PENG:
A program for transport properties of low-density binary gas mixtures

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Abstract
The fundamental properties of molecules bridge experiment and theory. Transport properties (diffusion, thermal diffusion, thermal conductivity and viscosity) of binary mixtures are measurable in experiments, and well-defined in theory, but difficult to compute with high accuracy. In addition to high-accuracy inter-molecular potential energy curves (PECs), a reliable and high-order solution program that compute the properties based on the PECs is required. In this work, we present a computer program called PENG that performs the collision integration numerically, and solves the Boltzmann equation in Chapman–Enskog fashion. The program has been devised to perform both parts of the solution procedure to arbitrary order, so that no hardcoded limitation will prevent a user from computing at higher precision, except the amount of RAM and the required computational time. PENG is well-designed in an Object-Oriented Programming (OOP) fashion, which make the program clear and easy to modify. In addition to the end-user oriented program, PENG is also compiled as a dynamic shared library that may readily be extended and embedded in users’ programs.

Keywords: Thermophysical properties; Program design; Collision integral; Dilute gases.

PROGRAM SUMMARY

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Program Title: PENG  
CPC Library link to program files: (to be added by Technical Editor)  
Developer’s repository link: (if available) https://github.com/zhaiyusci/peng  
Code Ocean capsule: (to be added by Technical Editor)  
Licensing provisions (please choose one): LGPL  
Programming language: C++  
Supplementary material:  
Nature of problem (approx. 50-250 words): Nowadays, quantum chemistry provides high-accuracy intermolecular interactions potential energy curves (PECs), and more and more accurate thermophysical properties of dilute gases can be measured experimentally. It is meaningful to build a bridge between thermophysical properties and PECs, so that people can refine the PECs and learn more about the nature of dynamics of gases. For a dilute binary gas mixture, the theory, the Boltzmann equation, and its solution has been available for a long time, but fewer numerical solution packages are available for the public. An easy-to-use and easy-to-extend software package is required.  
Solution method (approx. 50-250 words): To complete the work, we have created a program that computes the collision integrals \( \Omega^{(f,s)} \) for a set of temperatures, following which the thermophysical properties are computed using the Chapman-Enskog solutions of the Boltzmann equation. Both parts of the program are written in C++. The program is easy to use, and a well-designed framework is provided thanks to the Object-oriented design. Users with programming experience can readily extend the present work.  
Additional comments including restrictions and unusual features (approx. 50-250 words): In this version, the program is limited to the computation of the properties of mixtures of structureless atoms. For polyatomic molecules, additional work need to be done.  

1. Introduction  
Transport properties (thermal conductivity, thermal diffusion, diffusion, and viscosity) are important thermophysical features for gas mixtures.[1] As other dynamical phenomena, these properties are directly related to the interactions, i.e., the intermolecular potential energy functions/surfaces/curves (PEFs/PESs/PECs).  

It was unrealistic to compute the high-accuracy thermophysical properties fully from the first principle. Computational quantum chemistry nowadays can provide very accurate potential energy within a (relatively) short time. Larger memory, higher CPU speed and parallel programming have made the computation impossible in the old days possible.
Beside the *ab initio* researching paradigm, which is popular among computational scientists, we should also note that no matter how accurate theory is, it is meaningful to refine (or obtain) the theoretical results with help from experimental scientists. There is a long history of getting the parameters directly from experiments by fitting the model to measurement. *E.g.*, directly fitting PECs to spectra and virial coefficients is possible even for modern potential energy models, which have multiple parameters to represent realistic PECs flexibly and accurately.\footnote{2} Le Roy and coworkers proposed in Ref. \footnote{3} that it is possible to add gas transport properties into the data set to which the model is fitted, and they tuned their PECs manually to obtain a globally better description of all four kinds of properties.

Apparently, one of necessary steps of all such proposals is to build a PEC to transport properties software. There has been some\footnote{4} \footnote{5} \footnote{6} \footnote{7}, but most of them suffer from one or more problems listed below: (1) The programs were composed in an old-fashioned style, *e.g.*, out-of-date language/syntax, “all in main function” designing which hampered them being embedding in other applications, or “GOTO” dominated and thus unmaintainable logic. Meanwhile, due to an abuse of global variables, it is so difficult to adopt these codes that, in our experience, we must have three copies of the same code for computing $\Omega_{\alpha\beta}^{(\ell,s)}$ (here $\alpha$ and $\beta$ for different species) and compile them with different potential functions ($V_{\alpha\beta}$) into dynamically loadable libraries and load them in the following program for binary mixture transport properties. (2) Limited precision was hard coded in the programs, *e.g.*, small numbers of quadrature points are used, or only low-order solutions are implemented. Here “hard coded” does not mean a compile-time adjustable parameter, but that all the arrays therein are not dynamically allocated for high precision. (3) The software packages were not extensible, *i.e.*, only a single algorithm for integration was implemented in a code, and all parts are coupled together, and no interface was designed to load other codes. (4) Some programs lack maintenance, and cannot be compiled successfully on a modern GNU/Linux operating system out-of-the-box.

Of course, the drawbacks of the old programs are caused by historical reasons: lack of a high performance computer, performance must take priority over maintainability. Lack of objected oriented program (OOP) paradigm in computational physics, which came with Smalltalk in 1972, and became popular with C++ (released in 1983), Objective-C (released in 1984) and Java (released in 1995). FORTRAN, which is still the most popular programming language in high-performance computing, introduced OOP in Fortran 90.
Unfortunately, FORTRAN 90 and its successors are not as popular as its predecessor, FORTRAN 77. What makes it worse is that every single letter had to be recorded in punched-card format and as only a limited number of characters can be used in a line, thus overly shortened variable names were employed used by scientists in the old days, which unfortunately increase the difficulty of maintaining the programs.

We tried to construct a program friendly to both end users and developers in order to solve the problems above in the Platform of ENergetic Gases, PENG. We wrote the programs in a modernized way. The codes are in C++ (following C++ 17 standard), and the whole program is in OOP paradigm. Although we have provided the whole tool chain from PECs to transport properties, all the algorithms are highly decoupled, therefore experienced users (developers) can easily implement their own algorithms, and replace ours with little effort. Thus, it can serve as a platform for comparing different algorithms. We also decouple the user interface and the computing part, so that PENG can be embedded readily into other programs.

2. Theory

The macroscopic properties of dilute gases can be understood via statistical mechanics, in which the distribution function in the phase space is of the central role. For an \( N \)-atom system, the distribution function is of \( 6N + 1 \) dimension, which consists of \( 3N \) coordinates, \( 3N \) velocities, and time. For dilute gases, however, an approximation can be made that the distribution function of the whole system can be written as the product of all individual gas molecules, \( i.e., \) the one-body distribution function for \( i \)-th specie \( f_i \) in \( \mu \)-phase space, which is function of the Cartesian coordinates \( r_i \), velocities \( c_i \), and time \( t \).

To obtain the transport properties of a dilute binary gas mixture, we begin with the Boltzmann equation, which describes the dynamics of \( f_i \) \[8, 9, 10\]

\[
\left\{ \begin{align*}
\mathcal{D}_0 f_0 + J_0 (f_0 f) + J_{01} (f_0 f_1) &= 0 \\
\mathcal{D}_1 f_1 + J_1 (f_1 f) + J_{10} (f_1 f_0) &= 0
\end{align*} \right.,
\]

where \( \mathcal{D}_i \) is referred as the differential streaming operator

\[
\mathcal{D}_i = \frac{\partial}{\partial t} + c_i \cdot \frac{\partial}{\partial r_i} + F_i \cdot \frac{\partial}{\partial c_i},
\]
in which \( \mathbf{F}_i \) is external force, which is typically a function of coordinates. The \( J \)'s account for the encounters between gas molecules, where \( J_0 \) and \( J_1 \) covers the encounters between same type molecules, while \( J_{01} \) and \( J_{10} \) describe the ones between different molecules, e.g., \( J_0 \) and \( J_{01} \) are defined as

\[
J_0(f_0f) \equiv \iiint (f_0f - f_0'f')gdbd\epsilon dc,
\]

\[
J_{01}(f_0f_1) \equiv \iiint (f_0f_1 - f_0'f_1')gdbd\epsilon dc_1,
\]

and \( J_1 \) and \( J_{10} \) can be defined likewise. In the \( J \)'s definition, \( g \) is the magnitude of the pre-collision relative velocity, \( b \) is the “impact parameter” of the encounter, \( \epsilon \) is an angle corresponding to the azimuthal orientation of the scattering plane. A prime (′) indicates a function of a post-encounter velocity while the one without a prime indicates a pre-encounter velocity. \( J \) is related to intermolecular potential energy: microscopically, pre- and post-encounter velocities are the initial velocity of a direct encounter and reverse encounter, of which the kinetics is the same as the one of direct encounter but only of the backward direction in time, respectively, and the kinetics are of course, closely related with the intermolecular potential energy curves.

The Boltzmann equation is a non-linear integrodifferential equation: e.g., in the equation for \( f_i \), \( \mathcal{D}_i \) accounts for the differential part while \( J_i \) and \( J_{ij} \) (\( j = 1 - i \)) for the integral one. It is non-trivial to solve such equations. However, effort given by Hilbert\[11\], Chapman\[10\], and Enskog\[12\] have shown that we can use a perturbative way to approximate the solution, where \( J_i \) and \( J_{ij} \) can be treated as a perturbation term. In this manner, \( f_i, \mathcal{D}_i, J_i+J_{ij} \) can be expended as

\[
f_i = f_i^{(0)} + f_i^{(1)} + f_i^{(2)} + \ldots, \]

\[
\mathcal{D}_i f_i = \mathcal{D}_i^{(0)} + \mathcal{D}_i^{(1)} + \mathcal{D}_i^{(2)} + \ldots,
\]

where \( \mathcal{D}_i^{(r)} \) is defined as

\[
\mathcal{D}_i^{(r)} = \frac{\partial^{r-1}f_i^{(0)}}{\partial t} + \frac{\partial^{r-2}f_i^{(1)}}{\partial t} + \ldots + \frac{\partial_0 f_i^{(r-1)}}{\partial t} + \left( \mathbf{c}_i \cdot \frac{\partial}{\partial \mathbf{r}} + \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{c}_i} \right) f_i^{(r-1)},
\]

and

\[
J_i(f_if) + J_{ij}(f_if_j) = J_i^{(0)} + J_i^{(1)} + J_i^{(2)} + \ldots,
\]
in which
\[ J_i^{(r)} = J_i(f_i^{(0)} f^{(r)}) + J_i(f_i^{(1)} f^{(r-1)}) + \ldots + J_i(f_i^{(r)} f^{(0)}) \]
\[ + J_{ij}(f_i^{(0)} f_j^{(r)}) + J_{ij}(f_i^{(1)} f_j^{(r-1)}) + \ldots + J_{ij}(f_i^{(r)} f_j^{(0)}). \]  

These terms obey
\[ \mathcal{D}_i^{(r)} + J_i^{(r)} = 0, \quad r = 0, 1, 2, \ldots, \]  

We need also define the operator \( \partial_t / \partial t \), which is given in Appendix B.2. To sum up, \( \mathcal{D}_i^{(r)} \) is only related to \( f_i^{(0)}, f_i^{(1)}, \ldots, f_i^{(r-1)} \), and the only term contains \( f_i^{(r)} \) is related to \( J_i^{(r)} \). Thus, Boltzmann equation can be solved step by step from an initial trial of \( f_i^{(0)} \).

In the 0-th solution of \( f_i \), i.e., \( f_i^{(0)} \), we have \( J_i^{(0)} = 0 \), which corresponds to the uniform and steady gas, the distribution function is the Maxwellian velocity distribution
\[ f_i^{(0)} = n_i \left( \frac{m_i}{2\pi k_B T} \right)^{3/2} \exp\left\{ -m_i(c_i - c)^2 / 2k_B T \right\}, \]  

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( p \) is the hydrostatic pressure, \( m_i \) is the mass of the \( i \)-th atoms, \( c \) is the mass-weighted mean velocity of the gas, and \( n_i \) is the number of specie \( i \).

In the first order perturbation, \( f_i^{(1)} \) can be written as
\[ f_i^{(1)} = f_i^{(0)} \Phi_i^{(1)}. \]  

Thus,
\[ \mathcal{D}_i^{(1)} = - J_i^{(1)} \]
\[ = - J_i(f_i^{(0)} f^{(0)} \Phi_i^{(1)}) - J_i(f_i^{(0)} \Phi_i^{(1)} f^{(0)}) - J_{ij}(f_i^{(0)} f_j^{(0)} \Phi_j^{(1)}) - J_{ij}(f_i^{(0)} \Phi_i^{(1)} f_j^{(0)}) \]
\[ = - n_i^2 I_i \left( \Phi_i^{(1)} \right) - n_i n_j I_{ij} \left( \Phi_i^{(1)} + \Phi_j^{(1)} \right), \]  

where \( I_i \) and \( I_{ij} \) are pre-defined integrals, and are linear functionals of their argument, whose definitions are given in Appendix B.3. The \( \mathcal{D}_i^{(1)} \) can be written as
\[ \mathcal{D}_i^{(1)} = f_i^{(0)} \left\{ \left( C_i^2 - \frac{5}{2} \right) C_i \frac{\partial \ln T}{\partial r} + x_i^{-1} d_{ij} C_i + 2 \mathbf{E}_i \mathbf{E}_i : \frac{\partial \mathbf{c}}{\partial r} \right\}, \]  

where \( \mathbf{E}_i \) is the electric field.
where $C_i \equiv c_i - c$ is the peculiar velocity, $G_i \equiv (m_i/2k_BT)^{1/2}C_i$ is the dimensionless peculiar velocity, $x_i \equiv n_i/(n_i + n_j)$ is the mole fraction of the $i$-th specie, and

$$d_{ij} = -d_{ji} \equiv x_i \frac{\partial}{\partial r} \ln p_i - \frac{\rho_i \rho_j}{\rho_p} (F_i - F_j) - \frac{\rho_i}{\rho_p} \frac{\partial p}{\partial r}. \quad (14)$$

where $\rho = \rho_0 + \rho_1$ is the total density, $\rho_i \equiv n_i m_i$, and $p$ is the hydrostatic pressure ($p_i$ the partial pressure). Compare Eqs. (12) and (13), we can give the ansatz of $\Phi^{(1)}$

$$\Phi^{(1)}_i = -A_i \frac{\partial \ln T}{\partial r} - D_i d_{ij} - 2B_i : \frac{\partial c}{\partial r}, \quad (15)$$

where integrals of $A$, $D$, and $B$ should equal the corresponding coefficients in Eq. (13), i.e.,

$$f_i^{(0)} G_i^2 - 5/2) C_i = n_i^2 I_i(A_i) + n_i n_j I_{ij}(A_i + A_j), \quad (16)$$

$$( -1 )^i x_i^{-1} f_i^{(0)} C_i = n_i^2 I_i(D_i) + n_i n_j I_{ij}(D_i + D_j), \quad (17)$$

$$f_i^{(0)} G_i^2 G_i = n_i^2 I_i(B_i) + n_i n_j I_{ij}(B_i + B_j). \quad (18)$$

If there is no external force acting on the system, it can be shown that

$$d_{ij} = \frac{\partial x_i}{\partial r} = n^{-1} \nabla n_i. \quad (19)$$

Now let us consider the transport properties by get the expectation value with the first order approximation of $f_i$, i.e., $f_i^{(0)} + f_i^{(1)}$. Diffusion means that the two components of the gas have different average velocity

$$\overline{C}_0 - \overline{C}_1 = \frac{1}{n_0} \int f_0 C_0 \mathrm{d}c_0 - \frac{1}{n_1} \int f_1 C_1 \mathrm{d}c_1$$

$$= - \frac{1}{3} \left[ \left\{ \frac{1}{n_0} \int f_0^0 C_0 D_0 \mathrm{d}c_0 - \frac{1}{n_1} \int f_1^0 C_1 D_1 \mathrm{d}c_1 \right\} d_{01} + \left\{ \frac{1}{n_0} \int f_0^0 C_0 A_0 \mathrm{d}c_0 - \frac{1}{n_1} \int f_1^0 C_1 A_1 \mathrm{d}c_1 \right\} \frac{\partial}{\partial r} \ln T \right]$$

$$= \frac{1}{3} n \left\{ [D, D] d_{01} + [D, A] \frac{\partial}{\partial r} \ln T \right\}, \quad (20)$$

and we define the coefficient of diffusion as $D_{01} \equiv (n_0 n_1/3n)\{D, D\}$ and the coefficient of thermal diffusion as $D_T \equiv (n_0 n_1/3n)\{D, A\}$. We also
define the thermal-diffusion ratio \( k_T \equiv D_T/D_{01} \), and thermal diffusion factor \( \alpha_{01} \equiv k_T/x_0x_1 \).

If we look into the energy flux \( q \) of the system, we can get

\[
q = -\lambda \frac{\partial}{\partial r} T + \frac{5}{2} k_B T (n_0 \overline{C}_0 + n_1 \overline{C}_1) + k_B n T k_T (\overline{C}_0 - \overline{C}_1),
\]

where

\[
\lambda \equiv \frac{1}{3} k_B n^2 \{ \{ A, A \} \{ A, D \}^2 / \{ D, D \} \} \quad (22)
\]

is the coefficient of thermal conductivity, which reflect the correspondence of gas mixture to temperature gradient. We define \( \tilde{A}_i \equiv A_i - k_T D_i \), so

\[
\lambda = \frac{1}{3} k_B n^2 \{ \tilde{A}, \tilde{A} \}. \quad (23)
\]

Similarly, if we consider the pressure tensor, we have

\[
p^{(1)} = -\frac{4}{5} k_B n^2 T \{ B, B \} \frac{\partial}{\partial r} c, \quad (24)
\]

and the coefficient of viscosity \( \mu \) is defined as

\[
\mu \equiv \frac{2}{5} k_B n^2 T \{ B, B \}. \quad (25)
\]

Apparently, the key of getting the four coefficients is finding a robust way to get the integrals \( \{ A, A \}, \{ A, D \}, \{ D, D \}, \{ B, B \} \), and these vectors and matrices (\( \tilde{A}, D, \) and \( B \)) can be written as

\[
\tilde{A}_0 = \sum_{p=-\infty}^{\infty} ' a_p a_0^{(p)}, \quad \tilde{A}_1 = \sum_{p=-\infty}^{\infty} ' a_p a_1^{(p)}
\]

\[
D_0 = \sum_{p=-\infty}^{\infty} d_p a_0^{(p)}, \quad D_1 = \sum_{p=-\infty}^{\infty} d_p a_1^{(p)}, \quad (26)
\]

\[
B_0 = \sum_{p=-\infty}^{\infty} ' b_p b_0^{(p)}, \quad B_1 = \sum_{p=-\infty}^{\infty} ' b_p b_1^{(p)}.
\]
where \( \sum' \) means sum over all \( p \) but zero, and (for \( p > 0 \))

\[
\begin{align*}
\mathbf{a}_0 &= M_0^{1/2} \rho_1 \mathbf{C}_0 / \rho, \\
\mathbf{a}_0^p &= S^{(p)}_{3/2}(\mathbf{C}_0^2) \mathbf{C}_0, \\
\mathbf{a}_{0}^{-p} &= 0, \\
\mathbf{a}_1^p &= 0, \\
\mathbf{a}_{1}^{-p} &= S^{(p)}_{3/2}(\mathbf{C}_1^2) \mathbf{C}_1, \\
b_0^p &= S^{(p-1)}_{5/2}(\mathbf{C}_0^2) \mathbf{C}_0^0 \mathbf{C}_0, \\
b_0^{-p} &= 0, \\
b_1^p &= 0, \\
b_{1}^{-p} &= S^{(p-1)}_{5/2}(\mathbf{C}_1^2) \mathbf{C}_1^0 \mathbf{C}_1,
\end{align*}
\]

(27)

where \( S^{(n)}_m \) are Sonine polynomials (or in more common literature, associated Laguerre polynomials). Sonine polynomials can be written as

\[
S^{(n)}_m(x) = \sum_{p=0}^{n} \frac{(-x)^p}{p!} \binom{m+n}{m-p},
\]

(28)

and they have orthogonality, i.e.

\[
\int_0^{\infty} e^{-x} S^{(p)}_m(x) S^{(q)}_m(x) x^m \, dx = \begin{cases} 
0 & (p \neq q) \\
\Gamma(m+p+1)/p! & (p = q) \end{cases}.
\]

(29)

Using Sonine polynomials as bases, the solution to the integrals \( \{ \mathbf{A}, \mathbf{A} \}, \{ \mathbf{A}, \mathbf{D} \}, \{ \mathbf{D}, \mathbf{D} \}, \) and \( \{ \mathbf{B}, \mathbf{B} \} \) turns into linear algebra problems. Here, we use only the case of \( \mathbf{B} \) as an example. We define

\[
\{ \mathbf{B}, \mathbf{b}^{(p)} \} = \beta_p,
\]

(30)

and recalling Eq. (18)

\[
\begin{align*}
\beta_1 &= \frac{5n_0}{2n^2} = n^{-1} \frac{5x_0}{2}, \\
\beta_-1 &= \frac{5n_1}{2n^2} = n^{-1} \frac{5x_1}{2}, \\
\beta_q &= 0 \quad (q \neq \pm 1).
\end{align*}
\]

(31)

(32)

Thus,

\[
\{ \mathbf{B}, \mathbf{B} \} = \sum_p b_p \{ \mathbf{B}, \mathbf{b}^{(p)} \}
\]

\[
= b_1 \beta_1 + b_{-1} \beta_{-1}.
\]

(33)
Here note that we use \( S_{5/2}^{(p)} \) to expand \( \mathbf{B} \) leading to \( \beta_q \), \( q \neq \pm 1 \), because the expression of \( \{\mathbf{B}, \mathbf{b}^{(q)}\} \) has the structure of

\[
\int_0^\infty \exp\left\{ -\mathbf{C}^2 \right\} (\mathbf{C}^2)^{5/2} \mathcal{S}_{5/2}^{(q-1)}(\mathbf{C}^2) \, d(\mathbf{C}^2),
\]

which consists with the orthogonal property of Sonine polynomials. \( b_p \)’s are then the key to get \( \{\mathbf{B}, \mathbf{B}\} \). We further expand \( \mathbf{B} \) in \( \{\mathbf{B}, \mathbf{b}^{(q)}\} \) to turn Eq. (30) as

\[
\sum_{p=-\infty}^\infty \beta_p b_{pq} = \beta_q, \quad (34)
\]

where

\[
b_{pq} = \{\mathbf{b}^{(p)}, \mathbf{b}^{(q)}\}. \quad (35)
\]

This can be turned into a matrix multiplication considering we can only use limited \( p \) and \( q \). As defined in Eq. (25), the resulting value of viscosity will not be dependent on the total density \( n \) but will be on \( x_i \), because the \( n^2 \) in Eq. (25) and the \( n \)’s from \( b_i \) and \( \beta_p \) cancel. We will thus move the \( n \)’s to the final expression of these properties. (Actually, in the four properties studied, the diffusion and thermal diffusion are related to the density by an inverse proportional relation, while viscosity and thermal conductivity are independent on \( n \).) Clearly, the other integrals can be solved in this fashion.

The matrix elements \( a_{pq} \) and \( b_{pq} \) can then be given using the \( \Omega \) integrals, see below.

Formulae for diffusion \( D_{01} \) and thermal diffusion \( D_T \) are

\[
[D_{01}]_n = \left( \frac{k_B T}{p} \right) \frac{1}{2} x_0 x_1 \left( \frac{2 k_B T}{m} \right)^{1/2} d_0^{(m)},
\]

\[
[D_T]_n = - \left( \frac{k_B T}{p} \right) \frac{5}{4} x_0 x_1 \left( \frac{2 k_B T}{m} \right)^{1/2} \left( x_0 M_0^{-1/2} d_1^{(m)} + x_1 M_1^{-1/2} d_{-1}^{(m)} \right). \quad (36)
\]

Readers may find the equation here have additional \( k_B T/p = n^{-1} \) factor compared with the ones in Ref. [13], while we remove the \( n^{-1} \) from the definition of \( \delta_0 \) (see below). Diffusion is inversely proportional to the total density or pressure, and in practice people report these diffusion properties
under $p = 1$ atm, see, e.g., Ref. [14]. In PENG, we follow this convention and print the diffusion coefficients under 1 atm.

In equations above, subscript $n$ ([⋯]$_n$) means “the $n$-th order approximation of ⋅⋅⋅”, and superscription $(n)$ means element of the $n$-th order vectors (see below). We also have the $n$-th order vectors

$$
\mathbf{d}^{(n)} = (d_{-n}, \cdots, d_0, d_1, \cdots, d_n)^T,
\quad \delta^{(n)} = (0, \cdots, 0, \delta_0, 0, \cdots, 0)^T,
$$

(37)

where the superscript $\text{T}$ means transpose,

$$
\delta_0 = \frac{3}{2} \left( \frac{2k_bT}{m_0} \right)^{1/2}
$$

(38)

and

$$
\mathbf{d}^{(n)} = \left( \mathbf{D}^{(n)} \right)^{-1} \delta^{(n)}.
$$

(39)

The $\mathbf{D}^{(n)}$ matrix is

$$
\mathbf{D}^{(n)} =
\begin{pmatrix}
\begin{array}{cccccc}
 a_{-n-n} & \cdots & a_{-n-1} & a_{-n0} & a_{-n1} & \cdots & a_{-nn} \\
 \vdots & \ddots & \vdots & \vdots & \vdots & \cdots & \vdots \\
 a_{-1-n} & \cdots & a_{-1-1} & a_{-10} & a_{-11} & \cdots & a_{-1n} \\
 a_{0-n} & \cdots & a_{0-1} & a_{00} & a_{01} & \cdots & a_{0n} \\
 a_{1-n} & \cdots & a_{1-1} & a_{10} & a_{11} & \cdots & a_{1n} \\
 \vdots & \ddots & \vdots & \vdots & \vdots & \cdots & \vdots \\
 a_{n-n} & \cdots & a_{n-1} & a_{n0} & a_{n1} & \cdots & a_{nn}
\end{array}
\end{pmatrix},
$$

(40)

whose elements are

$$
\begin{align*}
a_{pq} &= a_{qp} = x_0^2 H_{pq}(0000) + x_0 x_1 H_{pq}(0001), \\
a_{p-q} &= a_{-q-p} = x_0 x_1 H_{pq}(0101), \\
a_{-q-p} &= a_{q-p} = x_1 x_0 H_{pq}(1010), \\
a_{-p-q} &= a_{-q-p} = x_1^2 H_{pq}(1111) + x_1 x_0 H_{pq}(1110), \\
a_{p0} &= a_{0p} = x_0 x_1 M_0^{1/2} H_{p0}(0001), \\
a_{-p0} &= a_{0-p} = -x_1 x_0 M_1^{1/2} H_{p0}(1110), \\
a_{00} &= 8 x_0 x_1 M_0 M_1 \Omega_{01}^{(1,1)},
\end{align*}
$$

(41)
where $H_{pq}(abαβ) = \left[ S^{(p)}_{3/2}(G_a^2) \otimes S^{(q)}_{3/2}(G_b^2) \right]_{αβ}$, for any positive $p$ and $q$.

Note that the last three lines were missed in Ref. [13]. The index $a$ and $b$ are for mass and $α$ and $β$ designate the collision integrals $Ω^{(ℓ,s)}_{αβ}(T)$. When $a = b = α = β$,

$$H_{pq}(abαβ) = 8 \sum_{ℓ=2}^{(p+q+1)(p+q+2−ℓ)} A_{pqst}^{"} Ω^{(ℓ,s)}_{αβ},$$  (42)

where

$$A_{pqst}^{"} = \left( \frac{1}{2} \right)^{(p+q+1)(p+q+2−ℓ)} \sum_{i=(ℓ−1)}^{\min[p,q,s,(p+q+1−s)]]} 8^i(p+q−2i)!$$

$$\frac{(−1)(s+i)}{(p−i)(q−i)!} \ell!(i+1−ℓ)! (s−i)!(p+q+1−i−s)! \times (s+1)! (2(p+q+2−i))! 2^{2s}$$

$$\frac{(2s+2)!}{4^{(p+q+1)}} (p+q+2−i)! [i+1−ℓ](p+q+1−i−s)−ℓ(s−i)].$$  (43)

When $a ≠ b, α ≠ β, a = α$ and $b = β$,

$$H_{pq}(abαβ) = 8 \sum_{ℓ=1}^{(p+q+1)(p+q+2−ℓ)} A_{pqst}^{"} Ω^{(ℓ,s)}_{αβ},$$  (44)

where

$$A_{pqst}^{"} = M_b^{(p+1/2)} M_a^{(q+1/2)} \sum_{i=(ℓ−1)}^{\min[p,q,s,(p+q+1−s)]]} 8^i(p+q−2i)!$$

$$\frac{(−1)(s+i)}{(p−i)(q−i)!} \ell!(i+1−ℓ)! (s−i)!(p+q+1−i−s)! \times (s+1)! (2(p+q+2−i))! 2^{2s}$$

$$\frac{(2s+2)!}{4^{(p+q+1)}} (p+q+2−i)! [i+1−ℓ](p+q+1−i−s)−ℓ(s−i)].$$  (45)

When $a = b$ while $α ≠ β$,

$$H_{pq}(abαβ) = 8 \sum_{ℓ=1}^{(p+q+1)(p+q+2−ℓ)} A_{pqst}^{"} Ω^{(ℓ,s)}_{αβ},$$  (46)
where

\[
A'_{pqst} = \min[p,q,s,(p+q+1-s)] \sum_{i=(\ell-1)} 8^i (p + q - 2i)! (p - i)!(q - i)!
\]

\[
\times \frac{1}{(s+1)! (p+q+1-i-s)!} \left( 2^{(2s+2)} \frac{(2(p+q+2-i))}{4(p+q+1)} \right)
\]

\[
\times \left( \sum_{w=0}^\infty F^{(i+1-\ell)} G^w \frac{w!}{w!} \right)
\]

\[
\times (p+q+2-i-s-w)_w (p+1-i-w)_w
\]

\[
\times (p+q+3-i-w)_w (q+1-i-w)_w
\]

\[
\times 2^{(2w-1)} \frac{M^i M^{i+a} M^{(p+q-2i-w)}_1}{(p+q+1-2i-w)_w}
\]

\[
\times \left[ 2M^i_\alpha F^{-1}(i+1-\ell)(p+q+1-i-s-w)
\right.
\]

\[
- 2M^{i+\epsilon}(s-i)
\]

\[
(47)
\]

in which \( F = (M^2_0 + M^2) / 2M_0 M_1 \) and \( G = (M_a - M_{1-a}) / M_{1-a} \). In formulae above, \( n! = \Gamma(n + 1) \) is the factorial, and \( (z)_n = \Gamma(z+n)/\Gamma(z) \) is the Pochhammer symbol. Note that we employ a zero-based index so that subscript \( 1-a \) represents the mass not appearing explicitly in \( a \) or \( b \).

The thermal conductivity \( \lambda \) of the binary mixture is given as

\[
[\lambda]_{n} = -\frac{5}{4} k_B \left( \frac{2k_B T}{m} \right)^{1/2}
\]

\[
\times \left( x_0 M_0^{-1/2} a_0^{(n)} + x_1 M_1^{-1/2} a_{-1}^{(n)} \right).
\]

\[
(48)
\]

The rule of super- and sub-scripts is the same as that for diffusion, and \( a^{(n)} \) and \( \alpha^{(n)} \) here are

\[
a^{(n)} = (a_{-n}, \cdots, a_{-1}, a_1, \cdots, a_n)^T,
\]

\[
\alpha^{(n)} = (0, \cdots, \alpha_{-1}, \alpha_1, \cdots, 0)^T.
\]

\[
(49)
\]
where
\[ \alpha_{-1} = -\frac{15}{4} x_1 \left( \frac{2k_B T}{m_1} \right)^{1/2}, \quad \alpha_1 = -\frac{15}{4} x_0 \left( \frac{2k_B T}{m_0} \right)^{1/2}, \] (50)
and
\[ a^{(n)} = \left( A^{(n)} \right)^{-1} a^{(n)}. \] (51)

Here, \( A^{(n)} \) is the \((0, 0)\) minor matrix of \( D^{(n)} \), i.e., remove the colored row and column in Eq. 40.

The viscosity \( \eta \) is similarly given by
\[ [\eta]_n = k_B T \left( x_1 b_1^{(n)} + x_2 b_{-1}^{(n)} \right), \] (52)
where \( N \) is the number density of the gas mixture,
\[ b^{(n)} = \begin{pmatrix} b_{-n}, & \cdots, & b_{-1}, & b_1, & \cdots, & b_n \end{pmatrix}^T, \]
\[ \beta^{(n)} = \begin{pmatrix} 0, & \cdots, & \beta_{-1}, & \beta_1, & \cdots, & 0 \end{pmatrix}^T, \] (53)
while
\[ b^{(n)} = \left( B^{(n)} \right)^{-1} \beta^{(n)}. \] (54)

The expressions for elements in \( \beta \) are (note that the redundant negative signs in Ref. 15 have been removed)
\[ \beta_1 = \frac{5}{2} x_0, \quad \beta_{-1} = \frac{5}{2} x_1. \] (55)

The shape of the matrix \( B^{(n)} \) looks the same as \( A^{(n)} \), namely,
\[ B^{(n)} = \begin{pmatrix} b_{-n-n} & \cdots & b_{-n-1} & b_{-n-1} & \cdots & b_{-n-n} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ b_{-1-n} & \cdots & b_{-1-1} & b_{-1-1} & \cdots & b_{-1-n} \\ b_{1-n} & \cdots & b_{1-1} & b_{1-1} & \cdots & b_{1-n} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ b_{n-n} & \cdots & b_{n-1} & b_{n-1} & \cdots & b_{n-n} \end{pmatrix}, \] (56)
with elements \((p > 0 \text{ and } q > 0)\)
\[ b_{pq} = a_{qp} = x_0^2 L_{pq}(0000) + x_0 x_1 L_{pq}(0001), \]
\[ b_{p-q} = a_{-q-p} = x_0 x_1 L_{pq}(0101), \]
\[ b_{-p-q} = a_{q-p} = x_1 x_0 L_{pq}(1010), \]
\[ b_{-p-q} = a_{-q-p} = x_1^2 L_{pq}(1111) + x_1 x_0 L_{pq}(1110). \] (57)
The $L_{pq}(ab\alpha\beta)$ is defined as

$$L_{pq}(ab\alpha\beta) = \left[ S_{5/2}^{(p-1)} (C_a^2) C_a C_a, S_{5/2}^{(q-1)} (C_b^2) C_b C_b \right]_{\alpha\beta}.$$  \hfill (58)

When $a = b = \alpha = \beta$,

$$L_{pq}(ab\alpha\beta) = \frac{16}{3} \sum_{\ell=2}^{(\text{min}[p,q]+2)} \sum_{s=\ell}^{(p+q+4-\ell)} B''_{pqsl} \Omega_{\alpha\beta}^{(\ell,s)},$$  \hfill (59)

where

$$B''_{pqsl} = \left( \frac{1}{2} \right)^{(p+q+2)} \frac{2^s}{4^{(p+q+2)}} \times \frac{(s+1)!}{(2s+2)!} \frac{[1 + (-1)^{\ell}]}{\ell!} \sum_{i=(\ell-2)}^{\text{min}[p,q,s,(p+q+2-s)]} (-1)^{s+i} \frac{(p+q-2i)!}{(p+q+2-i-s)!} \frac{(p+q+3-i)!}{(p+q+3-i)!} \frac{8^i}{(i+2-\ell)!} \times \left\{ \frac{(i+1-\ell)(i+2-\ell)}{(p+q+1-i-s)(p+q+2-i-s)} - \frac{1}{2} (s-i)(s-i-1) \right\} + \frac{3}{2} (\ell-1)\ell(s-i)(s-i-1) - 2\ell(i+2-\ell)(s-i)(p+q+2-i-s).$$ \hfill (60)

When $a \neq b, \alpha \neq \beta, a = \alpha$ and $b = \beta$,

$$L_{pq}(ab\alpha\beta) = \frac{16}{3} \sum_{\ell=1}^{(\text{min}[p,q]+2)} \sum_{s=\ell}^{(p+q+4-\ell)} B''_{pqsl} \Omega_{\alpha\beta}^{(\ell,s)},$$  \hfill (61)
where

\[
B''_{pq\ell} = M_b^{(p+1)} M_a^{(q+1)} \left( 1 - \delta_{s,(p+q+3)} \right) \\
\times \sum_{i=(\ell-2)} \frac{2^s}{4^{(p+q+2)}} 8^i (p+q-2i)! \\
\times \frac{(-1)^{(s+i)} (1 - \delta_{i,(-1)})}{(s-i)!(p+q+2-i-s)!} \\
\times \frac{(s+1)! [2(p+q+3-i)]!}{(2s+2)! (p+q+3-i)!} \frac{(-1)^{\ell}}{\ell!(i+2-\ell)!} \\
\times \left\{ (i + 1 - \ell)(i + 2 - \ell) \\
\times [(p+q+1-i-s)(p+q+2-i-s) \\
- \frac{1}{2}(s-i)(s-i-1)] \\
+ \frac{3}{2}(\ell-1)\ell(s-i)(s-i-1) \\
- 2\ell(i+2-\ell)(s-i)(p+q+2-i-s) \right\}.
\]

When \( a = b \) while \( \alpha \neq \beta \),

\[
L_{pq}(ab\alpha\beta) = \frac{16}{3} \sum_{\ell=1}^{(\min[p,q]+2)} \sum_{s=\ell}^{(p+q+4-\ell)} B'_{pq\ell} \Omega^{(\ell,s)}_{\alpha\beta},
\]

\( \text{Eq. (63)} \)
where

\[ B'_{pq\ell} = (1 - \delta_{s,(p+q+3)}) \]

\[ \times \sum_{i=(\ell-2)}^{\min[p,q,s,(p+q+2-s)]} \frac{2^{2s}}{4^{(p+q+2)}} \frac{8^i (p+q-2i)!}{(p-i)!(q-i)!} \]

\[ \times \frac{(-1)^{(s+i)} (1 - \delta_i,(-1))}{(s-i)! (p+q+2-i-s)! (2s+2)!} \]

\[ \times \frac{(2(p+q+3-i))!}{(p+q+3-i)!} \]

\[ \times \sum_{w=0}^{(\min[p,q,(p+q+2-s)]-i)} \frac{(p+1-i-w)_w (q+1-i-w)_w}{w! (p+q+1-2i-w)_w} \]

\[ \times \frac{(p+q+3-i-s-w)_w}{(2(p+q+3-i)-2w+1)_w} 2^{(2w-2)} G^w \]

\[ \times \frac{(p+q+4-i-w)_w}{(2(p+q+3-i)-w+1)_w} \]

\[ \times M^i a^{M_{1-a}} M_1^{(p+q-2i-w)} \frac{F(i+2-\ell) M^2_a}{\ell!(i+2-\ell)!} \]

\[ \times 4 \left\{ \frac{3 M^2_{1-a}}{2} \ell(\ell-1)(s-i)(s-i-1) \right. \]

\[ - \frac{2}{F} M^i a \ell(i+2-\ell)(s-i)(p+q+2-i-s-w) \]

\[ + \frac{1}{F^2} (i+1-\ell)(i+2-\ell) \]

\[ \times \left[ (p+q+1-i-s-w)(p+q+2-i-s-w) \right. \]

\[ - \frac{1}{2} M^2_{1-a} (s-i)(s-i-1) \left\} \right\} . \]

with \( F = (M_0^2 + M_1^2) / 2M_0M_1 \) and \( G = (M_a - M_{1-a}) / M_{1-a} \).

In the formulae above, the central components are the collision integrals \( \Omega^{(\ell,s)}_{\alpha\beta} \), which are determined by classical collisions between atom pairs. The numerical computation of \( \Omega^{(\ell,s)}_{\alpha\beta} \) is often performed in reduced units, where lengths are given as multiples of the collision radius \( \sigma \) and energies are multiples of the well depth \( \varepsilon \) of the PEC, e.g., the reduced PEC is \( V^\star(r^\star) = \varepsilon V(\sigma r^\star) \), in which the star (\(^\star\)) indicates a dimensionless reduced
quantity. Clearly, we can have all the quantities involved in classic collision in the “star” format by using the reduced units introduced above.

To compute $\Omega_{\alpha\beta}^{(\ell,r)}$ numerically, three integration must be carried out. The scattering angle $\chi$ is a function of initial kinetic energy of the collision $E^*$ and the collision parameter $b^*$, and is given by

$$\chi(E^*, b^*) = \pi - 2b^* \int_{r_m}^{\infty} \frac{dr^*}{r^{*2} F(r^*)},$$

with $b^* \in [0, +\infty), E^* \in [0, +\infty).$

with

$$F(r^*) = \left[ 1 - \frac{V^*(r^*)}{E^*} - \frac{b^{*2}}{r^{*2}} \right]^{1/2}. \quad (66)$$

The cross section $Q^{(\ell)}$ is a function of the initial kinetic energy $E^*$,

$$Q^{(\ell)}(E^*) = \frac{2}{1 - \frac{1+(-1)^{\ell}}{2(1+\ell)}} \int_0^{\infty} \left( 1 - \cos \ell \chi(E^*, b^*) \right) b^* db^*. \quad (67)$$

The collision integral $\Omega^{(\ell,s)}(T^*)$ is function of the reduced temperature $T^*$

$$\Omega^{(\ell,s)}(T^*) = \frac{1}{(s + 1)!} \int_0^{\infty} e^{-x} x^{s+1} Q^{(\ell)}(xT^*) dx, \quad (68)$$

and $\Omega^{(\ell,s)}(T)$ can be obtained using the expression

$$\Omega^{(\ell,s)}(T) = \frac{1/2 (s + 1)! \left[ 1 - \frac{1+(-1)^{\ell}}{2(1+\ell)} \right]}{\sqrt{2\pi \mu/kT}} \Omega^{(\ell,s)}(T^*). \quad (69)$$

Different numerical integration schemes can be implemented for these three integrals. Also, different schemes can be combined freely.

3. Program Implementation and Developers’ Guide

3.1. Structure of Peng

The main structure of the program is shown in Fig. 1. The program is designed in Object-Orient Program (OOP) paradigm. Before proceeding, some explanation about OOP should be given. Although it is often taught in books about OOP [16, 17, 18] that objects (classes) are abstractions of
objects (or things) in real life, it is a common practice \cite{19, 20} to present an algorithm as an object. Alternatively, readers may think such objects abstraction of computers of specific usage. For those readers who are familiar with procedural programming, *e.g.*, Fortran 77 users, OOP is an elegant way to have common variables, and multiplex the same code for different problems within the same program with minimal effort.

All codes in the core part of PENG are in the namespace `peng`. In this work, atom pair (class `AtomPair`) is the basic component in our mental model. For binary mixture of atoms 0 and 1, three kinds of pair should be considered: atom pair 00, 01, and 11. `AtomPair` class hold the basic information of the atoms in pair, which is recorded in `Atom` class, and the interatomic PEC, as a `FuncDeriv1D` object.

The `FuncDeriv1D` is an abstract for one-dimension functions $f(x)$ together with their derivatives. The most important two methods of this class are `value()` and `derivative()`. In the other part of the program, we always keep the calling to these two methods with the same $x$ together, if both value and derivative are needed. Thus, a cache mechanism may be used to store the intermediate variables to save computational time. Note that `FuncDeriv1D::derivative()` is not a pure virtual function, the program will fallback to a default numerical differential program if no analytical one is provided.

The original potential function will be passed to `Pot1DFeatures` to get $\sigma$ and $\varepsilon$ numerically, and a reduced potential $V^*$ will be returned by function `Pot1DFeatures::reduced_potential()`. $V^*$ will then be passed to class `ReducedPotentialQuadrature` for to get $\Omega^{(\ell,s)}(T^*)$, which is given by its `Omega()` method, which calls its `Q()` and `Chi()` methods automatically.

The three key methods of `ReducedPotentialQuadrature`, say, `Omega()`, `Q()`, and `chi()`, are sockets of the three classes, `OmegaImpl`, `QImpl`, and `ChiImpl`. Implementations of these three pure virtual classes can be loaded at compiling time with the template method `set_algorithm<TChi, TQ, TOmega>()` of `ReducedPotentialQuadrature`. For developers, these concrete classes are where one can extend PENG. Classes `OmegaGL`, `QCG`, and `ChiCG` are provided as examples of integration algorithms.

Once we have the program for $\Omega^{(\ell,s)}(T)$ ready, We may also obtain the transport properties, which are coded in class `TransportProperties`. Although we have our own $\Omega^{(\ell,s)}(T)$, we still leave an interface, class `OmegaComp`, and a concrete class `OmegaCache`, which uses `AtomPair` only when new combinations of $\ell$, $s$, and $T$ are passed in, or returns the cached value of $\Omega^{(\ell,s)}(T)$
from a local database otherwise, is implemented. This is because we do not want to limit the user to our implementations of collision integrals. Besides, $\Omega^{(\ell,s)}(T)$ are computed on-the-fly, to avoid unnecessary high-order computations, which are more difficult to compute than low-order ones.

Although Peng is designed as a library, a user interface (UI) is provided for end users. The UI is designed to be separated from the library, therefore, the codes of UI provide a good example for developers of how to use Peng in their own projects.

### 3.2. Algorithms implemented in Peng

To give the end users a usable software, and to test the framework, we have supplied some concrete classes for integration. Following Ref. [6], $\chi$ is rewritten as a function of $r_m$,

\[
\chi(E^*, r_m^*) = \chi \left( E^*, b^* = r_m^* \sqrt{\frac{E^* - V^*(r_m^*)}{E^*}} \right),
\]

and the integration in $[r_m, \infty)$ is mapped to $(0, 1)$ by $r \to \frac{r_m}{r}$, and the Chebyshev–Gauss (CG) quadrature rule [21] is used. Note that CG rule is for $(-1, 1)$. To use it under this circumstance, we assume the integrand of the $\chi$ quadrature is an even function, and we only take the positive half. The CG quadrature rule is based on Chebyshev nodes, which are nested. In our implementation, $3^n \ (n = 1, 2, \ldots)$ nodes are used, and the integration algorithm is written in class CGQuadrature.

The cross-section $Q^{(\ell)*}$ is

\[
Q^{(\ell)*}(E^*) = \frac{2}{1 - \frac{1 + (-1)^{\ell}}{2(1+\ell)}} \int_0^\infty (1 - \cos\ell \chi) \, b^* \, db^*
\]

\[
= \frac{1}{1 - \frac{1 + (-1)^{\ell}}{2(1+\ell)}} \int_0^\infty (1 - \cos\ell \chi) \, d(b^{*2})
\]

\[
= \frac{1}{1 - \frac{1 + (-1)^{\ell}}{2(1+\ell)}} \left[ \int_{r_m^*}^{r_{\ell}^*} + \int_{r_{\ell}^*}^\infty \right] (1 - \cos\ell \chi)
\]

\[
\times d \left( r_m^* \frac{E^* - V^*(r_m^*)}{E^*} \right).
\]

Due to orbiting [6, 11, 7, 5], the integration must be divided into two parts when the energy is less than $E_C^*$, corresponding to $r_{\ell}^*$, which is the minimum
of the function

\[ y(r^*) = V^*(r^*) + \frac{1}{2} r^{*2} \frac{dV^*(r^*)}{dr^*}. \]  

(72)

\( r'_k \) is the smallest for a specific \( E^* \), corresponding to \( b^* = 0 \). \( r^*_O \) and \( r^*_O' \) are roots of

\[ V^*(r^*) + \frac{b^*2 E^*}{r^{*2}} - E^* = 0. \]  

(73)

When \( E^* \) is larger than \( E^*_C \), \( r^*_O = r^*_O' = r^*_C \). The two integration may be carried out numerically using the CG quadrature rule, and have already been written in class QCG. Note that when orbiting happens, i.e., \(|\chi|\) is large (in the present implement, \(|\chi| > 20\pi\)), it is very difficult to obtain an accurate scattering angle numerically. Following Ref. [5], \( \cos^\ell(\chi) \) is replaced by the average value

\[
\cos^\ell(\chi) = \begin{cases} 
0 & (\ell \text{ is odd}) \\
\frac{(\ell-1)!!}{\ell!!} & (\ell \text{ is even})
\end{cases}
\]  

(74)

To compute \( \Omega^{(\ell,s)\star} \), generalized Gauss–Laguerre (GL) quadrature rule [21] is used, because the formula for \( \Omega^{(\ell,s)\star} \) is in the format of the GL rule, of which the grids and weight are given by an automatic quadrature rule generator [22]. Note that in generalized GL rule, different quadrature grids are used when \( s \) changes. The computed \( \Omega^{(\ell,s)\star}(T\star) \), implemented in OmegaGL, is then called by class AtomPair to obtain \( \Omega^{(\ell,s)}(T) \).

We notice that with our algorithms, the computational wall time is slightly longer than those of Refs. [5, 7, 6]. This is mainly because we did not take the interpolation approximation of \( Q \). In the reference implementations, \( Q \) used by \( \Omega \) is obtained from interpolation. However, we find that this made the final results unstable if transport properties at higher temperature are required, in which case the interpolation pivots may be changed. Of course, this problem can be solved by using a nested interpolation grids with spline, for example. However, we do have more powerful computers now, so direct computation of \( Q \) is affordable. Should the user require such an interpolation, one could embed our QCG class in their implementation of QImpl, or write their own.

All other details are written as inline comments in Peng’s source code, and the HTML format documentation can be generated using Doxygen [23].
Developers can follow these documents should they wish to add new algorithms. Beside the syntax check provided by compilers, we use Valgrind [24] to check that Peng does not suffer from problems from memory leakage or uninitialized variables.

4. End Users’ Guide

4.1. Potential Energy Curves

Firstly, “end users” should still be able to write simple C code, because Peng needs to call user-provided PECs. Due to name mangling, the lite way to employ user-provided PECs is to use a C interface, because it is de facto standard on GNU/Linux.

At least one function providing the value of PEC should be written, of which the signature is (in C)

\[
\text{double value(double r);}\
\]

For a real system, \( r \) should be in Angstrom and the return value in Kelvin.

It is often the case where the analytical derivative of the PEC can be provided. In such a case, also write the function

\[
\text{double derivative(double r);}\
\]

Do not provide an incorrect derivative when knowledge of the derivative is not available. If the program did not find the derivative function, it will compute the numerical derivative instead (see class FuncDeriv1D in the previous section).

The PECs for the three atom pairs should be in three separated files. For example, if we wish to tell Peng that we have a Lennard–Jones Potential, we write the following codes (in file lj.c),

```c
/**
 * File: lj.c
 * Lennard-Jones Potential (12-6)
 */

#include <math.h>

/* Some local cache */
static double rm6 = 0.0;
static double oldr = -1.0;
```
```c
void update_r(double r) {
    if (oldr != r) {
        rm6 = pow(r, -6);
        oldr = r;
    }
}

/* \(V(r) = 4(r^{-12} - r^{-6})\) */
double value(double r) {
    update_r(r);
    return 4 * (rm6 * rm6 - rm6);
}

/* \(V'(r) = 4(-12r^{-13} + 6r^{-7})\) */
double derivative(double r) {
    update_r(r);
    return 4 * (-12 * rm6 * rm6 / r + 6 * rm6 / r);
}

and compile it as a dynamic library

gcc -O3 -Wall -fPIC -shared -o lj.so lj.c

4.2. JSON input file

Other information, alongside the position of the prepared PECs, are written in input files. The input file are in JSON format, which is a popular human-readable format to record multiple types of data. E.g., the JSON file for He and Xe takes the form

```json
{
    "atoms": [
        {
            "name": "He",
            "mass": 4.00260325413
        },
        {
            "name": "Xe",
            "mass": 131.9041550856
        }
    ],
    "potentials": [
        {
            "name": "HeHe",
            "path": ".\hehe.so"
        }
    ]
}
```
The sample JSON file is self-explained, and we list the keys below. If unmentioned keys are written in the input file, e.g., `temperatures.bak` in the sample file, they will not affect the computation, thus, they can be used as comments.

1. **atoms**: Array of the two types of atoms, name is not really used, and mass in atomic mass unit [amu, $\frac{1}{12} m^{(12}C)$].
2. **potentials**: Array of the PECs, in the order of interactions between atoms[0]-atoms[0], atoms[0]-atoms[1], and atoms[1]-atoms[1].
3. **accuracy**: Maximum of allowed integration relative error.
4. **temperatures**: Array of the temperatures at which the properties are computed.
5. **molefractions0**: Array of the mole fractions of atoms[0], and the mole fraction of atoms[1] is computed accordingly.

6. **propertyorder**: The maximum order when compute the transport properties.

Once the JSON input file and the dynamical libraries of the PECs are prepared, The user can run Peng with

```
/path/to/peng.exe < input.json
```

Pre-formatted tables, with heads being elements and their mole fractions, as well as the approximation order of the computation, following with values of the computed results, will be printed to `stdout` with names and units of the results. Intermediate information, will be printed to `stderr`. The user needs a modern terminal support UTF-8 encoding to show the tables because Peng uses some Unicode characters in the unit literals. Users may find examples in the examples directory of the source codes.

**5. Case study: binary mixture of He and Xe**

With Peng, we can easily compute the transport properties from the first principle, which can be compared with experimental data. If the potential energy functions are based on high-level electronic structure theories and reasonable models, then the results should be reliable, and the theory can be used to confirm the experiments. E.g., for the binary mixture of He and Xe, we use three potential energy curves for the pairs He···He[25], Xe···Xe[26], and He···Xe[27]. These three state-of-the-art potential energy curves are very accurate, in which high-order coupled cluster theory are used with large basis sets and relativistic corrections has been made. For intermolecular interactions, the methodology used can provide spectroscopically accurate results. Thus, thermophysical prediction based on these potential energy curves is a very important reference for understanding theoretical data.

Because the masses of He and Xe differ with each other greatly, higher-order approximation of the Chapman–Enskog solution is needed[28] Viscosity of He and Xe mixture is interesting. Experiment[29] showed that the viscosity-temperature curves for mixtures of different mole fraction cross, and theoretical computation can confirm such cross at ∼ 300 K (Fig. 2). Here, we compute the viscosity to the fifth order. The curves converge quickly in general. Noticeably, viscosity for the mixture with mole fraction of He being
0.8687 converges slower than the other two do, $[\mu]_4$ is an accurate approximation (Fig. 3a), while for $x_{\text{He}} = 0.2677$, even $[\mu]_1$ is acceptable (Fig. 3c).

We can also compute the thermal diffusion factor $\alpha_{01}$ based on coefficients for diffusion and thermal diffusion, and compare them with available experimental data. In Fig. 4 the calculated $\alpha$ is is plotted. Interestingly, the $\alpha_{\text{XeHe}}(T)$ function is not monotonic. The calculated curve agrees with the experimental data[30]. However, such agreement is not very satisfactory. Considering the deviation between different experimental works (see Fig. 2 in Ref. [30]), computational data may be more reliable in this case.

We computed the diffusion coefficients to the third order of Sonine polynomial expansion of distribution function, and find that the curve converge uniformly. Also note that to get the curve, high accurate $\Omega$ integrals are needed. In this case, we cannot get a smooth curve unless a threshold of $1 \times 10^{-5}$ for integrals are used.

6. Summary and Outlook

We presented Peng, an extensible C++ library that compute the collision integrals between atom pairs, and transport properties (diffusion, thermal diffusion, thermal conductivity, and viscosity) based on the Chapman–Enskog solution of Boltzmann equation.

When designing the program, extensibility is kept in mind. The main three steps of computing classical collision integrals, angle of deflection $\chi$, cross-section $Q$, and collision integral $\Omega$ can be implemented as concrete class of virtual classes ChiImpl, QImpl, and OmegaImpl. Although we provide usable implementations based on Chebyshev–Gauss and Gauss–Laguerre quadrature rules, however, we will implement more algorithms, and contributions from the community are welcomed. Users can also only use the TransportProperties class to use with their own integration code with minimal effort. Peng gives the user the ability of computing thermophysical properties, and the method developers a platform to test their algorithms.

Of course, the present version of Peng can only compute classical collision integrals, and can only deal with monatomic gas binary mixtures, although these functions are rare in computer programs publicly available. In the future, more functions, e.g., computing quantum collision integrals [1,31], dealing with polyatomic gases [32], and more flexible quadrature rules (including doing the integration on multi-dimension sparse grids) can be added in newer version.
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Conflicts of interest

The authors declare no competing financial interest.

Author contributions

• Y.Z.: Investigation; Methodology; Software; Visualization; Writing - original draft.
• Y.L.: Software;
• H.L.: Supervision; Methodology; Software; Writing - review & editing.
• F.R.W.M.: Supervision; Methodology; Writing - review & editing.

Appendix A. Build Guide

PENG is easy to install. For end users, with a GNU/Linux computer connected to the Internet, simply type

```
make -j
```

in the root of the source code, a Bash script `external/prerequest.sh` will run to download the packages needed by PENG, and build them automatically before compiling PENG. For cases in which there is no Internet access, one needs the following packages

1. fmt ([https://fmt.dev/latest/index.html](https://fmt.dev/latest/index.html)),
2. JSON for modern C++ ([https://json.nlohmann.me/](https://json.nlohmann.me/)),
3. NLOpt ([https://nlopt.readthedocs.io/en/latest/](https://nlopt.readthedocs.io/en/latest/)),
4. Eigen ([https://eigen.tuxfamily.org/](https://eigen.tuxfamily.org/)).
Please find the detailed compiling flags in the shell script.

The code can be compiled with **GCC 12.1.1, Clang 14.0.6**, and **Intel ICC 2021.6.0** on an openSUSE x86_64 computer. It also works on Android (with Termux) and Microsoft Windows (with Windows Subsystem for Linux, WSL).

Appendix B. Mathematical preparations

Readers, especially those who do not familiar with the statistical theory for gases, may find this paper hard to understand because the mathematics. In this section, we will give the definitions of symbols, and some of their properties. We will, however, not provide the proof because of the length of this work.

**Appendix B.1. Scalars, vectors, and tensors**

In this work, following the tradition of [9], we use italic font (a) to represent a scalar, and bold italic font (a) to denote a vector. E.g., velocity \( \mathbf{c} = (u, v, w) \) is a vector, whose \( x, y, \) and \( z \) components are \( u, v, \) and \( w \). So a function \( f \) of \( \mathbf{c} \) would be of \( u, v, \) and \( w \). If we want to get the gradient of \( f \), it would be

\[
\frac{\partial}{\partial \mathbf{c}} f = \left( \frac{\partial f}{\partial u}, \frac{\partial f}{\partial v}, \frac{\partial f}{\partial w} \right). \tag{B.1}
\]

The scalar (inner) product of two vectors are written as \( \mathbf{a} \cdot \mathbf{b} \), which gives a scalar equals the sum of the products of each pair of the components of \( \mathbf{a} \) and \( \mathbf{b} \). The divergence of a function \( f \) can be, therefore, denoted by

\[
\frac{\partial}{\partial \mathbf{c}} f = \frac{\partial f}{\partial u} + \frac{\partial f}{\partial v} + \frac{\partial f}{\partial w}. \tag{B.2}
\]

If the dot does not present, \( \mathbf{a} \mathbf{b} \) is a second order tensor (matrix), which is denoted by bold Sans Serif font (\( \mathbf{w} \))

\[
\mathbf{w} = \mathbf{a} \mathbf{b} = \begin{pmatrix}
a_x b_x & a_x b_y & a_x b_z \\
a_y b_x & a_y b_y & a_y b_z \\
a_z b_x & a_z b_y & a_z b_z
\end{pmatrix} = \begin{pmatrix}
w_{xx} & w_{xy} & w_{xz} \\
w_{yx} & w_{yy} & w_{yz} \\
w_{zx} & w_{zy} & w_{zz}
\end{pmatrix} \tag{B.3}
\]

The divergence of a tensor is the sum of its diagonal elements, it is easy to turn a tensor as non-divergence, and is denoted by \( \overset{\circ}{\mathbf{w}} \)

\[
\overset{\circ}{\mathbf{w}} = \mathbf{w} - \frac{1}{3} (w_{xx} + w_{yy} + w_{zz}) \mathbf{U} \tag{B.4}
\]
for a tensor in $xyz$ space, where $\mathbf{U}$ is the unitary matrix. If the rows and columns of a tensor $\mathbf{w}$ is interchanged, we have the transposed one $\mathbf{\bar{w}}$. The symmetricalized $\mathbf{w}$ is then

$$\mathbf{\bar{w}} = \frac{1}{2}(\mathbf{w} + \mathbf{\bar{w}}).$$

(B.5)

This symbol, can be combined with the non-divergence symbol, as $\nabla \cdot \mathbf{\bar{w}}$.

Simple product of tensors is still a tensor, whose elements are

$$(\mathbf{w} \cdot \mathbf{w}')_{\alpha\beta} = \sum_{\gamma} w_{\alpha\gamma}w'_{\gamma\beta},$$

(B.6)

while the double, or scalar product is

$$\mathbf{w} : \mathbf{w}' = \sum_{\alpha\beta} w_{\alpha\beta}w'_{\beta\alpha}.$$  

(B.7)

Appendix B.2. $\partial_r/\partial t$ in $D^{(r)}$

The $r$-th order partial derivative of a function $F$ is defined using the chain rule

$$\frac{\partial_r F}{\partial t} = \sum_{\lambda \in \{n, c, T\}} \frac{\partial F}{\partial \lambda} \frac{\partial_r \lambda}{\partial t}.$$ 

(B.8)

We define $\partial_r \lambda/\partial t$ as, respectively,

$$\frac{\partial_r n}{\partial t} = \begin{cases} \frac{\partial}{\partial r}.(nc) & (r = 0) \\ 0 & (r > 0) \end{cases},$$

(B.9)

$$\frac{\partial_r c}{\partial t} = \begin{cases} -\left(c \frac{\partial}{\partial r}\right)c + F - \frac{1}{\rho} \frac{\partial}{\partial r} p^{(0)} & (r = 0) \\ -\frac{1}{\rho} \frac{\partial}{\partial r} p^{(r)} & (r > 0) \end{cases},$$

(B.10)

$$\frac{\partial_r T}{\partial t} = \begin{cases} -c \frac{\partial T}{\partial r} - \frac{2}{3k_Bn} \left(p^{(0)} : \frac{\partial}{\partial r} c + \frac{\partial}{\partial r} q^{(0)}\right) & (r = 0) \\ -\frac{2}{3k_Bn} \left(p^{(r)} : \frac{\partial}{\partial r} c + \frac{\partial}{\partial r} q^{(r)}\right) & (r > 0) \end{cases}.$$ 

(B.11)
Appendix B.3. Integrals related to $f^{(0)}$

Again, we write the Maxwellian velocity distribution function, \textit{i.e.}, the distribution function for a uniform and steady gas (Eq. (10))

$$f_i^{(0)} = n_i \left( \frac{m_i}{2\pi k_B T} \right)^{3/2} \exp \left\{ -\frac{m_i (C_i)^2}{2k_B T} \right\}.$$ 

Let $F$, $G$, $H$, $K$, \ldots be functions of velocity (we will label them with subscripts to specify the variable), and we define three kinds of integrals. $I$ is defined as

$$n_0^2 I_0(F) \equiv \iiint f_0^{(0)} f^{(0)} (F_0 + F - F_0' - F_0') gb db d\epsilon dc,$$ 

(B.12)

Clearly, the $I$ integrals are linear with respect to their variables, and note that $I$ is only partly integrated, thus $I_0$ and $I_{01}$ are actually functions of $c_0$, and likewise $I_1$ and $I_{10}$ are of $c_1$.

We can also construct complete integrals. The bracket integral $[F, G]$ are defined as

$$[F, G]_0 = [G, F]_0 \equiv \int G_0 I_0(F) dc_0.$$ 

(B.13)

For $F$ and $H$ are arbitrary function of $c_0$ and $G$ and $K$ are of $c_1$, we define

$$[F_0 + G_1, H_0 + K_1]_{01} \equiv \int F_0 I_{12}(H_0 + K_1) dc_0 + \int G_1 I_{21}(H_0 + K_1) dc_1 = [H_0 + K_1, F_0 + G_1]_{01}.$$ 

(B.14)

For binary mixture, we also use the following compound integral ($F$ and $G$ are both functions of $c_0$ and $c_1$)

$$n^2 \{F, G\} = n^2 \{G, F\}$$

$$\equiv n_0^2 [F, G]_0 + n_0 n_1 [F_0 + F_1, G_0 + G_1]_{01} + n_1^2 [F, G]_1.$$ 

(B.15)

It can be proved that $[F, G]$ and $\{F, G\}$ are linear with respect to the two variables $F$ and $G$. 

30
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Figure 1: The Unified Modeling Language (UML) diagram of PENG. Only the main components of the program are plotted. The extensible ones are colored in light orange.
Figure 2: Viscosity of He and Xe mixture. Red: \( x_{\text{He}} = 0.8687 \), blue: \( x_{\text{He}} = 0.5316 \), and green: \( x_{\text{He}} = 0.2677 \). The lines are computed results of this work and the pluses are measured data from Ref. [29]. Viscosity curves with different approximation are plotted with the same color, so lines of the same color overlap.
Figure 3: Convergence of viscosity of He and Xe mixture. Panel a: $x_{\text{He}} = 0.8687$, panel b: $x_{\text{He}} = 0.5316$, and panel c $x_{\text{He}} = 0.2677$. For different mole fraction, the convergence are different.
Figure 4: Thermal diffusion factor of He and Xe equimolar mixture. Red: first order; blue: second order; and green: third order approximation of $\alpha$. The purple pluses are experimental data from [30].