L &= (\rho, 0.9975, 0, 0), \\
(p, T, u_x, u_y)_M &= (\rho, 0.9975, 0, 0), \\
(p, T, u_x, u_y)_R &= (\rho, 0.9975, 0, 0),
\end{aligned}
\]

(26)

where the subscript “L”, “M”, and “R” indicate the regions \( x \leq \frac{1}{4}N_x, \frac{1}{4}N_x < x \leq \frac{3}{4}N_x, \) and \( x > \frac{3}{4}N_x \), respectively, \( \rho_i = 0.955 \) and \( \rho_f = 1.045 \) are theoretical vapor and liquid densities, respectively, at \( T = 0.9975 \). The temperature is dropped to \( T = 0.99 \) when the equilibrium state of the system is achieved. Then the temperature drops by a small value \( \Delta T = 0.01 \) each time once the equilibrium state of the system is achieved again. Simulations go on until the temperature is reduced to 0.85 then a series of coexistence points are obtained which is shown in the inset of Fig. 1. The solid line is directly calculated from van der Waals EOS using a Maxwell equal-area construction. It shows that the coexistence points simulated by the DBM are well agree with the theoretical coexistence curve. It verifies that the DBM provides a correct vDW thermodynamics.

Figure 1 also gives the interface density profiles at equilibrium state at \( T = 0.90 \). Three different coefficients of surface tension \( K \) are simulated and compared with analytical solutions. The lines in Fig. 1 are the analytical solutions and the symbols represent DBM simulations. It can be seen that the DBM results are in excellent agreement with the analytical solutions under different coefficients of surface tension. It proves that the calculation of surface tension in DBM is accurate.

To further test our model in two-dimension, Fig. 2 shows the verification of Laplace’s law. A circular droplet with a radius of \( r \) is surrounded by its vapor phase. The initial conditions are set as

\[
\begin{aligned}
(p, T, u_x, u_y)_\text{in} &= (1.5865, 0.92, 0, 0), \\
(p, T, u_x, u_y)_\text{out} &= (0.4786, 0.92, 0, 0),
\end{aligned}
\]

(27)

where the subscript “in” and “out” indicate the regions \( \sqrt{(x-x_L/2)^2 + (y-y_L/2)^2} \leq r \) and \( \sqrt{(x-x_L/2)^2 + (y+y_L/2)^2} > r \), respectively, where \( L_x \) and \( L_y \) are the length and width of computational region. The simulation region is \( L_x \times L_y = 1 \times 1 \). All the rest parameters and the simulation conditions are the same with those in Fig. 1.

According to Laplace law, the pressure difference \( \Delta P \) between the inside and outside of the circular domain is proportional to the reciprocal of radius \( 1/r \) when the surface tension is fixed.

\[ \Delta P = \frac{\sigma}{r}. \]

(28)

Fig. 2 \( \Delta P \) plotted versus \( 1/r \) for three different coefficients of surface tension as tests of Laplace’s law. The symbols are DBM results while the lines are linear fits with slopes \( k \).

3 Simulations and analysis

3.1 Isothermal and thermal phase separation

For a single-phase fluid such as steam water or molten metal, phase transition and separation occurs when the temperature suddenly drops to a two-phase coexistence zone. Such a process is commonly called quenching which is an important technology for heating processing. Under quenching condition, the fluid undergo two stages: the early spinodal decomposition (SD) and the late stage of domain growth (DG).

The characteristics of the late stage have been extensively studied by theoretical derivations, numerical simulations, and experiments. It has been known that the characteristic domain size \( R(t) \) grows as power with time \( t \), \( R(t) \sim t^\alpha \), at the domain growth stage in isothermal systems. However, there is less research on the early stage of phase separation. One reason is that how to exactly distinguish the SD stage from the DG stage is still an open problem. In 2011, a geometric criterion was given by using the Minkowski function. It was found that the boundary length \( L \) increases at SD stage and decreases at DG stage. As a result, the maximum point of \( L \) can be used to mark the critical time.
when the SD stage ends and the DG stage begins. However, profiles and maximum points of $L$ vary with the selected threshold values. In 2015, with the help of the total TNE strength, a physical criterion was proposed to distinguish the two stages of phase separation. In this work, we will show that the entropy production rate $S_{\text{sum}}$ can also be used to mark the transition from the SD stage to the DG stage and the maxima of $S_{\text{sum}}$ corresponds to the critical time $t_{\text{SD}}$.

Firstly, the isothermal and thermal phase separations are simulated and compared. The initial conditions are set as

$$$(\rho, u_x, u_y, T) = (1 + \delta, 0.0, 0.0, 0.85), \quad (29)$$$ where $\delta$ is a random density noise with an amplitude of 0.01. The computational grids are $N_x \times N_y = 100 \times 100$ with space step $\Delta x = \Delta y = 0.01$. Time step is $\Delta t = 1 \times 10^{-4}$ and relaxation time $\tau = 0.02$. The coefficient of surface tension is $K = 1 \times 10^{-5}$, the parameters in the vdW EOS are $a = \frac{9}{4}$ and $b = \frac{1}{4}$. The spatial derivations are calculated by NPS scheme and the time derivation is solved by the first order forward difference. Periodic boundary conditions are used in both directions. The temperature is reset to $T = 0.85$ at each time step for isothermal case. For thermal case, the temperature changes freely and is solved by the distribution function at each time step.

Figure 3 shows the density contour maps for isothermal and thermal conditions at several typical times. The first line and the second line correspond to the isothermal case and thermal case, respectively. The fluid separates into small regions with higher density at $t = 0.2$ and higher density region increases and the density in the lower density region decreases. From (b) ($t = 0.4$) we can see the liquid-vapor interfaces are clearer than those at $t = 0.2$, but there is no significant change for the domains of liquid or vapor. After the SD stage, the small domains merge with each other and larger domains are formed under the action of surface tension. The characteristic domain size grows fast which can be found from the density contour maps at $t = 2.0$ and $t = 8.0$. Compared with isothermal case, the thermal phase separation is much slower.

![Fig. 3](image)

Fig. 3 Density contour maps at several times for isothermal and thermal phase separation. The first line corresponds to case (I) isothermal phase separation and the second line case (II) thermal phase separation. The columns from left to right denote at the time (a) $t = 0.2$, (b) $t = 0.4$, (c) $t = 2.0$, and (d) $t = 8.0$, respectively.

To quantitatively analyze the phase separation process, we resort to the complex physical field analysis techniques including statistical methods, rheological methods, and morphological methods. Figure 4 gives the profiles of characteristic domain sizes $R(t)$, the second order thermal non-equilibrium strengths $D_2$ and the boundary lengths $L$ of the Minkowski function, and the entropy production rates $S_{\text{sum}}$ as functions of time $t$. Figure 4(a) shows the profile of $R(t)$ in a log-log scale. The critical time $t_{\text{SD}}$ is marked by arrows. The scaling law at the DG stage is obvious. Compared with the isothermal case the thermal phase separation has a larger $t_{\text{SD}}$ and a lower growth rate, which is in accordance with the evolution of density pattern in Fig. 3. From the previous study, we know the non-equilibrium strength and the boundary length can also be used as the criterion to discriminate the two stages of phase separation which is verified by Figs. 4(b) and 4(c). The non-equilibrium strength and the boundary length increase with time at the SD stage and decrease with time at the DG stage. The maximum points correspond to the $t_{\text{SD}}$. From Fig. 4(d) we can find that the profile of entropy production rate possesses the same characteristics, hence it provides another physical criterion for the two stages of phase separation. It should be noted that the values of $t_{\text{SD}}$ given by those different criterions may not be exactly the same. It is physically reasonable and reflects the different characteristic of the complex flows from different perspectives. Nevertheless, the same conclusion is reached that the $t_{\text{SD}}$ of isothermal phase separation is less than that of thermal case. In addition, we can see the non-equilibrium strength of thermal phase separation is weaker and the entropy production rate of thermal phase separation is lower than those of isothermal case from Figs. 4(b) and 4(d), respectively.

![Fig. 4](image)

Fig. 4 Four kinds of criteria to discriminate the stages of the spineal decomposition and domain growth. (a) Rheological characterization. (b) Non-equilibrium strength. (c) Morphological characterization. (d) The rates of entropy production.

### 3.2 Effects of heat conduction

To examine the effects of heat conduction, we simulate the thermal phase separation with different heat conductivities. In the usual DBM based on BGK model, the coefficients of viscosity $\mu$ and heat conductivities $\kappa$ are bound together. It has $\mu = \tau p T$ and $\kappa = c_p \tau p T$. The Prandtl number $Pr$ which is defined as $Pr = c_p \mu / \kappa$, is fixed, so the effects of viscosity and heat conduction are usually considered together. However, in the multiphase flow DBM, by introducing the $C_q$ in the extra term, the $Pr$ is adjustable.
Different heat conductivities can be obtained under the fixed relaxation time by changing the value of Pr.

All the simulation conditions are the same with those of thermal phase transition in Fig. 3. Different values of heat conductivities are obtained by change the $C_p$ in Eq. (2). Figure 5 shows the density contour maps with three different Pr at several typical moments. The three lines from top to bottom correspond to the cases with $Pr = 1.0$, $Pr = 0.5$, and $Pr = 0.2$, respectively. The four columns from left to right correspond to the snapshots at time $t = 0.2$, $t = 0.5$, $t = 2.0$, and $t = 8.0$, respectively. We can see the smaller the Pr is, the faster the phase separation evolves. Under the fixed viscosity coefficient, a smaller Pr corresponds to a bigger heat conductivity. Thus, we can conclude that the role of heat conduction is to accelerate the evolution of thermal phase separation.

To quantify the characteristics of the thermal phase separation process, the profiles of characteristic domain size $R(t)$ and the entropy production rate $S_{\text{sum}}$ as functions of time are plotted in Fig. 6. The $R(t)$ provides an approximately criterion to distinguish the two stages. First, $R(t)$ increases and reaches a platform and the platform remains until the end of the SD stage. Then the phase separation enters the DG stage and $R(t)$ grows in the form of a power law. The end of the platform corresponds to the critical time $t_{SD}$ which is marked by arrows in Fig. 6(a). The larger the Pr (or the smaller the heat conductivity) is, the bigger the $t_{SD}$ is. This means the effects of heat conduction are to shorten the duration time of the SD stage and to speed up the rate of phase separation. From the maximum points of entropy production rate in Fig. 6(b), the same conclusions can be obtained. In addition, it can be seen that the amplitude of $S_{\text{sum}}$ increases with the acceleration of the phase separation.

The relationship between $t_{SD}$ and heat conductivities (represented by $1/Pr$), and the relationships between entropy production rates and heat conductivities are shown in Fig. 7. Figure 7(a) gives the results of $t_{SD}$ simulated by DBM with different values of Pr and the fitting curve. When the heat conductivity satisfies $1 \leq 1/Pr \leq 5$, the curve is fitted by exponential function with an expression of

$$t_{SD} = 5.46 \exp\left(-\frac{1}{0.33Pr}\right) + 0.25.$$  

This expression verifies the previous conclusion that heat conduction helps to accelerate the thermal phase separation and the duration of SD stage $t_{SD}$ decreases exponentially with heat conductivity. Then we examine the effects of heat conduction on entropy production rate of NOEF $S_{\text{NOEF}}$, the entropy production rate of NOMF $S_{\text{NOMF}}$, and the total entropy production rate $S_{\text{sum}}$. The peak values of $S_{\text{NOEF}}$, $S_{\text{NOMF}}$, and $S_{\text{sum}}$ are selected to represent the corresponding amplitudes of the entropy production rates. They are indicated by $S_{\text{NOEF}}^\text{max}$, $S_{\text{NOMF}}^\text{max}$, and $S_{\text{sum}}^\text{max}$, respectively. Figures 7(b), 7(c), and 7(d) show the profiles of $S_{\text{NOEF}}^\text{max}$, $S_{\text{NOMF}}^\text{max}$, and $S_{\text{sum}}^\text{max}$ as functions of $1/Pr$, respectively. The symbols represent DBM results and the solid lines are obtained by fitting. All the fitting curves have the same function form but different fitting coefficients. The expressions are

$$S_{\text{NOEF}}^\text{max} = 0.094 \exp\left(-\frac{1}{0.517Pr}\right) + 0.0026,$$

$$S_{\text{NOMF}}^\text{max} = -0.074 \exp\left(-\frac{1}{1.577Pr}\right) + 0.044,$$

$$S_{\text{sum}}^\text{max} = -0.046 \exp\left(-\frac{1}{3.177Pr}\right) + 0.053.$$  

According to the fitting results, we learn that the amplitudes of entropy production rates of NOEF and NOMF both have an exponential relationship with the heat conductivity. However, the entropy production rate of NOEF decreases exponentially while the entropy production rate of NOMF increases exponentially with the increase of heat conductivity. The larger the conductivity, the lower the entropy production rate of NOEF and the higher the entropy production rate of NOMF. The sum of the entropy production rate increases exponentially with heat conductivity.

In Fig. 7 only the maximum points of entropy production rates are studied which are not adequately represent the entropy production properties. Figure 8 shows the profiles of entropy production rate and quantities of entropy production as functions of time. Figures 8(a) - 8(c) are profiles of entropy production rates for different heat conductivities represented by $1/Pr$ and figures 8(d) - 8(f) show quantities of entropy production which are the areas between the profiles of entropy production rate and the x-
axis. From Fig. 8 (a) we can see that the profiles of $\dot{S}_{\text{NOEF}}$ shift leftwards and the amplitudes decrease with the increase of heat conductivity. The entropy productions of NOEF also decrease with the increase of heat conductivity which can be found in Fig. 8 (d). The profiles of $S_{\text{NOMF}}$ in Fig. 8 (b) also shift leftwards while the amplitude increase with the increase of heat conductivity. From Fig. 8 (c) we can see that the entropy production of NOMF increases with the increase of heat conductivity. Figure 8 (c) shows the change of the amplitude of $S_{\text{sum}}$ is much more complex when the Prandtl number is around 1, though the increase of amplitude is significant when $Pr < 0.8$. This can also be found in Fig. 7 (d) where $S_{\text{max}}$ increases exponentially with heat conductivity when $Pr < 0.8$. The profiles of total entropy production are shown in Fig. 8 (f) from which we can see the change of the total entropy production with heat conductivity is not monotonic.

### 3.3 Effects of viscosity

In this section, we study the effects of viscosity coefficient on the thermal phase separation. The simulation conditions are the same with those in Fig. 6 (II). Various viscosity coefficients are obtained by changing the relaxation time $\tau$. The Prandtl number also changes with the relaxation time to keep the heat conductivity be fixed. Figure 9 shows the density contour maps with four different values of $\tau$ at several typical moments.

The four lines from top to bottom correspond to the cases with (I) $\tau = 0.02$ and $Pr=1.0$, (II) $\tau = 0.016$ and $Pr=0.8$, (III) $\tau = 0.01$ and $Pr=0.5$, and (IV) $\tau = 0.004$ and $Pr=0.2$, respectively. The four columns from left to right correspond to the snapshots at time (a) $t = 0.2$, (b) $t = 0.5$, (c) $t = 2.0$, and (d) $t = 8.0$, respectively. From the density contour maps at $t = 0.2$ we can see a smaller viscosity coefficient has a clearer interface, which means a weaker viscosity corresponds to a faster separation process. However, the difference in density contour map for different viscosity coefficients is not obvious at the later stage.

**Fig. 9** Density contour maps at several times for different coefficients of viscosity with the same heat conductivity. The first line corresponds to case (I) $\tau = 0.02$ and $Pr=1.0$, the second line case (II) $\tau = 0.016$ and $Pr=0.8$, the third line case (III) $\tau = 0.01$ and $Pr=0.5$, and the fourth line case (IV) $\tau = 0.004$ and $Pr=0.2$. The columns from left to right denote the density contour maps at the time (a) $t = 0.2$, (b) $t = 0.5$, (c) $t = 2.0$, and (d) $t = 8.0$, respectively.

Figure 10 (a) shows the profiles of characteristic domain size $R(t)$. The critical time points $t_{SD}$ are marked by arrows from which we know the role of viscosity is to prolong the SD stage. The rate of the phase domain growth can be represented by the slope of the $R(t)$ in the log-log scale from which we can see the viscosity has little effect on the rate of separation at the DG stage. The reason is that those simulation conditions here are all high viscosity, so the effect of viscosity change on the domain growth is not significant. The domain growth law states that, at DG stage, $R(t) \sim t^{1/2}$ for higher viscosity and $R(t) \sim t^{2/3}$ for lower viscosity. Although this conclusion is for isothermal conditions, we
find that a similar power law exists for thermal phase separation. The power exponent is not sensitive to the viscosity coefficient within a certain range. The profiles of total entropy production rate for different viscosity coefficients are shown in Fig. 10 (b). The maximum points of entropy production rate indicate the $t_{SD}$ which are consistent with those in Fig. 10 (a).

Fig. 10 The characteristic domain sizes (a) and the rates of entropy production (b) for different coefficients of viscosity.

The relationship between $t_{SD}$ and viscosity coefficients (represented by $\tau$) is shown in Fig. 11 (a). The symbols are DBM results and the solid line is fitted by exponential function with an expression of

$$ t_{SD} = 0.00106\exp\left(\frac{\tau}{0.00622}\right) + 0.25, $$

(34)

when the coefficient of viscosity $\tau$ varies in the range $[0.004, 0.2]$. This expression verifies that viscosity prolongs the SD stage and the duration of SD stage $t_{SD}$ increases exponentially with coefficients of viscosity within the range of simulation parameters. Then we examine the effects of viscosity on entropy production rate of NOEF $\dot{S}_{NOEF}$, the entropy production rate of NOMF $\dot{S}_{NOMF}$, and the total entropy production rate $\dot{S}_{sum}$. The peak values of entropy production rates $\dot{S}_{max_{NOEF}}$, $\dot{S}_{max_{NOMF}}$, and $\dot{S}_{max_{sum}}$ are plotted in Figs. 11 (b), 11 (c), and 11 (d), respectively, as functions of $\tau$. The symbols are simulation results and the solid lines are fitting curves. The exponential function is used to fit the profile of $\dot{S}_{NOEF}$ which reads

$$ \dot{S}_{NOEF, max} = 6.09\exp\left(\frac{\tau}{6.54 \times 10^{-3}}\right) \times 10^{-4} + 3.7 \times 10^{-3}. $$

(35)

The fitting curve shows maximum of entropy production rates of NOEF increase exponentially with the increase of viscosity coefficient. The profile of $\dot{S}_{NOMF, max}$ is fitted by linear function

$$ \dot{S}_{NOMF, max} = -0.747\tau + 0.0204. $$

(36)

Thus, the maximum of entropy production rates of NOMF decrease linearly with the increase of viscosity coefficient. The behaviour of the total entropy production rate is much more complex, so we choose a cubic polynomial to rough fit $\dot{S}_{sum_{NOMF}}$ which reads

$$ \dot{S}_{sum_{NOMF}} = (19.1\tau)^3 - (15.2\tau)^2 + 2.12\tau + 0.0152. $$

(37)

Figure 12 shows the profiles of entropy production rate and the amounts of entropy production as functions of time for several typical viscosity coefficients. The quantities of entropy production are the areas between the profiles of entropy production rate and the $x$-axis. From Fig. 12 (a) we can see that the profile of $\dot{S}_{NOEF}$ shifts to the right and the amplitude increases with the increase of viscosity coefficient. Figure 12 (d) shows that the entropy production of NOEF also increases with the increase of viscosity coefficient. The profile of $\dot{S}_{NOMF}$ in Fig. 12 (b) shifts to the right but the amplitude decreases with the increase of viscosity coefficient. The profiles of entropy production are almost overlapped in Fig. 12 (e) when $\tau \leq 0.01$ and the entropy production decreases with the increase of viscosity when $\tau > 0.01$. The change of the total entropy production rate with viscosity coefficients is non-monotonic. From Fig. 12 (f) we can see that a larger viscosity coefficient corresponds to less entropy production at the early stage but it corresponds to more entropy production at the later stage.

3.4 Effects of surface tension

The surface tension is also an important factor that affects the phase separation. In this section, the thermal phase separation processes with different coefficients of surface tension $K$ are simulated and investigated. The simulation conditions are the same as those in section 3.3.
with those in Fig. (II) except for the value of \( K \). Figure 13 shows the density contour maps with three different \( K \) at several typical moments. The three lines from top to bottom correspond to the cases with (I) \( K = 2 \times 10^{-5} \), (II) \( K = 1 \times 10^{-5} \), and (III) \( K = 5 \times 10^{-6} \), respectively. The four columns from left to right correspond to the snapshots at time (a) \( t = 0.2 \), (b) \( t = 0.5 \), (c) \( t = 2.0 \), and (d) \( t = 8.0 \), respectively. The role of surface tension is to promote the merger of the small domains at the DG stage. From Figs. 13 (a) and 13 (b) we can see the surface tension also plays an important part at the SD stage. A smaller coefficient surface tension corresponds to a clearer interface and a smaller characteristic domain size. Figures 13 (c) and 13 (d) belong to the DG stage where a smaller coefficient surface tension also corresponds to a small characteristic domain size.

The evolution of the characteristic domain sizes \( R(t) \) over time is given in Fig. 14 (a). The stronger the surface tension is, the larger the \( R(t) \) is. The critical time points \( t_{SD} \) are marked by arrows. The bigger the coefficient surface tension is, the later the critical time is. Therefore, similar to the viscosity, the role of surface tension is also to prolong the SD stage. Besides, the surface tension has a significant effect on the platform of \( R(t) \) at the SD stage. The bigger the coefficient surface tension is, the higher and wider the platform is. The platform is nearly vanished for the case \( K = 5 \times 10^{-6} \). The profiles of total entropy production rate for different coefficients of surface tension are shown in Fig. 14 (b). The maximum values of entropy production rate indicate the points of \( t_{SD} \) which are consistent with those in Fig. 14 (a). In addition, the amplitude of entropy production rate increases with the decrease of the coefficient of surface tension.

In order to study the effects of surface tension quantitatively, the profiles of \( t_{SD} \), \( S_{NOEF}^\text{max} \), \( S_{NOMF}^\text{max} \), and \( S_{\text{sum}}^\text{max} \) as functions of \( K \) are shown in Fig. 15. The profile of \( t_{SD} \) is given in Fig. 15 (a) where the symbols represent the results of DBM and the solid line is fitted by linear function as

\[
t_{SD} = 0.028K + 0.228. \tag{38}
\]

where \( K \) has a unit of \( 10^{-6} \) and \( K \) varies in the range \([4 	imes 10^{-6}, 2 \times 10^{-5}]\). This indicates that the critical time increases linearly with the increase of coefficient surface tension, which is consistent with the previous conclusion in the literature. The profiles of \( S_{NOEF}^\text{max} \), \( S_{NOMF}^\text{max} \), and \( S_{\text{sum}}^\text{max} \) are given in Figs. 15 (b), 15 (c), and 15 (d), respectively. The symbols represent the results of DBM and the solid lines are fitting curves. These curves are very similar and are all fitted by exponential functions with different parameters,

\[
S_{NOEF}^\text{max} = 18exp(-K/8.22) + 11.1, \tag{39}
\]

\[
S_{NOMF}^\text{max} = 8.6exp(-K/7.07) + 2.4, \tag{40}
\]

\[
S_{\text{sum}}^\text{max} = 26.5exp(-K/7.84) + 13.5, \tag{41}
\]

where \( S_{NOEF}^\text{max} \), \( S_{NOMF}^\text{max} \), and \( S_{\text{sum}}^\text{max} \) all have a unit of \( 10^{-3} \) and \( K \) has a unit of \( 10^{-6} \). From Eqs. (39)-(41) we can see the maximum of entropy production rates are all decrease exponentially with the increase of the coefficient of surface tension. It can be concluded that the effect of surface tension is to lower the entropy production rate.

Fig. 13 Density contour maps at several times for different coefficients of surface tension. The first line corresponds to case (I) \( K = 2 \times 10^{-5} \), the second line case (II) \( K = 1 \times 10^{-5} \), and the third line case (III) \( K = 5 \times 10^{-6} \). The columns from left to right are density contour maps at the time (a) \( t = 0.2 \), (b) \( t = 0.5 \), (c) \( t = 2.0 \), and (d) \( t = 8.0 \), respectively.

Fig. 14 The characteristic domain sizes (a) and the rates of entropy production (b) for different coefficients of surface tension.

Fig. 15 The profiles of critical time \( t_{SD} \) and the amplitudes of entropy production rates as functions of coefficient of surface tension. (a) critical time \( t_{SD} \), (b) entropy production rate of NOEF \( S_{NOEF} \), (c) entropy production rate of NOMF \( S_{NOMF} \), (d) total entropy production rate \( S_{\text{sum}} \). The symbols are results of DBM and the solid lines are fitting curves.
Figure 16 shows the profiles of the entropy production rates and the quantities of entropy production as functions of time. From Figs. 16(a)–16(c) we can see the entropy production rates \( S_{\text{NOEF}}, S_{\text{NOMF}}, \) and \( \Delta S_{\text{sum}} \) have the similar characteristics. With the increase of coefficient of surface tension, the profiles shift to the right and the amplitudes of the profiles decrease. A bigger coefficient of surface tension leads to a lower entropy production at the early stage. However, at the later stage, the change of the entropy production is much more complex. As shown in Figs. 16(d)–16(f), the effect of the surface tension on entropy production is not monotonous at the later stage.

As the coefficient of viscosity increases, \( S_{\text{NOEF}}^{\text{max}} \) decreases and \( S_{\text{NOMF}}^{\text{max}} \) increases. The decrease of the former is exponentially related to the increase of the latter. The competitive relationship between \( S_{\text{NOEF}}^{\text{max}} \) and \( S_{\text{NOMF}}^{\text{max}} \) is similar to that in Fig. 17(a), except that \( S_{\text{NOEF}}^{\text{max}} \) and \( S_{\text{NOMF}}^{\text{max}} \) change in opposite directions. In fact, both the increase of heat conductivity and the decrease of coefficient of viscosity are equivalent to the decrease of Prandtl number. Thus, combining Fig. 17(a) and Fig. 17(b), we find that \( S_{\text{NOMF}}^{\text{max}} \) decreases and \( S_{\text{NOEF}}^{\text{max}} \) increases with the increase of Prandtl number. Generally, a larger Prandtl number indicates that the effect of viscosity is stronger than the effect of heat conduction. However, in this study, it is interesting to find that a larger Prandtl number corresponds to a smaller \( S_{\text{NOEF}}^{\text{max}} \) and a larger \( S_{\text{NOMF}}^{\text{max}} \).

Fig. 17 The maximum entropy production rate \( S_{\text{NOMF}}^{\text{max}} \) versus \( S_{\text{NOEF}}^{\text{max}} \) under various (a) heat conductivities, (b) coefficients of viscosity, and (c) coefficients of surface tension. The arrows in subfigures (a), (b), and (c) indicate an increase in heat conductivity, coefficient of viscosity, and coefficient of surface tension, respectively. The symbols are DBM results and the solid lines are fitting curves.

Fig. 17(c) shows the profile of \( S_{\text{NOMF}}^{\text{max}} \) versus \( S_{\text{NOEF}}^{\text{max}} \) under various coefficients of surface tension. The arrow points to the direction along which coefficient of surface tension increases. The symbols are DBM results and the solid line is fitted by linear function

\[
S_{\text{NOMF}}^{\text{max}} = 0.466S_{\text{NOEF}}^{\text{max}} - 0.3. \tag{44}
\]

As the coefficient of surface tension increases, both \( S_{\text{NOMF}}^{\text{max}} \) and \( S_{\text{NOEF}}^{\text{max}} \) decrease. The reduction of \( S_{\text{NOMF}} \) is proportional to that of \( S_{\text{NOEF}}^{\text{max}} \). We can conclude that the effect of surface tension is to decrease the entropy production rate, and it mainly leads to the cooperation, instead of competition between \( S_{\text{NOMF}}^{\text{max}} \) and \( S_{\text{NOEF}}^{\text{max}} \).

The relationships between the quantities of entropy production \( \Delta S_{\text{NOMF}} \) and \( \Delta S_{\text{NOEF}} \) under various heat conductivities, coefficients of viscosity, and coefficients of surface tension are shown in Fig. 18. The profiles of \( \Delta S_{\text{NOMF}} \) versus \( \Delta S_{\text{NOEF}} \) under various heat conductivities are plotted in Fig. 18(a). The arrow points to the direction along which heat conductivity increases. We can see that both \( \Delta S_{\text{NOMF}} \) and \( \Delta S_{\text{NOEF}} \) increase with time. \( \Delta S_{\text{NOMF}} \) is approximately proportional to \( \Delta S_{\text{NOEF}} \) and the slope increases with the increase of heat conductivity. This shows that, with the increase of heat conductivity, the proportion of \( \Delta S_{\text{NOMF}} \) in the total entropy production \( \Delta S_{\text{sum}} \) increases and the proportion of \( \Delta S_{\text{NOEF}} \) decreases. Figure 18(b) shows the profiles of \( \Delta S_{\text{NOMF}} \) versus \( \Delta S_{\text{NOEF}} \) under various coefficients of viscosity. The arrow points to the direction along which coefficient of viscosity increases. It can be seen that \( \Delta S_{\text{NOMF}} \) is also approximately proportional to \( \Delta S_{\text{NOEF}} \). However, different from the effect of heat conductivity, the slope decreases with the increase of coefficient of viscosity. This is easy to understand because both the increase of

3.5 Cooperation and competition between two kinds of mechanisms for entropy production

In this section, we study the cooperation and competition between the two kinds of mechanisms, NOEF and NOMF, for entropy production under various heat conductivities, viscosities, and surface tensions. Figure 17 shows the relationship between the maximum entropy production rates \( S_{\text{NOMF}}^{\text{max}} \) and \( S_{\text{NOEF}}^{\text{max}} \). The profile of \( S_{\text{NOMF}}^{\text{max}} \) versus \( S_{\text{NOEF}}^{\text{max}} \) under various heat conductivities is plotted in Fig. 17(a). The arrow points to the direction along which heat conductivity (represented by \( 1/Pr \)) increases. The symbols are DBM results and the solid line is fitted by

\[
S_{\text{NOMF}}^{\text{max}} = \exp(-1.466S_{\text{NOEF}}^{\text{max}} + 1.61). \tag{42}
\]

There is a competition between \( S_{\text{NOMF}}^{\text{max}} \) and \( S_{\text{NOEF}}^{\text{max}} \) as the heat conductivity changes. When the heat conductivity increases, \( S_{\text{NOMF}}^{\text{max}} \) increases but \( S_{\text{NOEF}}^{\text{max}} \) decreases. The increase of the former is exponentially related to the decrease of the latter.

From Fig. 17(b), we can see a similar relationship between \( S_{\text{NOMF}}^{\text{max}} \) and \( S_{\text{NOEF}}^{\text{max}} \) under various coefficients of viscosity. The arrow points to the direction along which coefficient of viscosity increases. The symbols are DBM results and the solid line is fitted by

\[
S_{\text{NOMF}}^{\text{max}} = \exp(-1.063S_{\text{NOEF}}^{\text{max}} + 0.997). \tag{43}
\]
heat conductivity and the decrease of coefficient of viscosity correspond to the decrease of Prandtl number. From Fig. 18(a) and 18(b) we can conclude that the slope of the $\Delta S_{\text{NOMF}} - \Delta S_{\text{NOEF}}$ profiles increase with the decrease of Prandtl number. It means that, with the decrease of Prandtl number, the proportion of $\Delta S_{\text{NOMF}}$ in the total entropy production increases and the proportion of $\Delta S_{\text{NOEF}}$ decreases.

Figure 18(c) shows the profiles of $\Delta S_{\text{NOMF}}$ versus $\Delta S_{\text{NOEF}}$ under various coefficients of surface tension. The arrow points to the direction along which coefficient of surface tension increases. The $\Delta S_{\text{NOMF}}$ is also approximately proportional to $\Delta S_{\text{NOEF}}$. However, compared with heat conductivity and coefficient of viscosity, the coefficient of surface tension has less effect on the slope of $\Delta S_{\text{NOMF}} - \Delta S_{\text{NOEF}}$ profile. This is consistent with the conclusion in Fig. 17(c). The competition between $\Delta S_{\text{NOMF}}$ and $\Delta S_{\text{NOEF}}$ with the change of surface tension is much weaker.

4 Conclusion

Based on the multiphase flow DBM, we investigate the entropy production of thermal phase separation. The relationship between entropy generation rate and the non-equilibrium quantities is established. Two mechanisms, the non-organised energy fluxes (NOEF) and the non-organised moment fluxes (NOEF), are responsible for the entropy generation. A new physical criterion to separate the two stages of phase separation is presented. It is found that the entropy production rate increases with time at the spinodal decomposition stage and decreases with time at the domain growth stage. The maximum point of the entropy production rate corresponds to the critical time $t_{SD}$ of the two stages. Then, the effects of heat conduction, viscosity, and the surface tension on the entropy production are examined. Within the range of simulation parameters in this work, it is found that the amplitude of entropy production rate of NOEF decreases exponentially with the increase of the heat conductivity, increases exponentially with the increase of the viscosity coefficient, and decreases exponentially with the increase of the coefficient of surface tension. The amplitude of entropy production rate of NOMF increases exponentially with the increase of the heat conductivity, decreases linearly with the increase of the viscosity coefficient, and decreases exponentially with the increase of the coefficient of surface tension. The amplitude of sum entropy production rate is a combination of those of NOEF and NOMF. It increases exponentially with the increase of the heat conductivity and decreases exponentially with the increase of the coefficient of surface tension. The effect of viscosity coefficient on the total entropy production rate is non-monotonic. In addition, it is found that the competition between the entropy production of NOMF and that of NOEF is much more significant when the heat conductivity or coefficient of viscosity changes, which means a smaller entropy production of NOMF corresponds to a larger entropy production of NOEF. However, the entropy production of NOMF and that of NOEF change synchronously with the change of the coefficient of surface tension. Instead of competition, there exits a cooperation between NOMF and NOEF for entropy production under various coefficient of surface tension.

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