

Modeling real gas equations of state in high density combustion

Chenwei Zheng, Deshawn Coombs, Ben Akih-Kumgeh
Department of Mechanical and Aerospace Engineering
Syracuse University
Syracuse, New York, USA

1 Motivation and Objectives

Combustion systems increasingly operate at high pressure and low temperature conditions. These extreme operating conditions lead to high densities of the fuel and air mixtures which invalidate the ideal gas modeling often used in analysis. The ideal gas model can induce errors in predicted combustion properties. For more physically realistic reacting flow simulations, real gas effects must therefore be taken into account. It is preferable that any method used to address this problem be computationally convenient.

There are many models of real gas equations of state (EOS), starting from the more theoretically grounded Van der Waals equation to the very complex empirical EOS, such as the Benedict-Webb-Rubin (BWR) equation. It can be observed that most practical real gas EOS are modifications of the Van der Waals equation of state. Currently, in order to simplify computational tasks associated with EOS evaluations, some research projects use cubic equation of state such as the Redlich-Kwong (RK) model [1], Soave-Redlich-Kwong (SRK) [2] and Peng-Robinson (PR) model [3].

According to Reitz [4], the general form of cubic equation of states can be written as :

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + qbV + wb^2} \quad (1)$$

where V is the volume of the system and R is the universal gas constant, q and w are constants depending on the type of cubic EOS. For the PR-EOS their values are: $q = 2$, $w = -1$, and $q = 1$, $w = 0$ for the RK and the SRK-EOS. For pure species, a and b are functions of temperature. The expressions for EOS parameters are presented in Table 1, where T_c and P_c are critical temperature and critical pressure, ω is the acentric factor, κ is a constant that depends on the acentric factor and T_r is defined as reduced temperature, $T_r = T/T_c$.

Table 1: Parameters for cubic EOS

Equation	b	a	q	w
Redlich Kwong (RK)	$\frac{0.0867RT_c}{P_c}$	$\frac{0.4278R^2T_c^{2.5}}{\sqrt{T}P_c}$	1	0
Soave Redlich Kwong (SRK)	$\frac{0.08664RT_c}{P_c}$	$\frac{0.42747R^2T_c^{2.5}}{P_c} [1 + \kappa(1 - T_r^{0.5})]^2$ $\kappa = (0.480 + 1.574\omega - 0.176\omega^2)$	1	0
Peng Robinson (PR)	$\frac{0.07780RT_c}{P_c}$	$\frac{0.45724R^2T_c^2}{P_c} [1 + \kappa(1 - T_r^{0.5})]^2$ $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$	2	-1

The binary mixing rule with regards to a and b suggested by Peng and Robinson [3]:

$$\begin{aligned}
 a &= \sum_i \sum_j x_i x_j a_{ij} \\
 b &= \sum_i x_i b_i \\
 a_{ij} &= (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2}
 \end{aligned} \tag{2}$$

where δ_{ij} is an empirically determined binary interaction coefficient characterizing the binary formed by component i and component j . δ_{ij} is proposed at the range between -0.2 to 0.2 by Abudour et al [5].

Another method to deal with the mixing rule is the pseudocritical method based on corresponding state principle (CSP). To obtain equation of state, we first calculate the pseudocritical properties for the mixture. According to Polling et al. [6] the pseudocritical temperature T_{cm} can be estimated by the simplest mole fraction average method, Kay's rule [7]: $T_{cm} = \sum_{i=1}^n y_i T_{ci}$. As for the pseudocritical pressure, P_{cm} , a mole-fraction average of pure-component critical pressures is normally unsatisfactory. This is because the critical pressure for most systems goes through a maximum or minimum with composition. The only exceptions are if all components of the mixture have quite similar critical pressures or critical volumes. The simplest rule which can give acceptable P_{cm} values for two-parameter or three-parameter CSP is the modified rule of Prausnitz and Gunn [8]:

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_{cm}} = \frac{(\sum_{i=1}^n y_i Z_{ci}) R (\sum_{i=1}^n y_i T_{ci})}{(\sum_{i=1}^n y_i V_{ci})} \tag{3}$$

where all of the mixture pseudocriticals Z_{cm} , T_{cm} , and V_{cm} are given by mole-fraction averages (Kay's rule) and R is the universal gas constant.

The mixture pseudo acentric factor is commonly given by a mole fraction average Joffe [9]:

$$\omega_{cm} = \sum_{i=1}^n y_i \omega_{ci} \tag{4}$$

The need to account for real gas effects in Computational Fluid Dynamics (CFD) simulations have been realized, with the result that increasingly more studies consider this problem. The text by Sirignano [10]

describes the use of cubic equations of state by the spray combustion community. Recent comprehensive reviews of work on real gas behavior in multiphase reacting flows have been presented by Bellan [11], Yang [12] and Sazhin [13]. Also, vapor-liquid equilibrium (VLE) processes of n -alkanes from C_2 to C_{20} were described by Zhu and Reitz [4]. Both PR- and SRK-EOS were found to be superior to RK-EOS. Oefelein and Yang [14] employed Large Eddy Simulation (LES) to investigate two dimensional mixing and combustion of hydrogen and oxygen. Thermodynamic non-idealities and transport anomalies was evaluated directly from fundamental theories over the fluid regime. A 32-term BWR EOS proposed by Jacobsen and Stewart [15] was used in the vicinity of the critical point while elsewhere the SRK EOS from Poling et al. [6] was used.

With the need to include more chemical kinetic effects in combustion simulations, one encounters a high number of species whose critical properties are not well known or would be too cum for manual assignment. This paper develops a framework to generate parameters of real gas EOS from transport and thermodynamics data already used in combustion chemical kinetic models. We first demonstrate through simulations that using real gas EOS leads to differences in the flow field at combustion relevant conditions, compared to simulation based on ideal gas EOS. We then describe the method to obtain required real gas EOS parameters from chemical kinetic model and their associated data. We further highlight an existing problem in the way current transport data are estimated, since significant differences are observed.

2 Research Approach

The research consists of two parts. The first part aimed at justifying the motivation above. We show using LES of propane jet that resulting flow fields can be dependent on the type of EOS used. The second part discusses how the properties of a real gas EOS can be estimated from available combustion chemistry model resources.

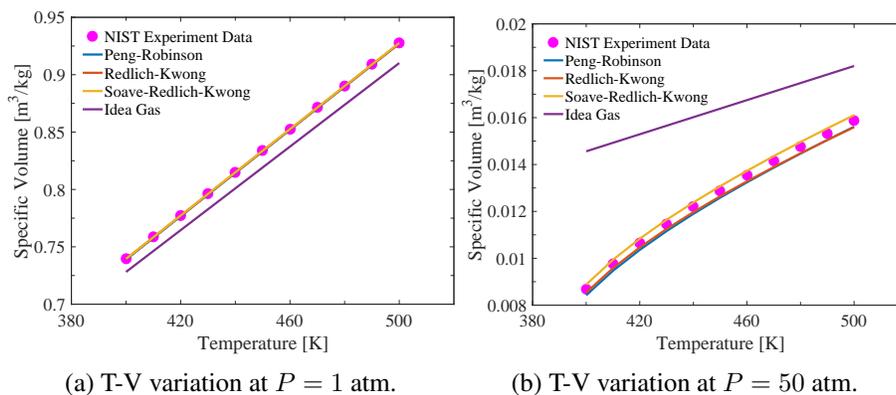


Figure 1: Variation of propane specific volume with temperature, highlighting importance of real gas EOS.

2.1 Propane EOS Estimation

Propane temperature and specific volume relationship is shown in Fig.1. Real gas EOS and ideal gas EOS results are compared with NIST experimental data. The temperature range is chosen based on the availability of experimental data.

Fig. 1a shows that at 1 atm, the specific volume predicted by real gas EOS is very close to experimental data, while the ideal gas EOS shows some deviation (up to 2%). When the pressure is increased to 50 atm as shown in Fig. 1b, the error in specific volume induced by the ideal gas assumption is about 70%, while the real gas EOS is close to the measured data. The impact of this on flow field predictions can be assessed by carrying out comparative flow simulations.

2.2 Simulation of a Propane Jet

The example problem we consider here consists of a propane jet introduced into a hot chamber of air. The conditions are such that the chamber is at $T = 900$ K, and the subsonic propane jet is at $T = 400$ K. Simulations are carried out at 1 atm and at 50 atm, using both ideal gas EOS and real gas (PR) EOS for air and propane. The real gas EOS require critical state parameters which for propane are $T_c = 369.85$ K, $P_c = 42.47$ bar, $\omega = 0.153$; and for air are $T_c = 132.55$ K, $P_c = 37.69$ bar, $\omega = 0$, here ω is the acentric factor. In order to properly resolve the flow field, the turbulence model chosen here is LES with the sub-grid-scale (SGS) model, Wall-Adapting Local Eddy (WALE). The mesh consists of 2,393,042 cells in total with a minimum cell size $\Delta x_{min} = 0.1$ mm. The injection velocity are the same between ideal gas EOS and real gas EOS, the speed of jet is 240.12 m/s with 1 ms injection duration. Simulation is carried out using the segregated solver of Star-CCM+. The time discretization is implicit, and to obtain good convergence of the solver at each time step the following unrelaxation factors were used, 0.8 for velocity, 0.2 for pressure, 0.9 for both the species and energy equations. A maximum of 50 iterations for the iterative matrix solvers was used to ensure the solution reached a converged state at each time step. The time step was set to which lead to a maximum local CFL number of approximately 2.4.

The resulting flow field can be compared using scalars such as the propane mass fraction and temperature. Figure 2a and 2b show the mass fraction field at 1 atm, which is to be compared with the fields in Fig. 2c and 2d, obtained at a pressure of 50 atm. We see that in both cases, the flow fields are different, since the spread and penetration depth in the case of PR-EOS are greater than those of ideal gas EOS. Further at high pressure, hence higher density, the difference is more pronounced as would be expected. At 1 atm, PR EOS is predicting slightly lesser density than ideal gas, the difference is within 1%. In Figure 2, the penetration depth of 1 atm is about 0.06 for either real gas eos and ideal gas EOS. However, the spread angle is different. The difference in the flow pattern can be introduced by the departure function in energy:

$$du = C_v dT + \left[T \cdot \left(\frac{\partial P}{\partial T} \right) \Big|_v - P \right] dv \quad (5)$$

$$dh = C_p dT + \left[v - T \cdot \left(\frac{\partial v}{\partial T} \right) \Big|_P \right] dP \quad (6)$$

where the second terms are the departure terms. While ideal gas EOS will result in zero for the departure term, Real Gas EOS can contribute a value in the function. Therefore, the energy function would be slightly different for the two EOS, and eventually causing the variation in the flow field. The temperature fields also reflect differences that align with the mixing field. These fields are affected through the use of the EOS to relate the pressure, density, and temperature, which appear in the conservation equations.

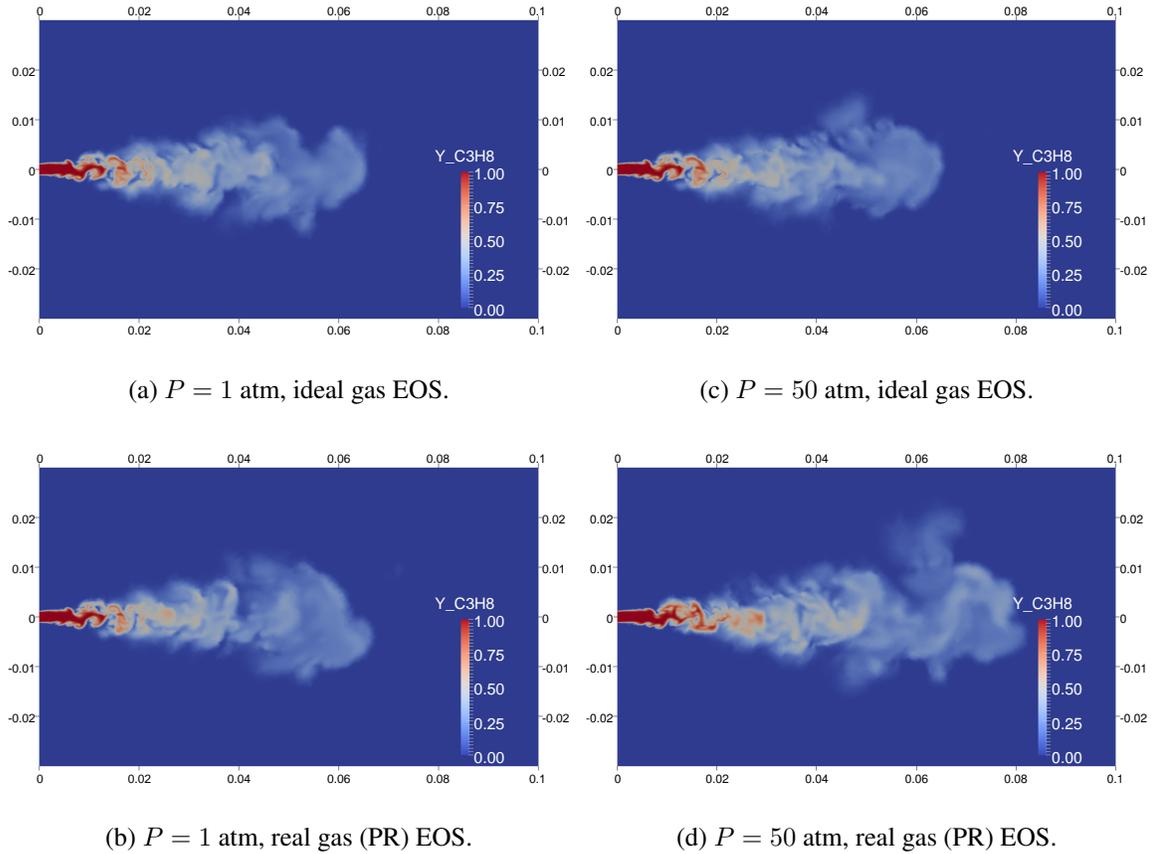


Figure 2: Propane mass fraction field at 1 ms after injection onset.

3 Method of EOS Parameter Estimation

Our goal is to determine for each species in a given mechanism its real gas EOS parameters, i.e. T_c , P_c , ω . Using an appropriate mixing rule, the EOS parameters for a given mixture combustion can be determined from those of individual species. There is a connection between the critical state properties and the parameters of intermolecular potentials (e.g. Lennard-Jones 12-6 potential). The latter are used in combustion flows to generate required transport properties (viscosity, conductivity and thermal diffusivity). One can reverse-engineer the transport data to obtain the critical state parameters needed for the EOS. Many empirical relations between parameters of intermolecular potentials and the critical state properties have been proposed [16]. Some require knowledge of the acentric factor while others do not. The most widely used of these equations are in the form:

$$\sigma \left(\frac{P_c}{T_c} \right)^{1/3} = a_\sigma - b_\sigma \omega; \quad \text{and} \quad \frac{\varepsilon}{k_B T_c} = a_\varepsilon - b_\varepsilon \omega \quad (7)$$

where ε is the depth of the potential well and σ is the intermolecular separation at which the potential energy is zero. In chemical kinetic models, the estimation rules proposed in Kee et al. [17] are often used. It appears that the Tee et al. [16] performs better than the Kee [17] when predicted transport variables are compared

Table 2: Parameters for estimation

Reference	Tee [16]	Kee [17]	Holley [18]
a_σ	2.3551	2.393	2.3551
b_σ	0.0874	0	0.3955
a_ε	0.7915	0.75	0.8063
b_ε	0.1693	0	0.6802

with observations. We note that T_c , P_c , ω are observable quantities whereas the accuracy of σ , ε can only be inferred from their prediction of transport properties. This circularity can lead to a verification problem. Holley et al. [18] have suggested updated coefficients for the Tee correlation. What this means is that with an appropriate correlation, one can obtain necessary T_c and P_c from transport data. The acentric factor, ω , poses a challenge that can only be resolved through structure-activity correlations. For instance, for alkanes, it can be established that ω depends on the number of carbon (N_c) [19]: $\omega = 0.004423[\ln(3.3063 + 3.4381N_c)]^{3.651}$. The necessary carbon number can be obtained from the model thermodynamic data file. Taken together, the above offers ways to generate critical state properties, hence EOS parameters from currently available resources.

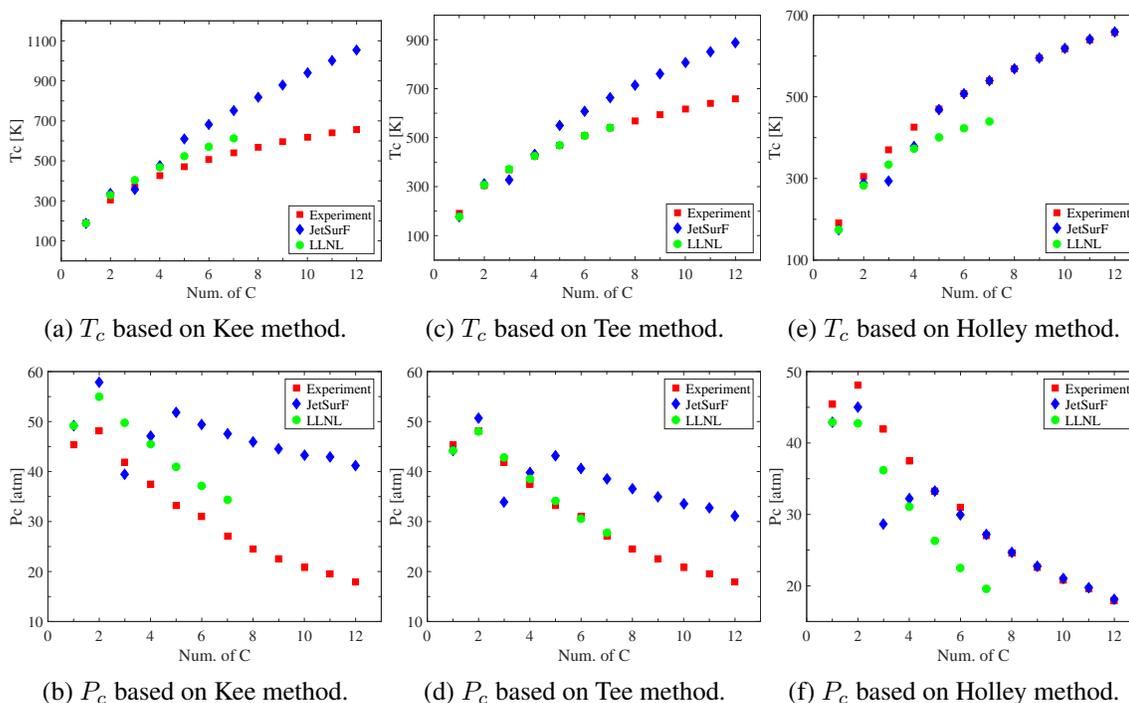


Figure 3: Critical properties estimation based on intermolecular constants.

4 Critical Properties Estimation

One might check the effectiveness of the proposed approach by comparing predicted critical state parameters with measured data for some species of relevance to combustion. An example is shown in Fig.3 for C1-C12 *n*-alkanes, with critical properties from the literature [6]. Intermolecular potential parameters σ and ε are chosen from the JetSurf 2.0 model [20] and LLNL *n*-Heptane mechanism. The observed differences in T_C and P_c trace back to differences in the transport data σ and ε , which are often not given critical attention in model evaluations.

As shown in the Figure 3, Tee's correlation with LLNL chemical kinetic database provides accurate critical properties. While for large carbon alkanes, Holley's correlation with JetSurf 2.0 shows good agreement with experimental data, for small carbon alkanes, the correlation results in inconsistency. Kee's correlation does not require acentric factor but errors occur as carbon number increases due to deviation from spherical shape. Therefore, we recommend using Tee's correlation with LLNL database.

5 Conclusion

In this paper, the problem of real gas equations of state for high density flow simulations is considered. The importance of such equations of state is underlined by comparing the large eddy simulation results of a propane jet into an air vessel realized using large eddy simulations with ideal and real gas equations of state. It is then suggested that parameters of a cubic equation of state, namely, the critical state variables, can be determined from the transport data of chemical kinetic models. It is further observed that the transport data of various chemical kinetic models are not necessarily consistent, suggesting further attention to this modeling problem.

Acknowledgement

The first author is supported through a Syracuse University initiative funded by the National Science Foundation under Grant No. DGE-1449617.

References

- [1] Redlich, O., Kwong, J. N. (1949). On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chemical reviews*, 44(1), 233-244.
- [2] Soave, G. (1972). Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science*, 27(6), 1197-1203.
- [3] Peng, D. Y., Robinson, D. B. (1976). A new two-constant equation of state. *Industrial Engineering Chemistry Fundamentals*, 15(1), 59-64.
- [4] Zhu, G. S., Reitz, R. D. (2002). A model for high-pressure vaporization of droplets of complex liquid mixtures using continuous thermodynamics. *International Journal of Heat and Mass Transfer*, 45(3), 495-507.

- [5] Abudour, A. M., Mohammad, S. A., Robinson Jr, R. L., Gasem, K. A. (2014). Generalized binary interaction parameters for the PengRobinson equation of state. *Fluid Phase Equilibria*, 383, 156-173.
- [6] Poling, B. E., Prausnitz, J. M., & O'connell, J. P. (2001). *The properties of gases and liquids* (Vol. 5). New York: Mcgraw-hill.
- [7] Kay, W. B. (1936). Density of hydrocarbon gases and vapors at high temperature and pressure. *Ind. Eng. Chem*, 28(9), 1014-1019.
- [8] Prausnitz, J. M., & Gunn, R. D. (1958). Volumetric properties of nonpolar gaseous mixtures. *AIChE Journal*, 4(4), 430-435.
- [9] Joffe, J. (1971). Combining rules for the third parameter in the pseudocritical method for mixtures. *Industrial & Engineering Chemistry Fundamentals*, 10(3), 532-533.
- [10] Sirignano, W. A. (2010). *Fluid dynamics and transport of droplets and sprays*. Cambridge University Press.
- [11] Bellan, J. (2000). Supercritical (and subcritical) fluid behavior and modeling: drops, streams, shear and mixing layers, jets and sprays. *Progress in energy and combustion science*, 26(4), 329-366.
- [12] Yang, V. (2000). Modeling of supercritical vaporization, mixing, and combustion processes in liquid-fueled propulsion systems. *Proceedings of the Combustion Institute*, 28(1), 925-942.
- [13] Sazhin, S. S. (2006). Advanced models of fuel droplet heating and evaporation. *Progress in energy and combustion science*, 32(2), 162-214.
- [14] Oefelein, J. C., Yang, V. (1998). Modeling high-pressure mixing and combustion processes in liquid rocket engines. *Journal of Propulsion and Power*, 14(5), 843-857.
- [15] Jacobsen, R. T., Stewart, R. B. (1973). Thermodynamic properties of nitrogen including liquid and vapor phases from 63K to 2000K with pressures to 10,000 bar. *Journal of Physical and Chemical Reference Data*, 2(4), 757-922.
- [16] Tee, L. S., Gotoh, S., Stewart, W. E. (1966). Molecular parameters for normal fluids. Lennard-Jones 12-6 Potential. *Industrial Engineering Chemistry Fundamentals*, 5(3), 356-363.
- [17] Kee, R. J., Coltrin, M. E., Glarborg, P. (2005). *Chemically reacting flow: theory and practice*. John Wiley Sons.
- [18] Holley, A. T., You, X. Q., Dames, E., Wang, H., Egolfopoulos, F. N. (2009). Sensitivity of propagation and extinction of large hydrocarbon flames to fuel diffusion. *Proceedings of the Combustion Institute*, 32(1), 1157-1163.
- [19] Han, B., Peng, D. Y. (1993). A groupcontribution correlation for predicting the acentric factors of organic compounds. *The Canadian Journal of Chemical Engineering*, 71(2), 332-334.
- [20] H. Wang, E. Dames, B. Sirjean, D. A. Sheen, R. Tango, A. Violi, J. Y. W. Lai, F. N. Egolfopoulos, D. F. Davidson, R. K. Hanson, C. T. Bowman, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, R. P. Lindstedt, A high-temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures, *JetSurF* version 2.0, September 19, 2010 (<http://web.stanford.edu/group/haiwanglab/JetSurF/JetSurF2.0/index.html>).