

The Statistical Modeling of Multicomponent-Fuel Drop Evaporation for Fuels Containing a Multitude of Species

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Abstract

A statistical formulation is described portraying the composition in an evaporating multicomponent-fuel liquid drop and in the gas phase surrounding it. The initial fuel composition is specified by a Gamma Probability Distribution Function (PDF) according to Continuous Thermodynamics results. Using a discrete-component model and the classical quasi-steady gas phase assumption with respect to the liquid, it is shown that when drops are immersed in a carrier gas containing fuel vapor, condensation of species onto the drop results in the development of a sometimes major peak in the drop-surface gas composition PDF. This PDF shape essentially agrees with that calculated using a superposition of two Gamma PDFs in the liquid.

Introduction

The modeling of multicomponent drop evaporation is a challenging task owing to the difficulty in portraying the coupled behavior of a multitude of chemical species. Detailed models of multicomponent-fuel (MC-fuel) drops were developed more than twenty years ago by [1] and [2] but even with current computational capabilities, the calculation time with these models remains daunting if many millions of drops must be considered, as in any practical spray application.

This study is devoted to the modeling of MC-fuel drops containing a very large number of species. Such a model was proposed by [3] and [4], and utilized by [5] and [6]. This model is based on a statistical representation of the fuel composition using Continuous Thermodynamics (CT). CT is a theory [7] [8] [9] [10] [11] in which the composition of a mixture is described by a probability distribution function (PDF) rather than by a series of discrete values of the concentration. Generally, this PDF is a function of all thermophysical properties of the chemical species, however, in practical applications it can be chosen to depend on one or several properties of interest of the mixture [10] such as the relative volatility [7], the normal boiling point, the number of carbon atoms per molecule, or most conveniently for many applications, the molar weight [11]. The simplification that the PDF depends only on the molar weight is possible for mixtures composed of homologous species [12] [11] and such distributions, based on the

Gamma PDF (Γ -PDF), are available for diesel fuel, gasoline and kerosene [11] [3]. Thus, the advantage of CT theory is that the mixture composition can be represented by a small number of parameters rather than by the prohibitively large number of parameters that would be necessary even for a fuel composed of 10-20 species. The theory is based on the appropriate representation of the chemical potential for a mixture containing numerous components and uses molecular thermodynamic methods to represent the Gibbs function in terms of this PDF. The concepts are fundamental and independent of the physicochemical model chosen to represent the chemical potential.

However, the drop model based on the Γ -PDF [3] [4] turned out to have some deficiencies, as reported by [5]. Specifically, unphysical results were obtained for drops evaporating in gas containing fuel vapor, or for large evaporation rates. The goal of this investigation is to formulate a model that is also based on statistical concepts, but that is more robust.

Highlights of the model

Aiming at a drop model that is usable in configurations where there are millions of drops, the goal is to develop a model that captures the crucial features of the MC-fuel but that is simple enough to be one of the building blocks of a larger model. Therefore, several assumptions are made, as follows: The drop is spherical of radius R . The liquid has a constant density ρ_l . Liquid evaporation is assumed to

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occur under thermodynamic equilibrium. The carrier gas surrounding the drop, denoted by the subscript a , obeys the perfect gas equation of state. The gas is postulated to be quasi-steady with respect to the liquid, which is justified by its much smaller characteristic time compared to that of the liquid. Furthermore, we are only interested in the average volumetric properties of the drop represented by its temperature T_d , and mass fractions of different species, $Y_{il} = M_i/M_d$, where $M_d = 4\pi R^3 \rho_l/3$ is the drop mass and the liquid is a mixture of N species i of individual mass M_i inside the drop, $\sum_{i=1}^N M_i = M_d$. The interest in average drop properties precludes consideration of differential species diffusivities, and therefore of any phenomena resulting from such processes. The study is performed at atmospheric pressure where solubility of the carrier gas into the liquid is negligible and the far field conditions are assumed quiescent.

The conservation equations for the discrete model are an extension of those in [13] and are detailed in [14]. A discrete representation of the mixture composition as a function of the molar weight is shown in Fig. 1a. The idea is to create ‘bins’ in the molar weight space and represent the mixture by these species or pseudo-species. The liquid drop model leads to a set for $N + 2$ equations and same number of unknowns: M_d , Y_{il} and T_d . The gas phase model in conjunction with the boundary conditions at the drop surface and in the far field leads to a analytic solution of the set of conservation equations. For a multitude of species one may define

$$\theta_l \equiv \sum_{i=1}^N (m_i X_{il}) = m_l, \quad \theta_v \equiv \frac{1}{X_v} \sum_{i=1}^N (m_i X_{ig}) = m_v, \quad (1)$$

$$\xi_{nl} \equiv \sum_{i=1}^N (m_i^n X_{il}), \quad \xi_{nv} \equiv \frac{1}{X_v} \sum_{i=1}^N (m_i^n X_{ig}), \quad (2)$$

which are the liquid mean molar weight, the vapor mean molar weight in the gas, the liquid n^{th} moment of the molar weight, the vapor n^{th} moment of the molar weight in the gas, respectively and $X_v \equiv 1 - X_{ag}$. Here m denotes the molar weight, X is the molar fraction, and subscripts v and g refer to the vapor and gas phase, respectively. These statistics enable the comparison between results from the statistical models based on a PDF and the discrete model. Moreover, a conservation equation for the evolution of $d\xi_{nl}/dt$ may be derived from the liquid-phase species equation.

In CT form, the mole fraction of a discrete species i is defined by the value of a continuous distribution function, f , in the vicinity of the molar mass point corresponding to

that species

$$X_i = f(m_i)\Delta m_i. \quad (3)$$

This definition holds for a mixture containing hydrocarbon species only. Such a mixture is, for example, a hydrocarbon liquid fuel such as diesel, gasoline or kerosene for which

$$X_{il} = f_l(m_i)\Delta m_i. \quad (4)$$

For a mixture containing hydrocarbons and non-hydrocarbon species, such distribution functions describing all components are not necessarily available. An example of such a situation is that of gasoline vapor in air. To utilize the CT formulation in this situation, one then defines the molar fraction of the non-hydrocarbon, here denoted by the subscript ag (ambient carrier gas) and that of the hydrocarbon mixture indexed by v , with $X_{ag} + X_v = 1$, and use the CT formulation for the hydrocarbon as

$$X_{iv} = X_v f_v(m_i)\Delta m_i. \quad (5)$$

Then from the discrete form $m_g = m_{ag}X_{ag} + \sum_{i=1}^N m_i X_{iv}$ one obtains the continuous form $m_g = m_{ag}(1 - X_v) + \theta_v X_v$ where N is the number of species in the fuel and the mean molar weight of the evaporated fuel and the second moment of the distribution are defined as

$$\theta_v = \int_0^\infty f_v(m_i) m_i dm_i, \quad \psi_v = \int_0^\infty f_v(m_i) m_i^2 dm_i. \quad (6)$$

Whitson [15] used the Γ -PDF

$$f_\Gamma(m_i) = \frac{(m_i - \gamma)^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} \exp\left[-\left(\frac{m_i - \gamma}{\beta}\right)\right] \quad (7)$$

to characterize the high molar-weight portion of crude oils, where $\Gamma(\alpha)$ is the Gamma function. The origin of f is specified by γ , and its shape is determined by two parameters, α and β . These parameters are related to the mean, θ_v , the variance, σ_v^2 , and the second moment, ψ_v , of f by $\theta_v = \alpha\beta + \gamma$, $\sigma_v^2 = \alpha\beta^2$, $\psi_v = \theta_v^2 + \sigma_v^2$.

Evidence [5] that the single- Γ -PDF has deficiencies in portraying the evaporation of drops immersed in a gas already containing low-molar-weight fuel vapor, as would be the case in all practical applications, prompted the proposal (details in [14]) to portray the fuel composition using a superposition of two Γ -PDFs

$$P_l(m_i; \alpha_1, \beta_1, \alpha_2, \beta_2, \epsilon) = (1 - \epsilon) f_\Gamma^{(1)}(m_i) + \epsilon f_\Gamma^{(2)}(m_i), \quad (8)$$

where $f_\Gamma^{(q)}(m_i) = f_\Gamma(m_i; \alpha_q, \beta_q)$ with $q \in [1, 2]$, ϵ is a weighing parameter ($0 \leq \epsilon \leq 1$) and $\int_\gamma^\infty P_l(m_i) dm_i = 1$. The problem of determining P_l can be stated as follows: Given an initial single- Γ -PDF characterized by θ_0, β_0 ,

γ and $\epsilon = 0$, is it possible to determine P_l as a function of time? To do so, one needs to solve for the vector $\eta \equiv (\alpha_1, \beta_1, \alpha_2, \beta_2, \epsilon)$ at each time step. Such an approximate solution relying on the reduction of the problem to ξ_{nl} for $n = [1, 4]$ with the last parameter empirically determined, is possible. The cumbersome mathematics is described in [14]. Ultimately, the solution must be found for 6 primary variables D, T_d, ξ_{il} for $i \in [1, 4]$ and $N + 6$ secondary variables $q_l^{(s)}, j_{jl}^{(s)}, \theta_{1l}, \beta_{1l}, \theta_{2l}, \beta_{2l}$ and ϵ . Comparing with the discrete problem where there are $N + 2$ primary variables, it is immediately apparent that there is an advantage in adopting this formulations if $N > 4$.

Inadequacy of the Single- Γ -PDF Model

To illustrate the deficiencies of the single- Γ -PDF model, consider a drop having an initial diameter $D_0 = 1$ mm at an initial temperature $T_{d,0} = 300$ K immersed in surroundings characterized by $T_g^{(\infty)} = 1000$ K and $Y_v^{(\infty)} = 0.82$ with the composition of the far field vapor specified by $\theta_v^{(\infty)} = 131.3$ and $\sigma_v^{(\infty)} = 24.4$, and $Le = 0.5$. We visualized in Fig. 1b the representation of a mixture composition by the single Γ -PDF. In all calculations, empirical or semi-empirical correlations used for the thermophysical properties are functions of m_i , or of m_i and T . For each thermophysical property, the same correlation is used for all models. All the correlations are presented in [14]. Plots comparing the predictions of the single- Γ -PDF and discrete models are presented in Fig. 2. The presence of a relatively large amount of vapor in the gas phase induces initial drop net condensation and the drop grows in size, as shown in Fig. 2a. After this initial transient, net evaporation begins during which, following a short transient, the linear D^2 -law is recovered. Noteworthy, there is excellent agreement between the discrete and the single- Γ -PDF model predictions for D^2/D_0^2 and T_d , and $X_v^{(s)}$ (where the superscript s denotes conditions at the drop surface) differs only after the drop residual mass is less than 15%. Examination of Fig. 2b reveals that the initial condensation results in a decrease in θ_l and a concomitant increase in σ_l which accounts for the species added to the liquid mixture. Further evaporation results in an increase in θ_l and a decrease in σ_l , as shown by the results from the discrete model. However, the single- Γ -PDF results display the opposite behavior in σ_l in that it increases. Thus, the qualitative trends of the discrete model are not captured by the single- Γ -PDF model. This fact is easily observable in Fig. 2c where the discrete model distribution displays another, smaller peak as evaporation proceeds, which the single- Γ -PDF model inherently cannot replicate. It is the emergence of this second peak that prompted the development of a new model

based on the superposition of two Γ -PDFs. Fig. 2d shows the discrepancies between the discrete and single- Γ -PDF model predictions for the vapor composition.

One notable result of these comparisons is that neither one of D^2/D_0^2 , T_d , or $X_v^{(s)}$ evolutions is a good indicator that a model captures the composition aspects of the liquid or the gas. This observation has important implications in that experimental results focussing on these three variables are not adequate to validate models. It is obvious that composition measurements are necessary to determine whether a model is appropriate.

The Double- Γ -PDF and Discrete Model Comparisons

A sample illustration (a detailed parametric study is presented in [14]) of the predictive potential of the double- Γ -PDF is shown in Figs. 3a -3h. In Fig. 3a are illustrated T_d and D^2/D_0^2 for $T_g^{(\infty)} = 600, 1000$ and 1200 K. In all cases the drop initially experiences net condensation before net evaporation begins. Although the extent of net condensation evident from the drop growth decreases with increasing $T_g^{(\infty)}$, the initial drop growth rate seems independent of $T_g^{(\infty)}$. The rate of heat transfer to the drop increases with $T_g^{(\infty)}$, and T_d and $X_v^{(s)}$ (see Fig. 3b) become larger earlier. During the initial net condensation $X_v^{(s)}$ becomes eventually larger than $X_v^{(\infty)}$ but a slight decline occurs during net evaporation. Comparisons between the discrete model and double- Γ -PDF predictions are presented in Figs. 3c through 3f for $\theta_l, \sigma_l, \theta_v^{(s)}$ and $\sigma_v^{(s)}$. The agreement between the two models is very good to excellent. Particularly, $\theta_v^{(s)}$ and $\sigma_v^{(s)}$, which are the quantities of interest in predicting the composition of the gas phase are very accurately predicted. During net condensation, σ_l increases and θ_l decreases due to the addition of the lighter, far-field species; as net evaporation initiates, the lighter species leave the drop, resulting in the reverse trend.

Finally, Figs. 3g and 3h portray a comparison between the discrete model and the double- Γ -PDF of the surface vapor at two times corresponding to a residual liquid mass of 60% and 20% respectively. At the smallest $T_g^{(\infty)}$ and early in the drop lifetime, the PDF visibly has a single peak which is located in the lower- m regime of the double- Γ -PDF, consistent with the fact that during slow drop heating the more volatile components are first released from the drop. Another, minor peak which was barely evident during the early drop lifetime develops in the larger- m regime during the later stages of the drop life. For the larger values of $T_g^{(\infty)}$ and at 60% of residual liquid mass, the lower- m regime peak is the minor of the two peaks, but becomes dominant later during the drop lifetime. The physical ex-

planation for this behavior is that at higher ambient temperature, the less volatile components may also evaporate because there is a larger heat flux into the drop leading to a higher drop temperature. Comparing the size of the two peaks, the longest net condensation period which occurs at the smallest $T_g^{(\infty)}$ naturally leads to the largest peak at the lower- m regime of the double- Γ -PDF. The double- Γ -PDF faithfully captures the discrete model both in the early and later stage of the drop lifetime and thus reproduces the differential species evaporation as a function of $T_g^{(\infty)}$. The importance of the dominant lighter components in the gas composition highlights the necessity of the double- Γ -PDF representation.

Conclusions

A new model is described to portray multicomponent-fuel drop evaporation through a statistical representation. This new model is based on the evolution of the single- Γ -PDF representing the initial liquid fuel composition to a superposition of two Γ -PDFs, a form which is called the double- Γ -PDF. It is shown here that unlike a precedent model in which the initial distribution of the species, specified by a single- Γ -PDF, was restricted to retaining its initial functional form, the present model, which is devoid of this restriction, can accommodate the wide range of behavior characteristic of the concomitant net evaporation/condensation of different species.

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References

- [1] Law, C. K., Prakash, S. and Sirignano, W. A., *Proc. Comb. Inst.* 16:605-617 (1976).
- [2] Lara-Urbaneja, P. and Sirignano, W. A. 1981, *Proc. Comb. Inst.* 18:1365-1374 (1981).
- [3] Tamim J. and Hallett W. L. H., *Chem. Eng. Sci.* 50(18):2933-2942 (1995).
- [4] Hallett W. L. H., *Combust. Flame* 121:334-344 (2000).
- [5] Lippert A. M. 1999. Modeling of multicomponent fuels with application to sprays and simulation of Diesel engine cold start, Ph. D. Thesis, University of Wisconsin, Madison.
- [6] Lippert, A. M. and Reitz, R. D. SAE Paper 972882, 1997
- [7] Bowman, J. R. and Edmister, W. C., *Ind. Chem. Eng.* 43:2625-2628 (1951).
- [8] Edmister, W. C. and Bowman, J. R., *Chem. Eng. Prog. Symp. Ser.* 48:46-51 (1952).
- [9] Aris R. and Gavalas G. R., *Phil. Trans. R. Soc. A* 260:351-393 (1966).
- [10] Briano, J. G. and Glandt, E. D., *Fluid Phase Equilibria* 14:91-102 (1983).
- [11] Cotterman, R. L., Bender, R. and Prausnitz, J. M., *Ind. Eng. Chem. Process Des. Dev.* 24:194-203 (1985).
- [12] Gal-Or, B., Cullinan, Jr., H. T. and Galli, R., *Chem. Eng. Sci.* 30:1085-1092 (1975).
- [13] Williams, F. A., *Combustion Theory*, Addison Wesley, 1965
- [14] Harstad, K. G., Le Clercq, P. C. and Bellan, J., A statistical model of multicomponent-fuel drop evaporation for many-droplet gas-liquid flow simulations, submitted to the *International Journal of Multiphase Flow*, 2002
- [15] Whitson C. H., *Soc. Pet. Eng. J.*, 23, 683-694 (1983).

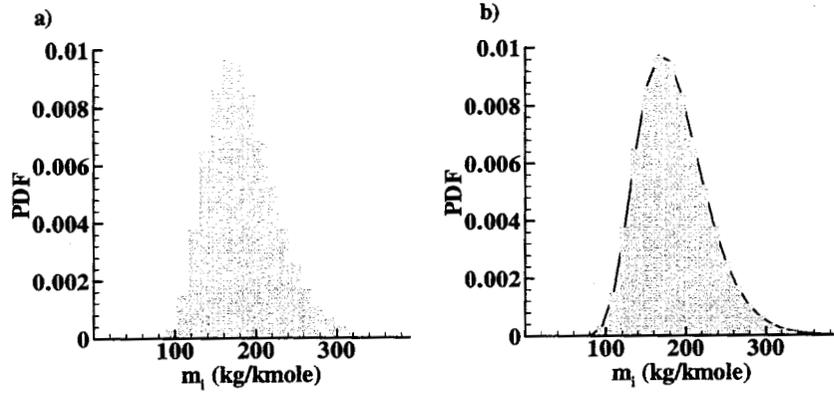


Figure 1: Probability Density Functions (PDFs) used in the computations. (a) Discrete pseudo-components $\gamma = 86$ kg/kmole, $\theta_{l,0} = 185$ kg/kmole, $\sigma_{l,0} = 43$ Only 18 out of the 32 components are 'visible' on this scale. (b) The single- Γ -PDF envelope of the initial discrete PDF.

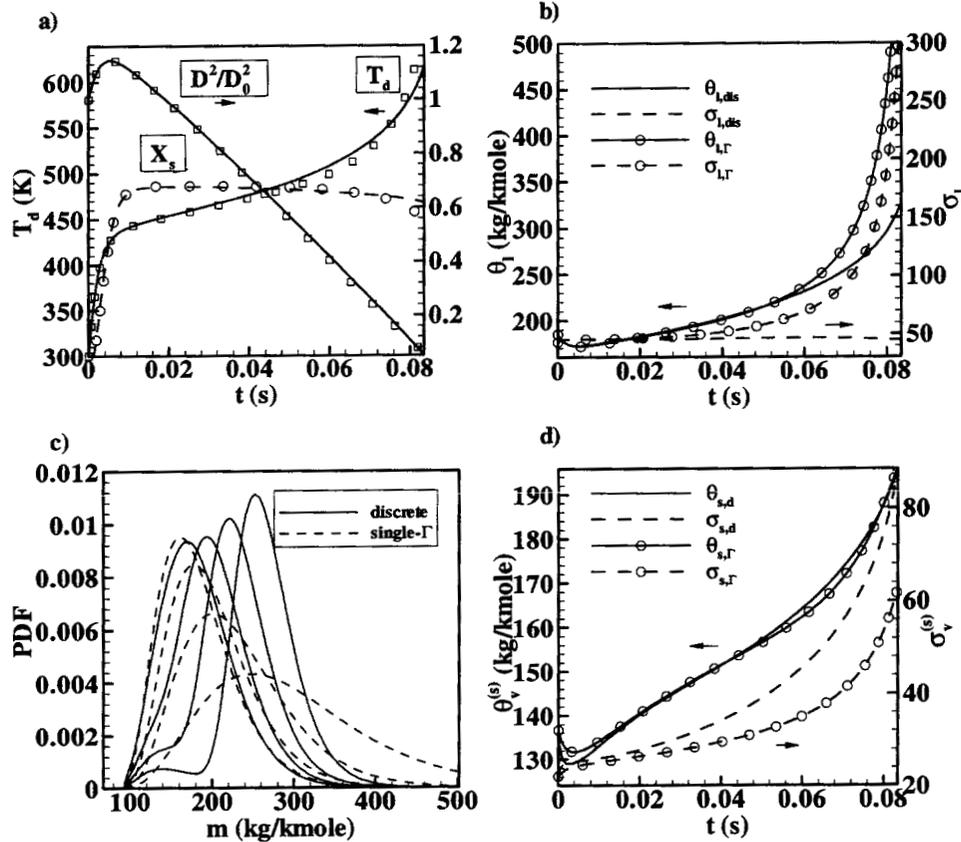


Figure 2: Evaporation of a diesel fuel drop, discrete model vs the single- Γ -PDF model. a) Drop temperature, relative surface area and drop surface vapor mole fraction; lines for discrete model, symbols for the single- Γ -PDF. b) liquid mean molar weight and standard deviation evolution in time, c) PDF at different stages of evaporation; from left to right 90%, 60%, 30% and 10% remaining mass, d) Surface mean molar weight and standard deviation evolution in time.

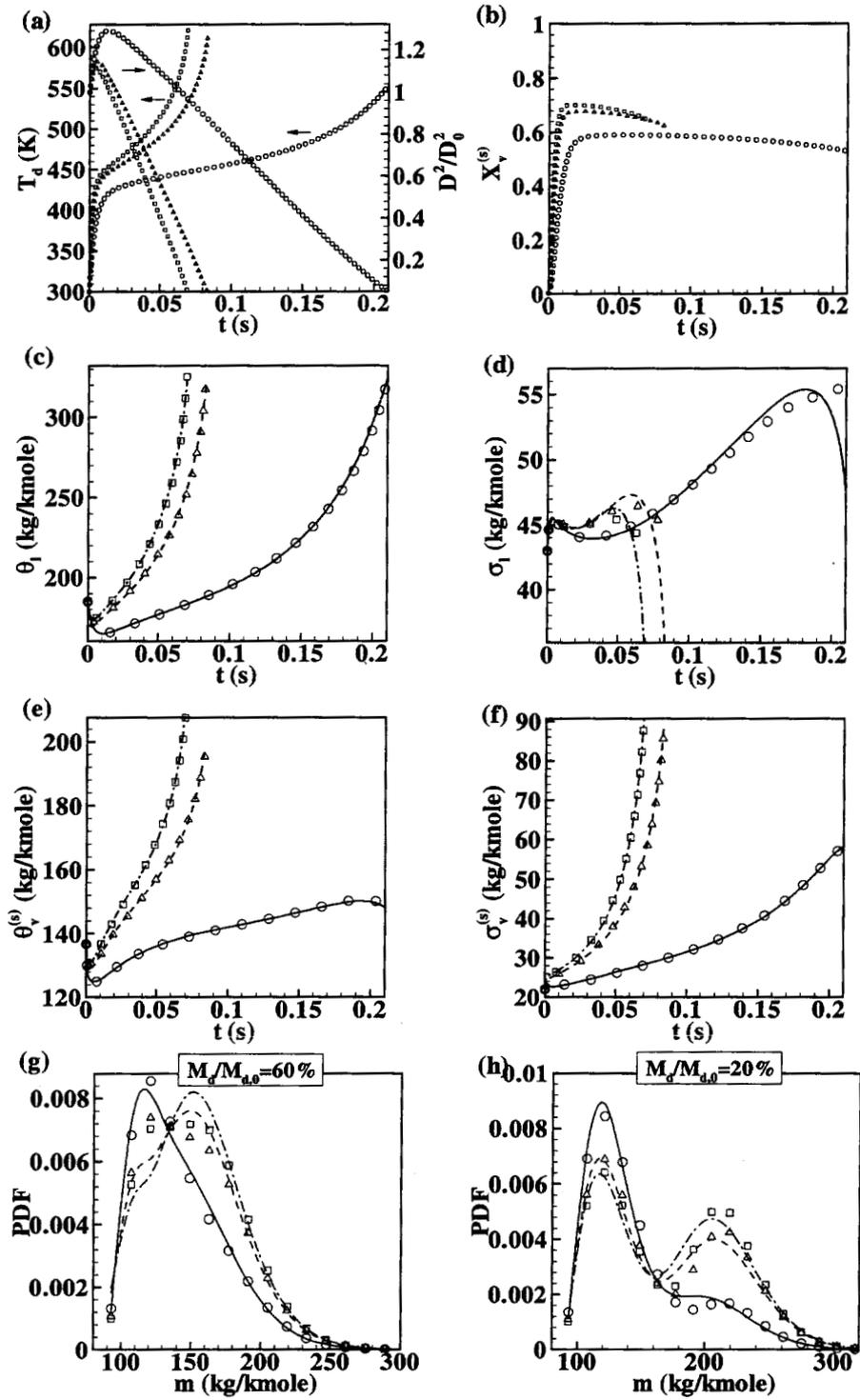


Figure 3: Drop history: — and \circ for $T_g^{(\infty)} = 600K$, --- and \triangle for $T_g^{(\infty)} = 1000K$ and - · - and \square for $T_g^{(\infty)} = 1200K$. Discrete (symbols) versus double- Γ -PDF (lines) model. (a) Drop temperature and relative surface area (discrete model only), (b) Drop surface vapor mole fraction (discrete model only), (c) Liquid mean molar weight, (d) Liquid PDF standard deviation, (e) Surface composition mean molar weight, (f) Surface composition PDF standard deviation, (g) Surface vapor PDFs at 60% residual drop mass, and (h) Surface vapor PDFs at 20% residual drop mass.