IOPscience

This content has been downloaded from IOPscience. Please scroll down to see the full text.

Download details:

IP Address: 93.80.122.29 This content was downloaded on 25/09/2015 at 09:25

Please note that terms and conditions apply.

Advances in Thermodynamics of the van der Waals Fluid

Advances in Thermodynamics of the van der Waals Fluid

David C Johnston

Department of Physics and Astronomy, and Ames Laboratory Iowa State University, Ames, IA 50011, USA

Morgan & Claypool Publishers

Copyright © 2014 Morgan & Claypool Publishers

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publisher, or as expressly permitted by law or under terms agreed with the appropriate rights organization. Multiple copying is permitted in accordance with the terms of licences issued by the Copyright Licensing Agency, the Copyright Clearance Centre and other reproduction rights organisations.

Rights & Permissions

To obtain permission to re-use copyrighted material from Morgan & Claypool Publishers, please contact info@morganclaypool.com.

ISBN 978-1-627-05532-1 (ebook) ISBN 978-1-627-05531-4 (print)

DOI 10.1088/978-1-627-05532-1

Version: 20140901

IOP Concise Physics ISSN 2053-2571 (online) ISSN 2054-7307 (print)

A Morgan & Claypool publication as part of IOP Concise Physics Published by Morgan & Claypool Publishers, 40 Oak Drive, San Rafael, CA, 94903, USA

IOP Publishing, Temple Circus, Temple Way, Bristol BS1 6HG, UK

Contents

Preface Author biography		viii
		ix
1	Introduction	1-1
•	Pafarancas	1.4
	Kelefelikes	1-4
2	Background and nomenclature: the ideal gas	2-1
	References	2-3
3	van der Waals intermolecular interaction parameters	3-1
4	Thermodynamic variables and properties in terms of the	4-1
	van der Waals interaction parameters	
4.1	Helmholtz free energy	4-1
4.2	Critical pressure, temperature and volume	4-2
4.3	Entropy, internal energy and heat capacity at constant volume	4-5
4.4	Pressure and enthalpy	4-6
4.5	Chemical potential	4-7
	Reference	4-7
5	van der Waals equation of state, reduced variables and	5-1
	laws of corresponding states	
5.1	van der Waals equation of state and reduced variables	5-1
5.2	Laws of corresponding states	5-2
5.3	Pressure versus volume and versus density isotherms	5-2
5.4	Influence of the van der Waals interactions on the pressure of the gas phase	5-3
5.5	Boyle temperature	5-7
5.6	Thermodynamic properties expressed in reduced variables	5-7
	5.6.1 Internal energy	5-7
	5.6.2 Helmholtz free energy	5-8
	5.6.3 Entropy and enthalpy	5-8
	5.6.4 Isothermal compressibility	5-9

	5.6.5 Volume thermal expansion coefficient	5-10
	5.6.6 Heat capacity at constant pressure	5-11
	5.6.7 Chemical potential	5-12
	References	5-13
6	Equilibrium pressure-volume, temperature-volume and	6-1
	pressure-temperature phase diagrams	
6.1	Pressure-volume phase diagram and Maxwell construction	6-4
6.2	Volume-temperature phase diagram	6-7
6.3	Lever rule	6-7
6.4	Pressure-temperature phase diagram	6-10
	References	6-11
7	Lekner's parametric solution of the coexistence curve and	7-1
	associated properties	
7.1	Thermodynamic behaviors on approaching the critical temperature from below	7-4
7.2	Thermodynamic behaviors for temperatures approaching zero	7-6
7.3	Coexisting liquid and gas densities, transition order parameter and temperature-density phase diagram	7-8
7.4	Latent heat and entropy of vaporization	7-10
7.5	Heat capacity at constant volume versus temperature within the liquid–gas coexistence region along an isochoric path	7-13
	References	7-18
8	Static critical exponents	8-1
8.1	Heat capacity at constant volume	8-3
8.2	Pressure versus volume isotherm at the critical temperature	8-3
8.3	Critical chemical potential isotherm versus number density	8-3
8.4	Liquid-gas transition order parameter	8-4
8.5	Isothermal compressibility	8-6
	8.5.1 Approach to the critical point along the critical isochore from above the critical temperature	8-6
	8.5.2 Approach to the critical point along either boundary of the gas-liquid coexistence region for temperatures below the critical temperature	8-6

8.6	Approach to the critical point along the critical isobar	8-7
	8.6.1 Isothermal compressibility	8-8
	8.6.2 Volume thermal expansion coefficient	8-8
	8.6.3 Heat capacity at constant pressure	8-8
	References	8-9
9	Superheating and supercooling	9-1
	References	9-3
10	Additional numerical calculations of thermodynamic properties	10-1
10.1	Isotherms versus density in the supercritical temperature region	10-1
10.2	Isobars versus temperature	10-5
	10.2.1 Results for pressures above the critical pressure	10-5
	10.2.2 Pseudocritical curves and the Widom line in the supercritical region	10-8
	10.2.3 Results for pressures less than the critical pressure	10-13
	References	10-16
11	Adiabatic free expansion and Joule–Thomson expansion	11-1
11.1	Adiabatic free expansion	11-1
11.2	Joule–Thomson expansion	11-3
	References	11-6
Арр	endices	
A	Tables of values	A-1
	Reference	A-11
B	Formulas for the discontinuities in isothermal	B-1
	compressibility, thermal expansion and heat capacity	
	versus temperature at constant pressure on crossing the	
	liquid-gas coexistence curve	
С	Formula for the heat capacity at constant volume in the	C-1
	coexistence region along the critical isochore	

Preface

This book evolved out of a course on thermodynamics and statistical mechanics that I taught at Iowa State University. One of the topics covered was phase transitions, and one of the types of phase transitions covered was the first-order liquid to gas transition described by the van der Waals mean-field theory of fluids. This theory was formulated by van der Waals in 1873 and, augmented by Maxwell in 1875, is the first theory that predicts a phase transition from interactions between particles. However, the thermodynamic properties of fluids (gases or liquids) derived from the van der Waals equation of state and free energy have not been thoroughly studied previously.

This book is a comprehensive exposition of the thermodynamic properties of the van der Waals fluid, which includes a review of past work together with presentation of my own recent extensive studies. The main goal of the book is to provide a graphical overview of the many interesting and diverse thermodynamic properties of the van der Waals fluid through plots of these properties versus various independent parameters. The data for these plots are obtained from formulas derived herein, some of which have previously appeared in the literature. Many results not amenable to graphical illustration are also included.

I hope that this book will be useful to instructors as a teaching resource and to students as a text supplement for thermodynamics and statistical mechanics courses as well as to others who are interested in the thermodynamics of the seminal van der Waals fluid.

> David C Johnston Ames, IA May 27, 2014

Author biography

Dr David C Johnston

Dr David C Johnston is a Distinguished Professor in the Department of Physics and Astronomy of Iowa State University in Ames, Iowa. He received his BA and PhD degrees in Physics from the University of California at Santa Barbara and the University of California at San Diego, respectively. Prior to joining Iowa State University, he carried out research at the Corporate Research Laboratories of Exxon Research and Engineering Company in Annandale, NJ. His research area is experimental solid state physics, with an emphasis on the measurement and theoretical modeling of the electronic, magnetic, thermal and superconducting properties of solids. He is a Fellow of the American Physical Society and a former Divisional Associate Editor of the journal *Physical Review Letters*.