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Predicting Pressure–Viscosity Behavior from Ambient Viscosity and Compressibility: Challenges and Opportunities

Uma Shantini Ramasamy · Scott Bair ·
Ashlie Martini

Abstract The potential for using an empirical expression to predict the piezoviscous response of a fluid from its pressure–volume behavior is explored. This approach is particularly promising since the variation of volume with pressure can be obtained relatively easily using atomistic simulations that are based on the molecular structure of the fluid. The accuracy of predictions made using the proposed method is evaluated, and its limitations are discussed in terms of sources of error and potential means of minimizing that error going forward.

1 Introduction

Viscosity, a fluid property that describes resistance to shear, is an important characteristic in lubrication. Viscous fluids present between two contacting surfaces, in nature and machines, reduce friction, and increase durability [1]. In hydrodynamic lubrication, viscosity drives the formation of a protective layer of sufficient thickness that separates

U. S. Ramasamy · A. Martini (✉)
School of Engineering, University of California Merced,
Merced, CA, USA
e-mail: amartini@ucmerced.edu

U. S. Ramasamy
e-mail: uramasamy@ucmerced.edu

S. Bair
Center for High-Pressure Rheology, George W. Woodruff
School of Mechanical Engineering, Georgia Institute of
Technology, Atlanta, GA, USA

the roughness of two contacting surfaces [2]. The formation and effectiveness of this layer are highly dependent on the effects of pressure, temperature, and shear rate within the interface on viscosity [3–5]. The increase of viscosity with pressure can significantly affect interface performance, particularly at the high pressures of elastohydrodynamically lubricated interfaces [6] and even in plain bearings. The rate at which a lubricant's viscosity increases with pressure is usually characterized by a pressure–viscosity coefficient, a material-specific constant derived from experimental viscosity data.

The pressure–viscosity response (PVR) of a fluid is a function of its chemical structure and composition [5], so obtaining pressure–viscosity coefficients for real lubricants usually requires highly accurate experiments to be performed for each fluid composition. To address this issue, it is desirable to be able to predict PVR efficiently using models. Such models can be divided into two categories, atomistic and empirical. Atomistic models, such as Molecular Dynamics (MD) simulation, provide explicit representation of molecular structure as well as chemistry and can be used to predict PVR for nanoscale volumes of fluid. Empirical models, on the other hand, are mathematical equations developed from experimental observations that relate PVR to other material-specific properties. As discussed next, there are advantages and disadvantages to each of these approaches and neither approach has been thoroughly validated.

MD simulations explicitly describe the molecular structures of fluids and predict the evolution of those structures over time. The high level of detail available from these simulations provides a means of leveraging the relationship between molecular structure and material properties. Viscosity (and so PVR) can be calculated directly from such simulations using either equilibrium

(EMD) or non-equilibrium (NEMD) methods; however, there are limitations with both approaches. Viscosity predictions through EMD are estimated at zero shear rate from either the Einstein relation or the Green–Kubo equation, both of which require the computation of time correlation functions. The accuracy of these functions depends on the size of the system used [7, 8] as well as the length of the relaxation time [9]. Since size and relaxation time are influenced by structure, computing viscosity using EMD can be prohibitively time intensive [7], particularly for complex lubricants. NEMD viscosity predictions are based on stress–strain relationships and are computed for systems subject to nonzero shear rates. While viscosity converges rapidly at large shear rates, simulations at low shear rates require a much longer simulation time. Due to the time scale limitation of MD in general and long relaxation time of complex molecules [10], NEMD of very large molecules may need to be run at unrealistically large shear rates. There may then be issues with extrapolating these results to lower shear rates since shear thinning can occur at the large shear rates accessible to MD simulations [11] that are not reflected in typical lower shear rate experimental measurements.

The alternative to MD-based approaches for predicting PVR is the use of empirical correlations [12–15]. These correlations are usually derived from experimental observations and enable PVR to be estimated from other material properties such as temperature–viscosity relationships, temperature–density relationships [12], and pressure–density relationships [12, 14, 15]. While these equations are a simpler option, they do not explicitly capture the dependence of PVR on molecular structure. Predictions from some of these models also have large errors [14], particularly if the fluid for which PVR is being predicted is very different from the fluids to which the models were fit. More importantly, these equations rely on experimental material property data, which limits their application for new lubricant mixtures unless prior experimental information is available.

Based on our evaluation of currently available methods, it is clear that there are pros and cons to estimating PVR using either MD simulations or empirical equations. MD simulations have structural precision that capture specific features of fluid molecules, but direct viscosity predictions demand large simulation sizes and long computational time, especially for complex fluids. Empirical models, on the other hand, are usually simple and straightforward mathematical equations, but they rely on experimental data and do not provide any insight on the dependence of molecular structure to pressure–viscosity behavior. To capitalize on the advantages of both methods, it would be beneficial to predict PVR from empirical models using

MD-predicted material properties, eliminating the need for experimental data.

This is the approach explored here. Specifically, we use a recently proposed empirical viscosity correlation to predict piezoviscous behavior from ambient viscosity and pressure–volume data [16]. A key feature of this approach is that the pressure–volume data can be relatively easily obtained from MD simulations, therefore obviating the need for any high-pressure experimental data to predict viscosity. The new method is evaluated in two stages. First, we evaluate the accuracy of the proposed viscosity correlation in terms of its ability to predict piezoviscosity from experimentally measured pressure–volume data. Second, pressure–volume data from MD simulation is used as input into the viscosity correlation to predict pressure–viscosity behavior. The ability of the model to make accurate predictions is found to vary from fluid to fluid. The limitations of the model are analyzed in terms of sources of error, and potential means of minimizing the error are discussed.

2 Methods

2.1 Empirical Model

Recently, a new empirical correlation was proposed that provides a bridge between two very different regimes of pressure–temperature–viscosity behavior for non-associating liquids [16]. These are the low-viscosity regime where the temperature dependence is Arrhenius and the pressure dependence is roughly linear and the high-viscosity regime where the temperature dependence is super-Arrhenius and the pressure dependence is roughly exponential. This correlation is given by [16]

$$\eta = A \exp\left(B\beta_V^q + C\beta_V^Q\right), \quad 0 < q < 1, \quad 1 < Q \qquad (1)$$

where η is viscosity, A, B, C, are various constants, q, Q are power law exponents, and β_V is the normalized Ashurst–Hoover scaling parameter

$$\beta_V = \left(\frac{1}{T}\right)\left(\frac{V_{\text{molec}}}{V}\right)^\gamma \qquad (2)$$

where T is temperature, V_{molec} is the specific volume of a single molecule, V is volume, and γ is the thermodynamic interaction parameter. A, B, C, q, Q and γ are material-specific constants.

V_{molec} is the mass-specific volume of a single molecule which can be obtained either empirically or computationally [16]. Empirical models, such as the Doolittle equation, have been used to derive V_{molec} from fitting to experimental data. This approach is outlined in Ref. [15] where V_{molec} is equivalent to the occupied volume (V_{occ} in Ref.

[15]). From atomistic modeling, V_{molec} can be estimated by dividing the van der Waals volume of one molecule, V_{molec}, by its mass.

Equation 1 represents a complete range of compressed fluid response and creates a master Stickel plot in which the points represent the location of the data rather than a fitted model. In addition, it also has an added advantage of not having singularities, a long standing problem for free-volume formulations in numerical simulations of elasto-hydrodynamic lubrication regimes [16]. Viscosity predictions made using Eq. 1 have been shown to be very accurate for several different liquids, from a refrigerant to a viscous diester [16]. However, the applicability of this method requires prior knowledge of material-specific parameters, thus limiting this approach to fluids with accessible or readily available B, C, q, and Q values.

In this work, we extend the potential utility of the method by assuming that B, C, q, and Q are universal constants for lubricant-like species. We identify values of B, C, q, and Q by fitting Eqs. 1 and 2 to experimentally measured data for squalane and diisodecyl phthalate, two commonly used reference fluids [16]. The parameters derived from fitting are $B = 44.52$, $C = 2.36e7$, $q = 0.094$, $Q = 2.18$ such that Eq. 1 becomes

$$\eta = A \exp\left(44.52\beta_V^{0.094} + 2.36e7\beta_V^{2.18}\right). \tag{3}$$

For a given fluid, we can fit values of the remaining constants, A and γ, using easily measured ambient viscosity and volume. Then, Eq. 3 can be used to predict the piezoviscous response of that fluid from its pressure–volume behavior.

Several different variables have been proposed to capture the PVR of a fluid, including the conventional pressure–viscosity coefficient, α_0, the secant pressure–viscosity coefficient, α_B, Blok's reciprocal asymptotic isoviscous pressure coefficient, α^*, and the modified Blok's coefficient, α_{film} [6, 15]. Here, we use Blok's reciprocal asymptotic isoviscous pressure coefficient, α^* given by [15]

$$\alpha^* = \left[\int_0^\infty \frac{\eta(P=0)dP}{\eta(P)}\right]^{-1} = \left[\frac{\eta_0}{\alpha_N \eta_N} + \sum_{i=1}^N \frac{\eta_0}{\alpha_i}\frac{\eta_i - \eta_{i-1}}{\eta_i \eta_{i-1}}\right]^{-1} \tag{4}$$

where η_i is viscosity at pressure P_i and $\alpha_i = \frac{\ln(\eta_i/\eta_{i-1})}{P_i - P_{i-1}}$. α_N and η_N are the pressure–viscosity coefficient and viscosity at the N-th pressure, respectively.

2.2 MD Simulation

Pressure-dependent volume data can be obtained from MD compressibility simulations. Compared to EMD and NEMD simulations for predicting viscosity, compressibility simulations can be performed with relatively small

model systems and do not depend on relaxation time, enabling them to be performed within relatively short durations. Recently, we developed a simulation method that successfully predicted the compressibility of several model lubricants [17, 18]. We will employ a similar approach here to estimate changes in density with pressure for 9-N-octylheptadecane (TOM) and 1-cyclopentyl-4(3-cyclopentylpropyl) dodecane (CPD).

The molecular structures of TOM and CPD, given in Fig. 1a, and simulation system, Fig. 1b, are constructed with Accelrys Materials Studio©. Subsequent simulations are implemented using Large Atomic/Molecular Massively Parallel Simulation (LAMMPS) software [19]. The system has periodic boundary conditions with initial dimensions of 4.0 nm × 4.0 nm × 4.0 nm. The all-atom optimized potentials for liquid simulations (OPLS-AA) force field [20] with a global cutoff of 1.2 nm is used to describe bond, angle, torsion, and non-bonded interactions between all atoms. A Nosé–Hoover thermostat and barostat are used to control temperature and pressure [21]. All simulations are run with a time step of 0.25 fs and a 1–4 intramolecular van der Waals scaling factor of 0.0. This scaling factor has been shown to increase the accuracy of density predictions for molecules with more than 12 carbon atoms [22].

The simulation cell is equilibrated under NVT (constant number of atoms, volume, and temperature) conditions, where temperature is set at 1,000 K, for approximately 125 ps, followed by NPT (constant number of atoms, pressure, and temperature) conditions, where pressure is set to 1 atm and temperature is kept constant at 300 K, for 5 ns. The initial density of the system is averaged over the last 0.5 ns of the NPT stage. Compression is then imposed on the system, where the dimensions of the simulation box are reduced at a constant engineering strain rate of 0.0001 ns⁻¹ in all three dimensions, to a maximum pressure of 400 MPa. At this strain rate, the x-, y-, and z-dimensions of the box are reduced to a maximum of 4.5 % of their initial length. During this compression process, six different simulation sizes are selected for further analysis. Each compressed system is re-equilibrated under NVT conditions at a temperature of 300 K for an additional 0.5 ns, and average pressure estimations are taken over the last 0.25 ns.

V_{molec}, the specific volume of a single molecule, can also be estimated from the simulations. Here, V_{molec} is estimated using the Connolly Volume Computation method [23] available in the Atom Volumes and Surfaces tool in Materials Studio©. The Connolly Volume Computation method is a geometric computation method that estimates volume-based information using analytical partition calculations [23]. A probe-like sphere scans the molecule to provide volume estimations. Variations in the probe radius provide different volume information, such as van der

Fig. 1 a Fully atomistic structure of TOM and CPD. **b** Cross-sectional view of the initial configuration of the model where the *black line* indicates the periodic boundary. *Colored spheres* represent individual atoms: *orange*—carbon; *green*—hydrogen (Color figure online)

9-N-octylheptadecane (TOM)

1-cyclopentyl-4(3-cyclopentylpropyl) dodecane (CPD)

(a)

(b)
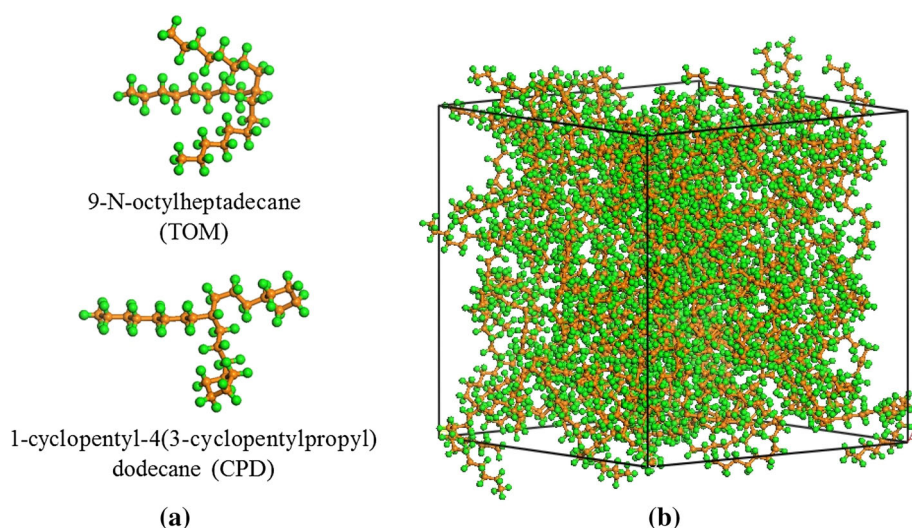
Waals volume, solvent-excluded volume, and interstitial volume [23]. In this work, the probe radius is set to zero and v_{molec} is estimated as the van der Waals volume of a single molecule.

3 Results and Discussion

3.1 Accuracy of the General Correlation

The capability of the general viscosity correlation to make accurate predictions is evaluated for five fluids: di-(2ethylhexyl)-sebacate (DOS), 1-cyclohexyl-3(2-cyclohexyl-ethyl)hendecane (CHH), 9-N-octylheptadecane (TOM), 1-cyclopentyl-4(3-cyclopentylpropyl) dodecane (CPD), and 80W-90. For these molecules, A and γ are estimated from fitting to temperature–viscosity and temperature–volume data (0–120 °C) at atmospheric pressure ($P = 0$ MPa); data for DOS, CHH, TOM, and CPD are available in the 1953 ASME Pressure–Viscosity Report [24] and for 80W-90 in previous technical reports [25, 26] as well as in the "Appendix" of this paper. V_{molec} is estimated from fitting pressure–temperature–volume and pressure–temperature–viscosity data [24–26] to the Doolittle equation [15]. Table 1 lists the parameters in Eqs. 2 and 3, and Table 2 reports the predicted PVR at various temperatures. The predictions for CHH have the largest error, ∼20 % at 0 °C, while predictions for 80W-90 have the smallest error, ∼0.4 % at 50 °C. These results show that although the model predictions are reasonable, the accuracy of the method varies from fluid to fluid and none of the predictions are perfect. The observed error may be due to inaccuracies in the form of Eq. 3, the fit universal constants in that equation, or the value of V_{molec}. These will be discussed further in the next section.

Table 1 V_{molec}, v_{molec}, A, and γ values required to predict PVR for DOS, CHH, TOM, CPD, and 80W-90

Molecule	V_{molec} (cc/g)	v_{molec} (nm^3)	A	γ
DOS	0.6602	0.468	8.257e−12	3.568
CHH	0.8756	0.507	1.257e−11	6.072
TOM	0.7673	0.449	8.257e−12	3.88
CPD	0.7646	0.443	7.471e−12	4.136
80W-90	0.699	-	1.190e−9	4.402

These values are derived from physical measurements of pressure–temperature–volume and pressure–temperature–viscosity data. v_{molec} is calculated by multiplying the fit value of V_{molec} by molecule mass; this is not available for 80W-90 since gear oils are composed of many species of hydrocarbons

3.2 Accuracy of the General Correlation with MD Data

Next, the general viscosity correlation, Eq. 3, is tested using pressure–volume data obtained from MD compressibility simulations of TOM and CPD at 20°C. When a system is compressed, its volume decreases with increasing pressures. Figure 2 shows these expected trends for TOM and CPD predicted by both MD simulations and the experimentally fit [24] Tait equation. V_{molec} is calculated as described in Sect. 2 using the Connolly Volume Computation. Then, using the simulation-predicted V_{molec} and ambient viscosity/volume data from experiment, we refit A and γ. Finally, we can predict PVR using Eq. 3 with the simulation predictions shown in Fig. 2. The results are summarized in Table 3.

The model predictions with the simulation data are less accurate than those predicted by the viscosity correlation with experimental volume data. To understand the observed error, we consider its possible sources, the empirical equation and MD simulations. The contribution

Table 2 Predicted α^* for DOS, CHH, TOM, CPD, and 80W-90 are compared to reported literature values [24, 25] (literature values in parenthesis)

Temperature (°C)	DOS (GPa^{-1})	CHH (GPa^{-1})	TOM (GPa^{-1})	CPD (GPa^{-1})	80W-90 (GPa^{-1})
0	13.94 (17.15)	33.77 (27.97)	15.25 (13.93)	18.88 (19.29)	–
20	–	27.57 (23.80)	12.69 (13.11)	15.93 (16.96)	–
25	11.50 (14.21)	–	–	–	–
30	–	–	–	–	23.82 (23.61)
38	11.26 (12.68)	24.79 (21.21)	11.78 (11.93)	14.48 (15.13)	–
50	–	–	–	–	20.80 (20.88)
80	–	–	–	–	17.48 (17.27)
99	8.48 (8.96)	14.02 (14.48)	9.29 (8.66)	10.33 (10.56)	–
120	–	–	–	–	14.58 (13.98)
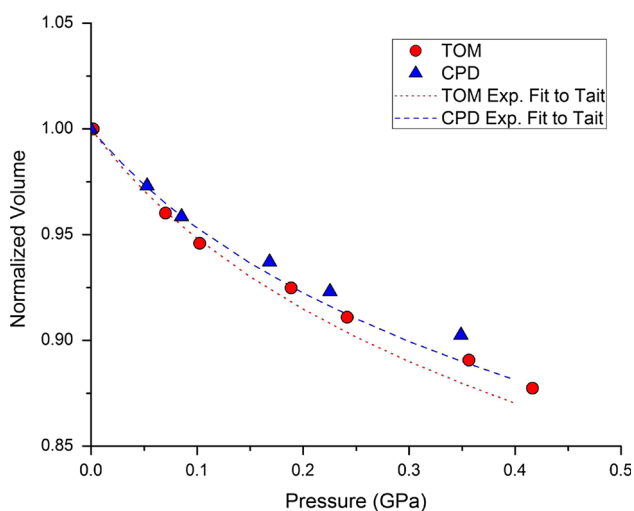
Fig. 2 Normalized volume (normalized by ambient volume) versus pressure plots for TOM and CPD. *Symbols* represent MD data, and the dashed lines represent the Tait equation fit to experimental data [24]

of these to the overall error can be isolated by calculating PVR with various combinations of input data. The results are shown in Table 4.

The best predictions are made, as expected, using the experimental data. As mentioned previously, the error that is observed in these cases is attributable to Eq. 3 itself, the universal constants, or the value of V_{molec} obtained by fitting experimental data to the Doolittle equation. The form of the equation, which combines two exponential power law terms, creates a viscosity master curve and is able to capture the Stickel curve up to high compressions. Additionally, this equation also includes molecular volume

characteristics, V_{molec}, which makes it robust and transferrable to specific molecules [16]. Therefore, this is not expected to be a major source of error. The accuracy of the constants may be improved slightly by fitting them to data from more fluids. However, we have found that the best-fit values of B, C, q, and Q are relatively constant for the different fluids we considered here. Lastly, the molecular volume obtained from a fit to the Doolittle equation. The Doolittle equation is known to be limited in its ability to reproduce experimental accuracy [27]. Therefore, we expect this to be the primary source of error associated with correlating experimental pressure–volume data to PVR.

Introducing MD simulation into the method increases the error in the predicted PVR. This error is attributable to two factors, the molecular volume and pressure–volume data. We compare the pressure–viscosity coefficient predictions made using V_{molec} from MD and P–V from experiment to those made using V_{molec} from experiment and P–V from MD. The results shown in Table 4 indicate that the error in the pressure–volume data is greater for TOM, while the error in the molecular volume is greater for CPD. In both cases, the error associated with the V_{molec} is reasonable in the sense that this value is well known to significantly depend on the details of its calculation, and there is no standard method. In fact, it was shown that molecular volume predictions from several different commonly used software packages (Materials Studio, PcModel, and TSAR) are inconsistent, primarily because of different atomic radii used in the volume computation method [28]. In general, there may be issues with the limited ability of V_{molec} to capture the role of molecular size in resisting intermolecular motion; e.g., the molecular volume of a

Table 3 v_{molec}, V_{molec}, A, γ, and α^* values predicted by MD for TOM and CPD at 20 °C. α^* predictions are compared to the reported literature values [24]

Molecule	v_{molec} (nm^3)	V_{molec} (cc/g)	A	γ	α^*_{MD} (GPa^{-1})	$\alpha^*_{Lit.}$ (GPa^{-1})
TOM	0.440	0.7520	7.471e−12	3.690	11.44	13.11
CPD	0.417	0.7203	5.425e−12	3.530	12.71	16.96

Table 4 Predicted α^* and the resulting error in those predictions for TOM and CPD using P–V (20 °C) and V_{molec} from either experiment or MD simulation

Molecule	V_{molec}	P–V	α^* (GPa^{-1})	$\alpha^*_{Lit.}$ (GPa^{-1}) [24]	Error (%)
TOM	Exp	Exp	12.69	13.11	3.2
	MD	Exp	12.2		6.9
	Exp	MD	11.92		9.1
	MD	MD	11.44		12.7
CPD	Exp	Exp	15.93	16.96	6.1
	Exp	MD	14.63		13.7
	MD	Exp	13.75		19
	MD	MD	12.71		25.1

ringed structure may exclude the volume in the center of the ring, but that volume is not available for neighboring molecules to occupy.

This error associated with the pressure–volume predictions may be due to limitations of the empirical potential that describes the atomic interactions and behavior of bonds. The empirical model used here, OPLS, is parameterized (fit to experimental data or first principles calculations) under ambient conditions [20]. This can limit its ability to accurately predict the conformation of molecules under high pressures. Going forward, this may be addressed by identifying alternative empirical models tuned for pressurized systems or fitting such a model specifically for this purpose.

4 Conclusions

This paper presented a method to predict PVR from empirical models using MD-predicted material properties. Specifically, we used a recently proposed empirical viscosity correlation to predict pressure–viscosity behavior from ambient viscosity and pressure–volume data. The method takes advantage of the molecular-scale features of MD simulation and the ability of empirical models to relate PVR to properties easily accessible using MD. The accuracy of the proposed method was evaluated with experimentally-measured and MD-derived volume data. The errors observed as well as the limitations of the method were then discussed.

It is clear that further work is necessary to enable this method to be used in practice. Further, since the analysis reported here was performed for simple fluids, additional challenges may arise if the method is applied to more complex lubricant molecules (e.g., those with polar interactions). Regardless, the approach presented in this study, which combines MD simulation with empirical models, holds significant promise. If the method can accurately

predict PVR and pressure–viscosity coefficients for known lubricants, it could then be applied to make predictions for molecules with new or novel chemical structures, therefore enabling molecular-scale lubricant design. Further, the proposed approach suggests a means of fundamentally understanding the relationship between a fluid's molecular structure and its pressure–viscosity behavior.

Appendix

See Tables 5 and 6.

Table 5 Viscosity (mPa s) for 80W-90 [25]

Pressure (MPa)	Temperature (°C)			
	30	50	80	120
0	232	73.7	20.08	6.98
50	797	224	52.6	15.51
100	2,372	594	117.2	30.2
150	6,838	1,417	240	55.2
250	48,661	7,520	928	158.1
500		375,318	22,072	1,839
750		Solid	407,406	14,792
1,000			8,283,860	123,772
1,200				678,516

Table 6 Calculated relative volume for 80W-90 [26]

Pressure (MPa)	Temperature (°C)			
	30	50	80	120
0	0.9856	1	1.0216	1.0503
50	0.9600	0.9718	0.9890	1.0110
100	0.9404	0.9506	0.9652	0.9836
150	0.9245	0.9336	0.9466	0.9627
250	0.8996	0.9073	0.9182	0.9315
500	0.8578	0.8637	0.8720	0.8819
750	0.8300	0.8350	0.8419	0.8501
1,000	0.8091	0.8135	0.8196	0.8267
1,200	0.7954	0.7995	0.8051	0.8115

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