Generalized Van der Waals Equation forLiquid-Vapor Equilibria in a Stationary GravitationalField

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Abstract

ThebehaviorofliquidsundergoingphasetransitioninthegravitationalfieldisstudiedbyconsideringthegeneralizedVanderWaalsequation.Consideringthetwosimplemodelsforliquid-vaporboundaryofapureclassicalfluid,thegeneralizedVanderWaalsequationshowshowthethreecriticalparameters(criticaltemperature,criticalvolumeandcriticalpressure),sufficetodescribe the reduced state parameters (reduced temperature, reduced volumeand reduced pressure), the concentration profile and the liquid-vapor boun-dary position, which can be used to observe transition phenomenon. Thismodel shows how the form of the equation can influence the vertical phaseseparation induced by the stationary gravitational field, and on the gas con-densationeffects.

Keywords

Liquid-Vapor,PhaseTransition,GravitationalField,ClassicalFluid,ConcentrationProfile

1. Introduction

Inrecentyears,manypiecesofresearchhavebeenmadeinordertoinvestigatetheeffectofuniformandnon-uniformgravitationalfieldsontheperfectgas[1][2]. That is, in order to bring out more about the field, the phase transition remainsthemostimportantandfundamentalfeatureinthermodynamicswhichisconsideredasalinkbetweentheliquidandvapor.Towardstheendofthelast century when the extensive studies of Andrew [3] used the Van der Waals equation[4] to explain the influence of temperature and pressure on fluid’s density.Thus thefirst theoreticaldescription of the vapor-liquidphase transition withVan der Waals equation of State was available. The Van der Waals equation ofstate is useful in theschemeof generalization of thestudyby consideringa realgas [5] [6] [7]. A generalization of this problem is the consideration of a real gas.In Refs [8] it has shown how the interesting features of a real gas and the possi-bility of condensation due to the existence of liquid-vapor equilibrium. Other-wise, the problem of classical liquid-vapor equilibrium has been intensively in-vestigated in the presence of a gravitational field by using a Van der Waals equa-tion ofstateespecially imposing conditionof equilibriumfor a certain pressureattheinterface,thevaporpressure$p$,thatfortheincompressibleliquid.Thecriticalpointischaracterizedbyfixedtemperature,pressureanddensityandal-so is an example of a continuous phase transition in the case of the vapor-liquidsystem [9]. It is so, because the vapor-liquid critical point is one of the manycritical points associated with transitions where density (as one of its specificthermodynamicproperties)changescontinuouslyinthecourseoftransition.Thisapproachwhichisvalidfortemperaturesmuchlowerthanthecriticaltemperatureofthesubstanceremainslessgeneral.

Theinfluenceoftheconstantgravitationalfieldontheliquid-vaporequilibrium for a pure substance has been investigated and pictured as in **Figure1**,where the parameters of the cell that will be used in the calculations are also de-fined. This pictured shows implicitly the effect of the existing constant gravita-tional field it is like on earth and how the denser liquid phase becomes located inthe lowerpart of the container[10] [11]. It has been alsofound in Ref [10]thatthe absence of gravity assuming thermal equilibrium, and the liquid assumes asphericalshapebyminimizingthesurfaceenergysurroundedbythevapor.

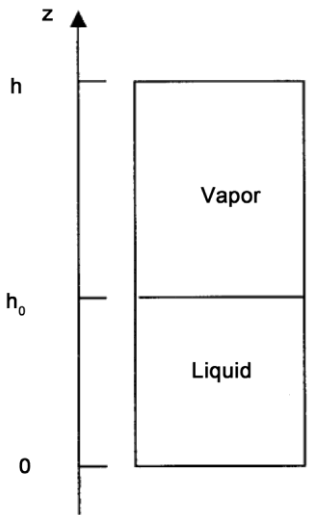

Figure1. Thecellforthestudyof liquid-vaporequilibrium.Thecellheightis$h$,andtheliquid-vaporboundaryisath_0[1].

Followingtheworkdonein[1],wheretheeffectofgravityontheexistenceand position of the liquid-vapor boundary of a pure substance is quantitativelydiscussed on the basis of two simple models: a perfect gas and incompressibleliquid model, and a Van der Waals fluid model, the model has been extended inthis paper by considering the generalized Van der Waals equation on the existenceandpositionoftheliquid-vaporboundaryofapuresubstance,usedinor-der to find the effect of gravity on a pure substance. That is, we verify the beha-vior of a liquid-vaporboundary in the stationary gravitational fieldwith empha-sis on the reduced parameters such as reduced pressure, reduced molar concen-trationand reducedtemperature.

The approach used here is holistic in the sense that they involve all parametersofthesystemunderconsideration.

The organization of the paper is as follows: In Section 2, we present a briefdescription of the simple modelthat is the perfect gas andthe incompressibleliquid for simulation of theeffectof the constantgravitationalfield on thepuregassystem.InSection3,thegeneralizedVanderWallsequationisusedinordertoevaluatethereducedsaturatedpressure,thereducedtemperatureintermsofthe reducedliquidandgas concentrations then conclude ourfindings inSection4 where the theoreticalresults,as wellas the numericalresults anddiscussion,aretreatedinordertoconcludeinSection5.

2. Theoretical Study of the Perfect Gas and IncompressibleLiquidintheConstantGravitationalField

Weconsideredrespectivelyavapor-liquidasthesubstanceinasmallcontainerandinthetallcontainer,inordertoputoutinourinvestigation,theinfluenceofenvironment.

2.1. EnvironmentasSmallContainer

Figure1here represents themodelof container(whichis a sealedcylindricalglass tube containing a given amount of a fluid, for example (H_2O, CO_2 or plasma)usedforourinvestigation.Consideringacontainerofvolume Vcontainingasubstanceofmass,$m$thatisusedtodeterminethepositionoftheliquidvapor interface, h_0,foragiventemperature.Iftheheightofthetube(container)is$h$, $V_G$andV_L thevolumesoccupiedbythegasandliquidphases,respectively, thentheliquid-vaporinterfacewillbelocatedataheight,

$$h_0=f_L h \tag{1}$$

wheref_L isthevolumefractionoftheliquid.

$$f_L=V_L/V=\frac{\bar{\rho}-\rho_G}{\rho_L-\rho_G} \tag{2}$$

withρ_L andρ_G thephasemassdensitiesobtainedfromthegivenrelationof themass

$$m_L=\rho_L V_L=m-m_G=m-\rho_G\left(V-V_L\right) \tag{3}$$

and $\bar{\rho}=m/V$ theaveragedensityofthesubstanceinthecell.Foraperfectgas phase,thevapormassdensityisgivenby

$$\rho_G=\rho_{sat}=MP_{sat}/RT \tag{4}$$

where$M$ is the molar mass P_{sat} isthevapor pressureatthegiventemper-andature$T$.

2.2. EnvironmentasaTallContainer

Here,theheightofthecontainerislarge,thegasphasewillbeinhomogeneous,thatis, thepressurewill obeythebarometric formula

$$P(u)=P_{sat}\exp(-Mgu/RT) \tag{5}$$

where$g$istheaccelerationofgravity,and $u=z-h_0$ theheightabovetheliq-uid-vaporboundary.Hence,thegasdensityinEquation(4)becomes

$$\rho_G(u)=\rho_{sat}\exp(-Mgu/RT), \tag{6}$$

where ρ_{sat} isgivenby

$$\rho_{sat}=MP_{sat}/RT \tag{7}$$

UsingEquations(5),(6)and(7),theaveragegasdensityinEquation(4)canbeevaluated as

$$\rho_G=\frac{\int_{h_0}^{h}\rho_G(z)\mathrm{d}z}{h-h_0}=\frac{P_{sat}}{g(h-h_0)}\left[1-\exp\left(-\frac{mg(h-h_0)}{RT}\right)\right] \tag{8}$$

andhenceEquation(1)becomes

$$h_0=\frac{\bar{\rho}-\frac{P_{sat}}{g(h-h_0)}\left[1-\exp\left(-\frac{Mg(h-h_0)}{RT}\right)\right]}{\rho_L-\frac{P_{sat}}{g(h-h_0)}\left[1-\exp\left(-\frac{Mg(h-h_0)}{RT}\right)\right]} \tag{9}$$

Forlarge $h(h-h_0\to\infty)$,Equation (9)simplifies to

$$h_0=\frac{P_0-P_{sat}}{g\rho_L} \tag{10}$$

where $P_0=\bar{\rho}g h$ isthepressureatthebottomofthecell(Thatis,atz=0).

An interestingapplicationofEquation(10)istheestimation of the effectofchangeintheearth'saveragetemperatureontheoceanlevel.FromEquation (10)wehave

$$\Delta h_0=-\Delta P_{sat}/g\rho_L \tag{11}$$

As it has also been shown in [1], for pure liquid water and an initial uniformtemperature of 15˚C,an increase of 1˚C implies a drop of1 cm in the water lev-el, while upon heating to 50˚C, 100˚C,and374˚C (just below the criticalpoint)the water level is predicted to decrease, by 1 m, 10 m and 2.2 km, respectively.These calculations show that the loss of liquid water upon moderate heating isnegligibleincomparisontothepredictedincreaseduetothemeltingofallthe

Earths’permanentice(intheformofglaciers,icecaps,andGreenlandandAntarcticicesheets),whichwouldcauseanestimatedincreaseoftheaveragelevelof70m .

Adifferentwayofchanging$h_0$isbymodifyingtheaccelerationofgravity, forexamplebymeansofacentrifuge.Asampleinitiallyat $g=0$ canbeentirelygaseous,whileonceitissubjectedtoagravitationalfield,aliquidphasemayappearforextremelystronggravitationalfieldsfurtherphasesmightshowup, suchasoneormoresolidphases.Theliquidphasestartstoformwhen$g=g_{\min}$ islargeenoughthatthepressureatthebottomofthecontainer, $P(0)$equals thesaturationpressure P_{sat}.Takingintoaccountthat,intheabsenceofagravitationalfield,thepressure,P,anddensity, ρforanidealgasarerelatedby Equation(5)weobtainfromEquation(9)anequationfor$P$and $g_{\min}$.

$$P=P_{sat}\frac{RT}{Mg_{\min}h}\left[1-\exp\left(-Mg_{\min}h/RT\right)\right] \tag{12}$$

Forinstance,tostartcondensingwatervaporina $h=10\mathrm{cm}$ cellinitiallyata pressureof$0.8P_{sat}$ andatroomtemperature, $g_{\min}=5\times10\mathrm{m}\cdot\mathrm{s}^{-2}$.

Ifthecontainerisessentiallyinfinite$(h\rightarrow\infty)$ butthemassofthegasisfinite,thenEquation(12)simplifiesto

$$g_{\min}=P_{sat}/\bar{\rho}h \tag{13}$$

Wenoticethat $g_{\min}$ isproportionaltothe $1/\bar{\rho}$,where $\bar{\rho}$istheaverage densityofthegasinsidethecellfor$g=0$.FortheamountofwaterontheEarth, $\bar{\rho}h\cong3\times10^{6}\mathrm{kg}\cdot\mathrm{m}^{-2}$andusing $P_{sat}(15\square\mathrm{C})=1.7\times10^{3}\mathrm{Pa}$,onegets$g_{\min}=6\times10^{-4}\mathrm{m}\cdot\mathrm{s}^{-2}\square9.8\mathrm{m}\cdot\mathrm{s}^{-2}=g_{\mathrm{Earth}}$

3. GeneralizedVanderWaalsEquation

Matter irrespective of the state at which it is found is stable only over a certainrange of temperatures and pressures. That is, it can move to another phase underequilibriumconditions,wheretheboundariesinthephasediagramdelineatethis behavior. The three different phases of matter can coexist in equilibriumonly at the “triple point”. Elsewhere only two phases can coexist *i.e.* Solid andLiquidalongthefusioncurveorLiquidandVaporalongthevaporizationcurve.Butthevaporizationcurveterminatesabruptlyatthecriticalpoint.Atthispoint,thetemperature,pressure,andmolarvolumeassumecharacteristicvaluesTc,PcandVcforany givensubstance.

The generalized Van der Waals equation can be obtained respectively in termsofvolumeEquation(14)andmolarconcentrationEquation(15)as

$$\left(P+\frac{a}{v^{n}}\right)(v-b)=RT \tag{14}$$

$$p=\frac{RT}{1/C-b}-aC^{n} \tag{15}$$

where$P$isthepressure,$v$isthemolarvolume.$a$and$b$aretwodifferentparameterscharacteristicsofeachsubstance.Theparameter$a$reflectsthelong-range attractive interactions (Van der Waals forces) while the parameter b reflects the short-range repulsive ones.

The Van der Waals equation is a cubic equation in the volume, which means that it has three solutions for a given pressure if the temperature, T, is less than the critical temperature T_c. The solutions of are the molar volume of the liquid, while the third molar volume (the third root) lying between these two has no physical meaning. If $T > T_c$ only one of these roots is real, while if $T = T_c$ the three roots merge into one. The parameters a and b can be related to the critical pressure P_c, the critical molar volume, v_c and the critical temperature, T_c, Obtained by the following relations:

$$\frac{\partial P}{\partial V} = 0$$

$$\frac{\partial^2 P}{\partial V^2} = 0$$

$$T_C = \frac{4an(n-1)^{n-1}}{K_B b^{n-1}(n+1)^{n+1}}, \quad V_C = \frac{(n+1)b}{n-1}, \quad P_C = \frac{a(n-1)^{n+1}}{b^n(n+1)^{n+1}}$$

4. Phase Transition Parameters

4.1. Theoretical Results

In order to determine the phase transition parameters using Van der Waals equation, the hydrostatic equation has to be considered. In a gravitational field, the pressure of a fluid (gas or liquid) within a vertical cell depends on the height, h_0 obeys the balance equation,

$$\frac{\mathrm{d}}{\mathrm{d}z} P(z) = -mgC(z) \tag{16}$$

To determine reduced parameters that would help to observed phase transition, we then combine Equations (15) and (16) to obtain a generalized barometric formula in the following differential form:

$$\frac{\mathrm{d}}{\mathrm{d}z} C(z) = -\frac{MgC(z)}{RT/[1-bC]^2 - naC(z)^{n-1}} \tag{17}$$

If we have assumed that the temperature is constant inside the cell and by introducing the new dimensionless variables that is the reduced gravitational energy $E_r = Mgz\left(RT_c\right)$, the reduced concentration $C_r = cv_c$, the reduced pressure $p_r = p/p_c$ and the reduced temperature $T_r = T/T_c$, in Equation (17), Equation (15) becomes

$$p_r = \frac{4nT_r}{(n-1)^2\left[\left(\frac{n+1}{n-1}\frac{1}{c}\right) - 1\right]} - \left(\frac{n+1}{n-1}\right)c^n \tag{18}$$

The concentration profile is also obtained as

$$\frac{\mathrm{d}c}{\mathrm{d}E_r} = -\frac{c}{\left(1-\frac{n-1}{n+1}\right)^2 c - \frac{(n+1)^2}{4} c^{n-1}} \tag{19}$$

Equation(19)showsthatthereducedconcentrationprofileisafunctiononlyofthereducedtemperature.Itisassumedthattheboundarybetweenthetwo phasesisattheheight $z=h_0$,sothattheliquidinthecellisbetween $0<z\leq h_0$ and the gas isatz□h_0.

In respect of the condition that the two phases are in equilibrium when theirpressures and chemical potentials are equal, from Equation (18) the followingequationsthatdescribethesaturationpressurefortheliquidandgaseousphasesrespectively:

$$p_r^{sat}=\frac{4nT_r}{(n-1)^2\left[\left(\frac{n+1}{n-1}\right)\frac{1}{c_L^*}+1\right]}-\left(\frac{n+1}{n-1}\right)c_L^{*n} \qquad (20a)$$

$$p_r^{sat}=\frac{4nT_r}{(n-1)^2\left[\left(\frac{n+1}{n-1}\right)\frac{1}{c_G^*}+1\right]}-\left(\frac{n+1}{n-1}\right)c_G^{*n} \qquad (20b)$$

where c_L^* and c_G^* arethereducedliquidandgasconcentrationatthegas–liquid boundary,$z=h_0$.

In order now to express the reduce pressure and the reduce temperature onlyas a function of the reduce molar concentration, we used Maxwell equal areaapproach.

$$p_r^{sat}\left(v_G-v_L\right)=RT\ln\left(\frac{v_G-b}{v_L-b}\right)-\frac{a}{1-n}\left(v_G^{1-n}-v_L^{1-n}\right) \qquad (21)$$

whereV_L andV_G arethemolarvolumesintheliquidandgasstatesat $z=h_0$,with$v_L=\left(\frac{n+1}{n-1}\right)bc^*/_L$ and $v_G=\left(\frac{n+1}{n-1}\right)b\ c^*./_G$

Inreducedvariables,Equation(21)canberewriteintheform:

$$4nT_r\ln\left(\frac{\left(\frac{n+1}{n-1}\right)\frac{1}{c_G}-1}{\left(\frac{n+1}{n-1}\right)\frac{1}{c_L}-1}\right)+(n+1)\left(c_G^{n-1}-c_L^{n-1}\right)=\left(n^2-1\right)p_{sat,r}\left(\frac{1}{c_G}-\frac{1}{c_L}\right) \qquad (22)$$

IfwecombineEquation(22)withEquation(20),weobtain

$$\ln\left(\frac{\left(\frac{n+1}{n-1}\right)\frac{1}{c_G}-1}{\left(\frac{n+1}{n-1}\right)\frac{1}{c_L}-1}\right)=\frac{\left(c_L-c_G\right)}{\left(c_L+c_G\right)}\left(\frac{n+1}{\left[(n+1)-(n-1)c_L\right]}+\frac{n+1}{\left[(n+1)-(n-1)c_G\right]}\right) \qquad (23)$$

Fromthesamesetofequations,thereducedsaturationpressureandthereducedtemperaturegives

$$p_r^{sat}=\frac{c_G^*c_L^*\left(c_L^{*n-1}-c_G^{*n-1}\right)\left[(n+1)-(n-1)\left(c_L^*+c_G^*\right)\right]}{(n-1)\left(c_L^*-c_G^*\right)} \qquad (24)$$

and

$$T_r = \frac{\left(c_L^{*n} - c_G^{*n}\right)\left[(n+1)-(n-1)c_L^*\right]\left[(n+1)-(n-1)c_G^*\right]}{4n\left(c_L^* - c_G^*\right)} \quad (25)$$

4.2. NumericalResultsandDiscussions

4.2.1. PhaseTransitionObservationinTermsofReducedPressure

FromEquation(18)theobtainedreducedpressureasafunctionofreducedtemperature is numerically investigated (see **Figure 2**) in order to show how thegeneralized form of the Van der Waals equation can be used to easy control phasetransition.

Figure2reducedpressureasafunctionofreducedmolarvolumefractionof waterisshownforatubeof10cmheightandfor $g=9.8\text{m}\cdot\text{s}^{-2}$ asituationthat corresponds to a top reduced gravitational energy. The behavior of the curvesshowsthatthereducedpressureincreaseswithanincreaseinreducedmolarvolume until the corresponding critical point($P_c=$ 0.63) after thatit decreasesprogressivelytotheinfinity.ThecriticalpointthatcorrespondsthephasetransitionpointisobservedatthereducedtemperaturevalueT_r =0.9.Itisthenobservedthatthedashedcurvesforvaporandthegreencontinuouslineforliquid showandintersectionpointatacertainreducedtemperaturevalue $T_r=0.9$ which a point of transition respectively from vapor to liquid and from liquid tovapor.Theintersectionpointcharacterizesthesupercriticalpointoftransitionafterwhichthenatureofthesubstancechanges totallytoanother.

4.2.2. PhaseTransitionObservationinTermsofReducedConcentration

Figure3presentsthereducedconcentrationasafunctionofreducedtemperatureandHeightintheconditionthatred $g=9.8\text{m}\cdot\text{s}^{-2}$ thatcorrespondstothetop ucedgravitationalenergy.

From**Figures 3(a)-(c)**,itisobservedthatthesubstancechangesprogressivelyfor its vapor nature to the liquid nature as the reduced temperature and theheight increases. The total transition of the vapor substance to the liquid substancecorrespondstothesupercriticalpoint.

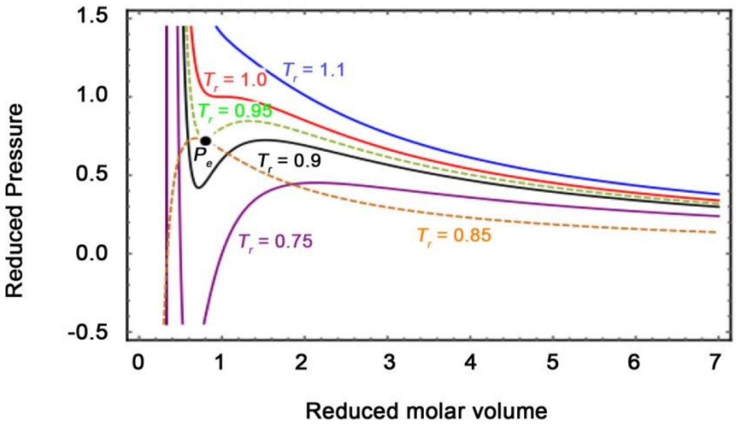

Figure2. Reducedpressureasafunctionofreducedmolarvolume,fordifferentvaluesofreducedtemperature.

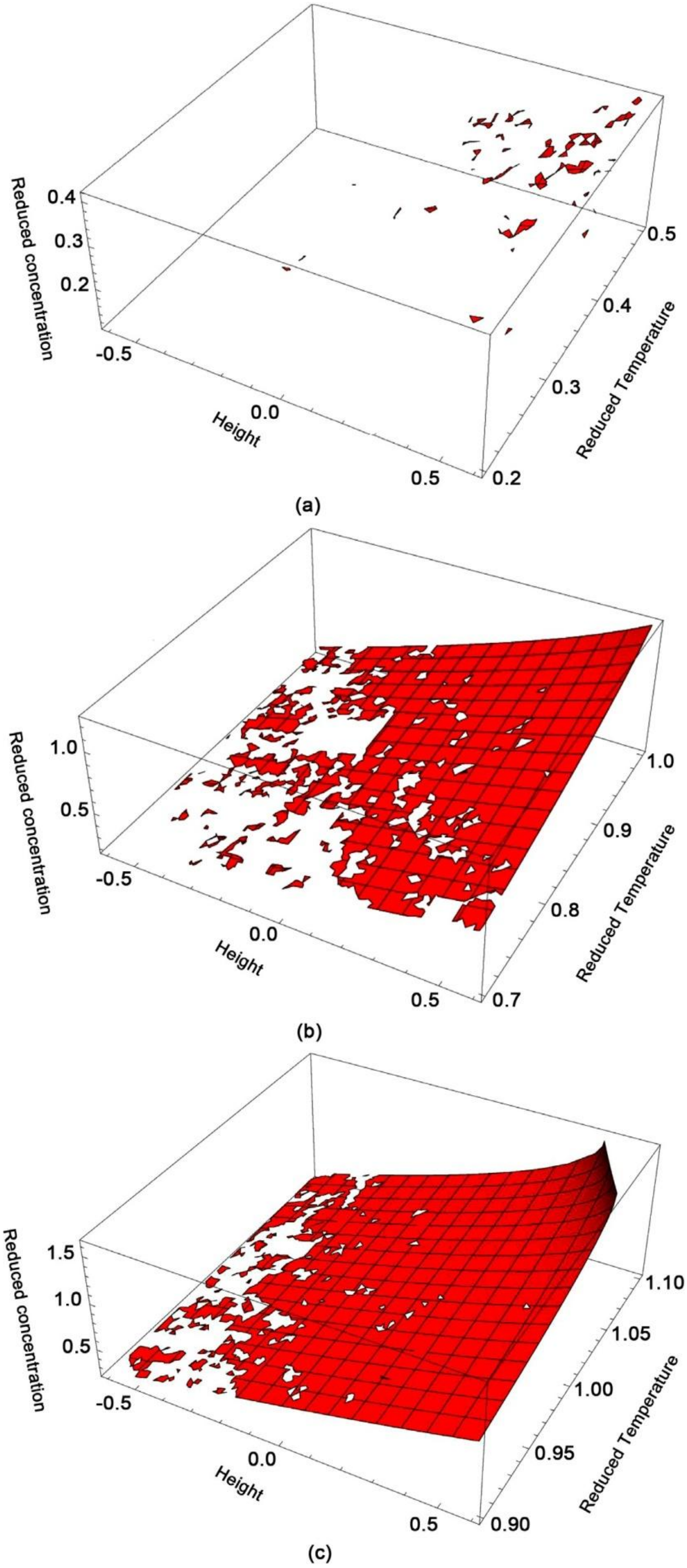

Figure3. Reducedconcentrationasafunctionofreduced temperatureandHeight.

5. Conclusions

Inthiswork,theeffectofgravityontheexistenceandpositionoftheliq-uid-vaporboundaryofapuresubstancewasquantitativelydiscussedonthebasisoftwosimplemodels:1)aperfectgasandincompressibleliquidmodel,and 2)aVanderWaalsfluidmodel.Theworkhasbeencarriedtakingintoaccountthe generalized Van der Waal equation unlike the simple Van der Waal modeltreated in [1] in order to investigate the effect of the gravitational field on theliquid-vapor boundary. From the results obtained, it observed that the vapor-liquidboundary has a phase separation at the critical point defined by the critical pa-rameters whichare obtainedby the firstandsecondderivatives of the genera-lized Van der Waal equation of state with respect to Volume (isolation of iso-therms). The first model has been shown to be a special case of the latter, fortemperatures much lower than the critical temperature while for the second case(b),ithas shown thatthe results can be obtainedin termsof only two indepen-dent dimensionlessparameters. Thereduced temperature controlsthereducedconcentration vertical profile as well as the height. It is equally observed that forheights lower than h_o (**Figure3(a)**) the phenomenon of phase transition is notobserved. Another interesting result of the present treatment is the possibility ofdirectly describing the appearance of the familiar vertical phase separation in thecell. Without the introduction of a gravitational field in the laws governing thebehaviorofafluid,theappearanceofthephaseboundaryneedstobeassumed.It alsoallowsustoquantitatively discuss the conditionsunder whichgravitationalfieldswill inducecondensationofagas.

For future works an investigation on the phenomenon of phase separationinvolving a variable or position-dependent gravitational field on a vapor-liquidboundarycanbecarriedout. Equallystudiescanbemadetoinvestigatethebe-havior of the vapor-liquid boundary using Berthelot's equation of state in thepresenceofdifferentfields.

ConflictsofInterest

Theauthorsdeclarenoconflictsofinterestregardingthepublicationofthispa-per.

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